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THE DONOR ABILITY OF TERTIARY PHOSPHINE
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DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
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By

Philip Edward Nicpon, B.S.

The Ohio State University
1966

Approved by

Adviser
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<td>Infrared spectrum of [Cu(Et₄P₂S₂)ClO₄, (KBr).</td>
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<td>31.</td>
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<td>Infrared spectra in ν&lt;sub&gt;CS&lt;/sub&gt; region (Nujol null) for (a) [Pd(PN)Br₂]⁺ and (b) [Pd(PN)(NCS)(SCN)].</td>
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<td>Infrared spectra of [Pd(PP)(NCS)(SCN)] in ν&lt;sub&gt;CN&lt;/sub&gt; region, (a) Nujol null (b) CH₂Cl₂ solution.</td>
<td>284</td>
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<td>286</td>
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<td>39.</td>
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<td>287</td>
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40. Electronic absorption spectrum of \([\text{Pd}(\text{PP})_2] \)
\([\text{Pd}(\text{SeCN})_4]\) (Nujol mull) .................. 288
CHAPTER I

INTRODUCTION

A. Nature of the Phosphorus and Arsenic Chalcogenide Bond in R$_3$PX and R$_3$AsX

1. General

An understanding of the nature of the phosphorus and arsenic chalcogenide bonds in tertiary phosphine and arsine chalcogenides (R$_3$PX and R$_3$AsX) is necessary in order to compare the donor properties of tertiary phosphine or arsine oxides with the analogous sulfides and selenides.

Tertiary phosphine chalcogenides contain approximately tetrahedral bond angles around the four-covalent phosphorus atom (74, 318, 327). This could involve mainly a $\sigma$-bond with $sp^3$ hybridization of phosphorus as shown in I. Alternatively, the presence of empty, d-orbitals on phosphorus and filled p-orbitals on the chalcogenide atoms make some double bond character between these two atoms possible by $p_\pi$-$d_\pi$ interaction; i.e., II. Hudson reviews (136) the theoretical aspects of d-orbital bonding by

\[ \text{R}_3\text{P}^+ - \text{X}^- \]

I

\[ \text{R}_3\text{P}=\text{X} \]

II
phosphorus in these compounds. A controversy exists over which model better describes the nature of the phosphorus-chalcogenide bond, the semi-polar (I) or double bond form (II). The experimental evidence indicates that the relative contribution from (I) or (II) is sensitive to the nature of the other substituents bonded to phosphorus. The same reasoning applies to the bonding in tertiary arsine chalcogenides although much less experimental evidence is available.

In contrast to tertiary phosphine and arsine oxides, tertiary amine oxides are best described only in terms of a semi-polar bond (III) because of the non-availability of empty d-orbitals on nitrogen (138).

2. Experimental evidence

Thermochemical data

The dissociation energies (PO, PS) of some tertiary phosphine oxides and sulfides are given in Table 1. The high PO dissociation energies suggest $p_d$ bonding. In contrast, the $N^+ \rightarrow O^-$ bond energy in tertiary amine oxides is on the order of 50-70 kcal/mole (138). It has also been suggested (229) that the lower PS dissociation energy in tertiary phosphine sulfides, when compared with the analogous oxides (Table 1), indicates that the bond order is less in thiophosphoryl (PS) than in phosphoryl (PO) bonds. Hudson has calculated, on the basis of
Table 1

Dissociation Energies of Some $R_3PO$ and $R_3PS$ Compounds (118)

<table>
<thead>
<tr>
<th>$R_3PX$</th>
<th>$D,E.(PX)$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_3$PO</td>
<td>139</td>
</tr>
<tr>
<td>(n-Pr)$_3$PO</td>
<td>138</td>
</tr>
<tr>
<td>(n-Bu)$_3$PO</td>
<td>137</td>
</tr>
<tr>
<td>Ph$_3$PO</td>
<td>128</td>
</tr>
<tr>
<td>(n-Pr)$_3$PS</td>
<td>91.6</td>
</tr>
<tr>
<td>(n-Bu)$_3$PS</td>
<td>91.5</td>
</tr>
</tbody>
</table>

electrostatic considerations and including the extra energy of the double bond, a PO dissociation energy in agreement with the values found (137).

The decomposition temperature of triphenylphosphine oxide is $454^\circ$, whereas that of triphenylphosphine sulfide is about $380^\circ$ (150), indicating that the phosphine sulfide is thermally less stable than the corresponding oxide.

No analogous thermochemical data is available for tertiary phosphine selenides or tertiary arsine chalcogenides. Indirect evidence suggests that the tertiary arsine sulfide bond may be stronger than the analogous oxide bond because triphenylarsine oxide may be easily converted to the sulfide simply by refluxing in carbon disulfide, whereas the same reaction does not occur with triphenylphosphine oxide (293). In fact, tertiary phosphine
sulfides are fairly easily converted to the analogous oxides (231).

Hydrogen bonding and adducts with Brönsted acids

Tertiary phosphine oxides exhibit hydrogen bonding properties (2,24,104,105,106,149,210). In addition, the compound HCl·POH may be formulated as POH+Cl in which complete proton transfer occurs (278); i.e., the phosphine oxide behaves as a Brönsted base (190).

No one has investigated the ability of tertiary phosphine sulfides and selenides or tertiary arsine chalcogenides to undergo such reactions. Surely, the sulfur or selenium atoms would not be as electronegative as oxygen therefore, one would not expect hydrogen bonding or Brönsted base behavior to occur with these.

Infrared measurements

The phosphoryl group stretching frequency occurs in the region 1350-1170 cm⁻¹ (17). The PO force constant, as well as vibrational frequency, is dependent on the electronegativity of the groups attached to phosphorus (16). The PO vibrational frequency (force constant) increases as the electronegativities of the substituent group increases. This supports the existence of a double bond between phosphorus and oxygen since increasing the electronegativity of the groups attached to phosphorus would strengthen the π-backbonding while it would decrease the strength
of the PO link in the semi-polar bond, \( P^+ \rightarrow O^- \), and lead to a reduced force constant.

Gordy has devised an empirical rule (98) for estimating force constants of two connected atoms. The method depends on the bond order between the two atoms, the electronegativity of these two, and their internuclear distance. The estimated force constant can then be inserted into the fundamental equation for a harmonic oscillator along with the reduced mass to obtain an estimate of the vibration frequency (Eq. 1).

\[
v_{\text{cm}}^{-1} = 1307 \sqrt{\frac{k}{\mu}}
\]  \hspace{1cm} (Eq. 1)

In Equation 1, \( k \) is the force constant \( \times 10^{-5} \) in dynes/cm and \( \mu \) is the reduced mass. An upper and lower limit is obtained for a double and single bond by use of this equation with the proper estimated force constants.

Thus, for tertiary arsine oxides, a pure double bond would give rise to a vibrational frequency of 964 cm\(^{-1}\) and a pure single bond would lead to one of 776 cm\(^{-1}\) (246). The experimental value found (246) for several tertiary arsine oxides is in the range 871-903 cm\(^{-1}\) indicating an AsO bond order somewhat greater than one.

The PS vibration depends upon the electronegativity of the substituents on the phosphorus atom (337) analogous to tertiary phosphine oxides, although it has also been suggested that the position of \( \nu_{\text{PS}} \) in \( \text{A}_3 \text{PS} \) compounds depends only on the mass of the A groups and on the force constants of the PA bonds (130).
Steric factors are believed to be of only secondary importance in determining $\nu_{PS}$ (337).

Gore, using the method discussed earlier, placed the $\nu_{PS}$ region between 500 and 750 cm$^{-1}$ (99). Zingaro found (337) $\nu_{PS}$ at 610 ± 20 cm$^{-1}$ for a variety of tertiary phosphine sulfides. Trimethyl- and triethylphosphine sulfide are outside these limits and occur at 568 and 535 cm$^{-1}$, respectively. The low position of $\nu_{PS}$ in the latter two cases is believed (337) to be due to strong intermolecular forces which tend to enhance ionic character of the bond and reduce the phosphorus-sulfur bond order (IV).

Infrared and Raman studies indicate (45,60,90,101) that tetraalkyldiphosphine disulfides exist as the trans structure (V).

Crystal structure determinations of tetraethylidiphosphine disulfide (74) and the neso- form of 1,2-dimethyl-1,2-diphenyldiphosphine disulfide (327) verify the phosphorus-phosphorus bond and the trans configuration (V).

A series of tertiary phosphine selenides exhibit the
ν_{PSe} vibration in the region 496-510 cm^{-1} (337). Zingaro estimates 388-559 cm^{-1}, based on Gordy's rule limits, as the region for ν_{PSe} employing a bond order of one and two, respectively (337). The values indicate that a bond order greater than one is present between phosphorus and selenium in these compounds. As with the analogous phosphine sulfide compounds, ν_{PSe} for trimethyl- and triethylphosphine selenide occurs at 441 and 422 cm^{-1}, respectively, which is outside the above range; intermolecular bonding is probably important here also.

Similarly, a series of tertiary arsine sulfides exhibit ν_{AsS} peaks in the region 470-490 cm^{-1} (341). Using Gordy's method to estimate force constants, a pure arsenic-sulfur double bond should occur at 555 cm^{-1} whereas the position for a single bond would be 372 cm^{-1} (341). Likewise, an upper limit of 520 cm^{-1} and a lower limit of 372 cm^{-1} is predicted for ν_{ArSe}, whereas experimentally the vibration occurs in the range 331-360 cm^{-1} (343). This indicates an arsenic-selenium bond order of one.

Dipole moments

Dipole moments for some tertiary phosphine and arsine chalcogenides are recorded in Table 2. These are larger than values for analogous phosphines and arsines and are similar to those of tertiary amine oxides (140); they seem to indicate a semi-polar bond (277). However, a variety of aliphatic tertiary phosphine oxides have dipole moments of 4.36 ± 0.01 D (62) independent of the inductive nature of the aliphatic group. The
### Table 2

Dipole Moments of Some Tertiary Phosphine and Arsine Chalcogenides

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu$, Debyes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_3P$</td>
<td>1.39</td>
<td>277</td>
</tr>
<tr>
<td>$\phi_3PO$</td>
<td>4.28(4.44)</td>
<td>277(62)</td>
</tr>
<tr>
<td>$\phi_3PS$</td>
<td>4.73</td>
<td>277,146</td>
</tr>
<tr>
<td>$\phi_3PSe$</td>
<td>4.83</td>
<td>146</td>
</tr>
<tr>
<td>$\phi_3As$</td>
<td>1.07</td>
<td>277</td>
</tr>
<tr>
<td>$\phi_3AsO$</td>
<td>5.50</td>
<td>277</td>
</tr>
</tbody>
</table>

The slight increase in dipole moment for triphenylphosphine oxide, sulfide, and selenide might not necessarily mean more ionic character in the order Se > S > O, but may simply reflect the longer phosphorus-chalcogenide bonds.

Other dipole moments are known for a variety of tertiary aromatic phosphine sulfides containing various substituted phenyl groups (92). The dipole moments of para-substituted phosphine sulfides increases with increasing electron donor character of the para substituent and this is attributed to a larger contribution of mesomeric form VII.
There is no dipole data available for any tertiary arsine chalcogenides or tertiary phosphine selenides (except for triphenylphosphine selenide).

Ultraviolet spectra

Jaffé found (145) that phenyl groups are conjugated only weakly with phosphorus or arsenic in triphenylphosphine- and triphenylarsine oxide. Each phenyl group makes an independent and additive contribution to the molar extinction coefficient.

The published U.V. spectra of triphenylphosphine and its oxide and sulfide (131) appear similar, except for extinction coefficients. Other workers have noted differences between oxide and sulfide derivatives of tertiary aromatic phosphines (92,141) and have suggested that the amount of π-bonding in the sulfides is considerably smaller than in the oxides, thereby promoting conjugation of the other bonded groups to a greater extent (VIII).

There is practically no change in $\lambda_{max}$ for tertiary aromatic phosphine oxides and sulfides with change of solvent from
cyclohexane to ethanol (7). Therefore, it was concluded that the phosphorus-chalcogenide bond is semi-polar; i.e., both ground and excited states are zwitterionic (IX,X) and would be stabilized almost to the same extent in a polar solvent.

Tetramethyl- and tetraethyldiphosphine disulfide absorb at 244.0 and 247.5 nm, respectively, in the U.V. (59). Here no complicating phenyl absorptions are possible. It is suggested (59) that the band may be due to an n → π* transition involving a non-bonding orbital on a sulfur and a π* molecular orbital of the phosphino sulfide bond. However, this is not conclusive since tetranethyldiphosphine absorbs in the same region (107). No other ultraviolet data is known for tertiary aliphatic phosphine or arsine chalcogenides.

Bond lengths

It has been suggested (270) that the N⁺ → O⁻ bond length in tertiary amine oxides is approximately equal to the calculated single bond length, whereas a considerable contraction occurs for the phosphorus-oxygen bond in tertiary phosphine oxides. Hudson reviews correlations between phosphorus-oxygen bond lengths and structure (139).

Two different bond lengths are observed and given in...
Table 3 for skeletal P-S and exocyclic P=S bonds in $P_xS_y$ compounds, the latter being shorter. Other compounds, thought to contain P=S groups, likewise show bond lengths similar to the exocyclic phosphorus-sulfur bonds.

Table 3

Bond Lengths for Some Phosphorus and Arsenic Chalcogenide Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>PX or AsX Bond Distance (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_4S_3$</td>
<td>2.09</td>
<td>121,186</td>
</tr>
<tr>
<td>$P_4S_5$</td>
<td>2.08-2.19</td>
<td>1.94</td>
</tr>
<tr>
<td>$P_4S_7$</td>
<td>2.08</td>
<td>1.95</td>
</tr>
<tr>
<td>$P_4S_7$</td>
<td>2.04-2.12</td>
<td>1.89</td>
</tr>
<tr>
<td>$P_4S_10$</td>
<td>2.08</td>
<td>1.95</td>
</tr>
<tr>
<td>$P_2S_6Br_2$</td>
<td>2.10</td>
<td>1.98</td>
</tr>
<tr>
<td>$P_4S_3I_2$</td>
<td>2.10</td>
<td>----</td>
</tr>
<tr>
<td>$P_4Se_3$</td>
<td>2.24</td>
<td>----</td>
</tr>
<tr>
<td>Et$_3$PSe</td>
<td>----</td>
<td>1.96</td>
</tr>
<tr>
<td>Et$_3$PS</td>
<td>----</td>
<td>1.86</td>
</tr>
<tr>
<td>Et$_2$P(S)P(S)Et$_2$</td>
<td>----</td>
<td>1.94</td>
</tr>
<tr>
<td>$\phi$(Me)P(S)P(S)(Me)$\phi$</td>
<td>----</td>
<td>1.98</td>
</tr>
<tr>
<td>Me$_2$As-S-As(S)Me$_2$</td>
<td>2.214</td>
<td>2.075</td>
</tr>
<tr>
<td>Me$_2$As-S-As(S)Me$_2$</td>
<td>2.279</td>
<td></td>
</tr>
<tr>
<td>KS$_2$P(OMe)$_2$</td>
<td>----</td>
<td>1.96</td>
</tr>
</tbody>
</table>
Potassium dimethyldithiophosphate, $\text{K}_2\text{P(OMe)}_2$, contains two phosphorus-sulfur bonds of equivalent length in the region for double bonding (52). One would expect a single and a double bond to be present (XI); delocalization apparently makes these two phosphorus-sulfur bonds equivalent (XII). Jørgensen suggests (158) that both phosphorus-sulfur bonds of diethyldithiophosphate have very little double bond character.

The phosphorus-selenium bond distance in triethylphosphine selenide (318) is 0.28 Å shorter than that in $\text{P}_4\text{Se}_3$ (166) indicating some multiple bond character in the former compound. A similar contraction is noted for an arsine sulfide compound (35, see Table 3).

**Nuclear magnetic resonance spectra**

Structural information may be determined from the $\text{P}^{31}$ N.M.R. spectra of certain phosphorus compounds. For instance, the presence of two multiplets, a doublet and a quartet, in the $\text{P}^{31}$ N.M.R. spectra of $\text{P}_4\text{S}_3$ (34) and $\text{P}_4\text{Se}_3$ (143) indicates a structure containing two sets of one and three equivalent phosphorus atoms ($I = 1/2$ for $\text{P}^{31}$).

Useful information may also be obtained from $\text{P}^{31}$ chemical shifts in various compounds. The position of a peak varies
because of differences in the magnetic shielding of the phosphorus nucleus by its valence electrons and trends in the chemical shifts have been interpreted qualitatively in terms of molecular electronic structures (110,112,154,320).

Electron shielding (i.e., chemical shift) of a nucleus is influenced by the electronegativity and the double-bonding ability of attached groups; these are opposing effects (112,264). An increase in ionic character decreases the phosphorus shielding (negative chemical shift) whereas an increase in double bond character between phosphorus and substituent groups increases the nuclear shielding (positive chemical shift) (112,320).

The chemical shifts for phosphorus compounds fall in two ranges. Shifts in tetra-coordinated compounds fall in a relatively narrow range, generally with greater nuclear magnetic shielding (greater positive shift) than in tri-coordinate phosphorus compounds (110,112,154,320). The large variations in tri-covalent phosphorus compounds are due to variance in bond angles and to changes in the s-contribution of the bonding σ-hybrid (320) while the smaller chemical shifts found for quadruply connected phosphorus compounds are believed due to changes in the distribution of π-bonds among the four σ-bonds (319,320). Thus, in quadruply connected phosphorus, differences in shielding at the phosphorus atom is caused by the action of substituents to shift π-bonds within the σ-bonded sp³ hybrid (320).
On the basis of chemical shift data, Gutowsky and McCall have postulated (112) that the double bond phosphorus-oxygen contribution is greater than the analogous phosphorus-sulfur bond in P(X)Cl$_3$. The same trend is illustrated when mixed organic, halide, or RO(RS) groups are attached to phosphorus (Table 4); that is, the order of positive chemical shift decreases in the following series: $\gamma_3^PPO > \gamma_3^PPS > \gamma_3^PP$.

The same general trend is exhibited by tertiary phosphine oxides and sulfides (Table 4) except that the analogous tertiary phosphine gives a P$^{31}$ resonance at a field position higher (more positive) than for the quadruply connected phosphorous; i.e., the order of chemical shift is $\gamma_3^P > \gamma_3^PPO > \gamma_3^PPS$. In addition, if one compares the chemical shift data for triethylphosphine chalcogenides, the order is Et$_3^PPO > Et_3^PSe > Et_3^PPO > Et_3^PSe$. These data would indicate that the double bond character in the phosphorus-selenium bond is greater than in the phosphorus-oxygen bond. The higher positive shift for the tertiary phosphines make p$^{31}$ chemical shifts suspect for determining bond order in tertiary phosphine chalcogenides.

Burdett and Burger found the P$^{31}$ resonance at higher fields in UO$_2^{++}$ complexes than in the free P=O ligands (28). By the above arguments, these data would indicate greater phosphorus-oxygen double bond character although the infrared $v_{PO}$ decreased upon complexation.

The value of $J_{C^{13}-H}$, the C$^{13}$-H coupling constant, depends on the electronegativity of attached groups and use of this
Table 4

Chemical Shift Data ($^{31}$P) for Various Phosphorus Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak Position, ppm</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCl$_3$</td>
<td>-220</td>
<td>260,320</td>
</tr>
<tr>
<td>P(O)Cl$_3$</td>
<td>-4(4-1.9)</td>
<td>320(260)</td>
</tr>
<tr>
<td>P(S)Cl$_3$</td>
<td>-28.8</td>
<td>260</td>
</tr>
<tr>
<td>Et$_2$PCl</td>
<td>-119</td>
<td>215</td>
</tr>
<tr>
<td>Et$_2$P(O)Cl</td>
<td>-76.7</td>
<td>215</td>
</tr>
<tr>
<td>Et$_2$P(S)Cl</td>
<td>-108.3</td>
<td>215</td>
</tr>
<tr>
<td>O$_2$PCl$_2$</td>
<td>-161.5</td>
<td>215</td>
</tr>
<tr>
<td>O$_2$P(O)Cl$_2$</td>
<td>-33.7</td>
<td>215</td>
</tr>
<tr>
<td>O$_2$P(S)Cl$_2$</td>
<td>-74.8(-80.0)</td>
<td>215(320)</td>
</tr>
<tr>
<td>OEtPCl</td>
<td>-97.0</td>
<td>215</td>
</tr>
<tr>
<td>OEtP(O)Cl</td>
<td>-59.0</td>
<td>215</td>
</tr>
<tr>
<td>OEtP(S)Cl</td>
<td>-93.7</td>
<td>215</td>
</tr>
<tr>
<td>(EtO)$_3$P</td>
<td>-139</td>
<td>320</td>
</tr>
<tr>
<td>(EtO)$_3$PO</td>
<td>-1.0</td>
<td>320</td>
</tr>
<tr>
<td>(EtO)$_3$PSe</td>
<td>-71.0</td>
<td>320</td>
</tr>
<tr>
<td>(O$_2$)$_3$P</td>
<td>-126.8</td>
<td>260</td>
</tr>
<tr>
<td>(O$_2$)$_3$PO</td>
<td>+18.0</td>
<td>320</td>
</tr>
<tr>
<td>(O$_2$)$_3$PS</td>
<td>-53.4</td>
<td>260</td>
</tr>
</tbody>
</table>
Table 4 (Contd.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peak Position, ppm</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{EtS})_3\text{P}$</td>
<td>$-115.6$</td>
<td>260</td>
</tr>
<tr>
<td>$(\text{EtS})_3\text{PO}$</td>
<td>$-61.3$</td>
<td>260</td>
</tr>
<tr>
<td>$(\text{EtS})_3\text{PS}$</td>
<td>$-92.9$</td>
<td>260</td>
</tr>
<tr>
<td>$\text{MeP}_3\text{P}$</td>
<td>$+61.0$</td>
<td>123</td>
</tr>
<tr>
<td>$\text{Me}_3\text{PS}$</td>
<td>$-59.1$</td>
<td>215,251</td>
</tr>
<tr>
<td>$\text{Et}_3\text{P}$</td>
<td>$+20.4$</td>
<td>260</td>
</tr>
<tr>
<td>$\text{Et}_3\text{PO}$</td>
<td>$-48.3$</td>
<td>260</td>
</tr>
<tr>
<td>$\text{Et}_3\text{PS}$</td>
<td>$-54.5(-68.1)$</td>
<td>251 (260)</td>
</tr>
<tr>
<td>$\text{Et}_3\text{PSe}$</td>
<td>$-45.8$</td>
<td>260</td>
</tr>
<tr>
<td>$\text{Bu}_3\text{PO}$</td>
<td>$-43.2$</td>
<td>260</td>
</tr>
<tr>
<td>$\text{Bu}_3\text{PS}$</td>
<td>$-48.0$</td>
<td>212</td>
</tr>
<tr>
<td>$\varnothing_3\text{P}$</td>
<td>$+5.9$</td>
<td>260</td>
</tr>
<tr>
<td>$\varnothing_3\text{PO (CHCl}_3\text{)}$</td>
<td>$-27.0$</td>
<td>251</td>
</tr>
<tr>
<td>$\varnothing_3\text{PS}$</td>
<td>$-42.6$</td>
<td>251</td>
</tr>
<tr>
<td>$\text{Me}_2\text{PPMe}_2$</td>
<td>$+59.5$</td>
<td>214,251</td>
</tr>
<tr>
<td>$\text{Me}_2\text{P(S)P(S)Me}_2$</td>
<td>$-34.7$</td>
<td>251</td>
</tr>
<tr>
<td>$\text{Et}_2\text{PPEt}_2$</td>
<td>$+34.3$</td>
<td>214,251</td>
</tr>
<tr>
<td>$\text{Et}_2\text{P(S)P(S)Et}_2$</td>
<td>$-49.4$</td>
<td>251</td>
</tr>
</tbody>
</table>

$^\dagger$ relative to 85% $\text{H}_3\text{PO}_4$. 
fact showed that the phosphorous-oxygen bond of trimethylphosphine oxide is best described as a double bond since the results indicate neutral phosphorus rather than P$^+$ (113). Similarly, trimethylamine oxide was shown by this method to consist of a N$^+\rightarrow O^-$ linkage in contrast to its phosphorus analog.

The existence of a P-P bond in tetramethyldiphosphine disulfide was doubted on the basis of $J_{p-p}$, the P-P coupling constant, determined from proton magnetic resonance spectra (116). Cowley has shown, however, that the mass spectrum of tetramethyldiphosphine disulfide provides strong support for a P-P bond (59).

Miscellaneous data

By using an internally consistent LCAO-MO method, Wagner calculated (323) that a nearly pure coordinate single bond exists in trimethylphosphine oxide, in contrast with the $J_{c-13-H}$ data.

Similar conclusions (single bond) as to the nature of the PO and PS bond in tertiary phosphine oxides and sulfides have been reported in the older literature by workers employing other data such as parachors (310) and bond refraction constants (91, 230).

The ionic character of the P=O and P=S bonds is estimated at about 80% and 8%, respectively, on the basis of the difference in electronegativity values between phosphorus and the
two chalcogenides (130). Similar reasoning would predict about 0% ionic character for the P=Se bond.

3. Conclusion

The experimental evidence can be used to justify either the coordinate linkage (I) or the double linkage (II) according to the particular investigator's prejudice. It would seem better to consider the phosphorus and arsenic chalcogenide bonds in these as resonance hybrids between the two canonical forms (XIII,XIV) and not specify the relative amounts of each form in

\[
\begin{align*}
R_2P^{+}\_X^- & \Rightarrow R_2P=X \\
R_2As^{+}\_X^- & \Rightarrow R_2As=X
\end{align*}
\]

a given system; although, for brevity, the double bond form will be used to describe these compounds henceforth.

B. Comparison of the Donor Properties of Tertiary Phosphine and Arsine Oxides with Analogous Sulfide and Selenide Systems

1. Adducts with molecular halogens and \( \text{SO}_3 \)

Tertiary phosphine oxides as well as tertiary phosphine sulfides and selenides form addition compounds with molecular halogens (338,342). Also, recently the analogous tertiary arsine chalcogenides have been shown to form crystalline adducts with iodine or interhalogens (246). In addition, tertiary phosphine and arsine chalcogenides form adducts with sulfur trioxide; the following have been reported: \( \mathcal{O}_3\text{PO}\cdot\text{SO}_3 \) (15).
\[ \Phi^3 \text{PS} \cdot \text{SO}_3 \ (15), \ \Phi^3 \text{AsO} \cdot \text{SO}_3 \ (15), \ (C_{6}H_{11})_3 \text{AsS} \cdot \text{SO}_3 \ (15), \ \text{and} \]
\[ \text{Me}_3 \text{PO} \cdot \text{SO}_3 \ (30,195). \] Triphenylphosphine selenide probably initially formed an \( \text{SO}_3 \) adduct (215) but was oxidized to triphenylphosphine oxide.

These tertiary phosphine and arsine chalcogenides exhibit Lewis base character toward iodine and sulfur trioxide. Therefore, one might reasonably expect them to act as Lewis bases toward other Lewis acids; e.g., toward transition metal ions.

2. **Tertiary phosphine and arsine oxides**

Indeed, the P=O and As=O groups form addition compounds with a variety of Lewis acids and these are reviewed in Lindqvist's monograph (189). These oxide donors behave as Lewis bases towards covalent halides and some oxyhalides of the following elements: B(III), Al(III), Ga(III), Si(IV), Sn(IV), Ti(IV), V(III), Zr(IV), Hf(IV), Nb(V), Ta(V), As(V), As(III), Sb(V), Sb(III), Bi(III), Se(IV), and Te(IV).

In addition, tertiary phosphine and arsine oxides also form complexes with a variety of transition metal ions. Tertiary phosphine oxide complexes of the following metals have been isolated: Mn(II) (8,95), Fe(III) (8), Ni(II) (10,54,70, 71,96), Co(II) (8,10,55,70,71), Cu(II) (8,10,71,94), Zn(II) (8,10,70), VO^{++} (134), Mo(V) (133,167), W(VI) (167), and Hg(II) (195). Likewise, complexes of the following metals with tertiary arsine oxides have been prepared: Mn(II) (95,276), Fe(III) (276),
Co(II) (97,276), Ni(II) (93,96,276), Cu(II) (94), VO^{++} (134),
Re(III) (209), Hg(II) (276), and with molybdenum in various
oxidation states (132,133,304).

Organic phosphates, (RO)_3PO, and tertiary phosphine oxides
are used for solvent extraction of various uranium(IV and VI),
neptunium(IV), and plutonium(IV) species (188,240,258,333).
Solid tertiary phosphine oxide complexes of UO_2(NO_3)_2 (31,122)
and Th(NO_3)_4 (268) have been isolated.

Bifunctional ligands of the type R_2P(O)(CH_2)_nP(O)R_2
(where R is an alkyl or alkoxy group and n is 1-4) are also
used for solvent extraction of uranium(VI), thorium(IV), and
some Lanthanide elements (257,258,267,306). Some complexes of
these have also been isolated (267,268). It is conceivable that
ligands of this type, where n is one, might undergo enolization
and behave in a manner similar to \( \beta \)-diketones. When
R = n-C_3H_7O-, n-C_4H_9-, or Cl these function as neutral bidentate
ligands, even in the presence of base (295,324), and apparently
do not enolize sufficiently to be effective analogs of \( \beta \)-dike­
tones. However, Kosolapoff found (168) that the following
reaction, which is analogous to alkylation of a \( \beta \)-diketone, oc­
curs (Eq. 2).

Tertiary phosphine and arsine oxides bond to acceptor atoms through electron pairs on oxygen. The structures of three complexes show that the M-O-P(As) bond angles are not linear. The Sb-O-P bond angle in SbCl$_5$·Me$_3$PO is 144.9° (191); the Hg-O-As bond angles in HgCl$_2$·2Ø$_2$AsO are 136.7° and 134.4° (192); and the Sb-O-As bond angles in SbCl$_3$·2Ø$_2$AsO are 140.9° and 137.2° (193).

3. **Tertiary phosphine (arsine) sulfides and selenides**

Addition compounds with other Lewis acids

Besides molecular halogens and sulfur trioxide, tertiary phosphine (arsine) sulfides and selenides have not been systematically studied as bases toward other Lewis acids. However, it is known that aluminum compounds such as AlCl$_3$, AlBr$_3$, and EtAlCl$_2$ are the only active Lewis acid catalysts in the reaction of P(S)Cl$_3$ and aromatic hydrocarbons under Friedel-Crafts conditions (228). It is reported that these aluminum compounds give stable addition compounds with P(S)Cl$_3$ (219). Other Lewis acid catalysts, such as ZnCl$_2$, FeCl$_3$, and TiCl$_3$ do not give
addition compounds with $P(S)Cl_3$, and they are not reactive in Friedel Crafts reactions.

Complexes with transition metal ions

Investigations of the donor ability of tertiary phosphine (arsine) sulfides and selenides towards transition metal ions are few compared with those of the analogous $P=O$ and $As=O$ donors. Indeed, at the start of this investigation, no tertiary arsine sulfide or selenide complexes had been reported although Zingaro and Merijanian have noted that color changes occur in solution when such type molecules are mixed with solutions of transition metal salts. They were unable to isolate any complexes, however. Bannister and Cotton reported that triphenylphosphine sulfide and selenide do not form complexes with a variety of transition metal ions. However, they were able to obtain two palladium (II) complexes of the type $PdL_2Cl_2$. They also found that tin(IV) forms the complex $SnCl_4\left(PSe\right)_2$ but could not isolate analogous sulfide complex. Only analytical data was reported for these complexes. The palladium(II) complexes were reportedly too insoluble for measurements which might have elucidated their structure. Two recent review articles by Jørgensen (160) and Livingstone (207) quote these results and state that ligands of this type appear to be poor donors toward metal ions. Philip and Curran have also reported the same deficiency of donor character for triphenylphosphine sulfide but were able to obtain a one to one
complex with mercury(II) bromide. Only one other phosphine sulfide complex was reported in the literature at the start of this investigation; triethylphosphine sulfide was reported to form the complex $2\text{HgBr}_2 \cdot \text{Et}_3\text{PS}$ (235).

No infrared data was reported for the above complexes. One report for halogen addition compounds of tertiary phosphine sulfides (338) is based on wrong P=S assignments. Other errors still occur in the literature. For example, Zingaro averaged the position of two peaks in the P=S region of triphenylphosphine sulfide and listed a value of $627 \text{ cm}^{-1}$ for this vibration (337); other workers have reported the correct assignment at $637 \text{ cm}^{-1}$ (147). The extra peak at $614 \text{ cm}^{-1}$ is very weak in triphenylphosphine and somehow gains intensity in the sulfide; it does not appear to be a P=S vibration.

4. Additional evidence for donor ability of sulfide and selenide systems

Seleno- and thionophosphates $(\text{RO})_3\text{PX}$

Other evidence indicates that the "poor donor ability" of these sulfide and selenide systems is simply due to a lack of research in this area. The older work of Pishchimuka (279, 280, 281), recently repeated by Hilgetag and Teichmann (125, 126, 299, 314), illustrates that certain metals; i.e., Au(III), Sn(IV), Fe(III), Al(III), and Ti(IV) isomerize thionophosphates $(\text{RO})_3\text{PS}$, to thiolophosphates $(\text{RO})_2(\text{RS})\text{PO}$. The same
reaction occurs with selenophosphates \((RO)_3PSe\). Although heating is known to cause isomerization in certain cases (124), the reaction is accelerated markedly by the presence of metal ions. For instance, Hilgetag and co-workers could isolate only complexes of the type \([(RO)_2(RO)PO]_2 [SnX_4]\), even though they originally started with \((RO)_3P=S\). However, mercury(II) was reported to yield thionophosphate complexes, where the ligand is bonded through the sulfur atom; i.e., \(2HgCl_2 \cdot SP(OMe)_3\). Silver(I) causes cleavage of an alkyl group to yield adducts of the type \((RO)_2P(S)OAg\) but the initial complex is thought to involve sulfur coordination of the \((RO)_3P=S\) group (127).

Dialkylidithio- and dialkyldiselenophosphatos \((RO)_2PX_2^-\)

In contrast to the above studies, diethyldithiophosphate, \((EtO)_2PS_2^-\), bonds both sulfur atoms to transition and post-transition metals without isomerization. Complexes formed by this ligand and similar ones have been reviewed by Jørgensen (157) and Livingstone (199).

Most metals form neutral inner complexes with diethyldithiophosphate which have physical properties similar to the acetylacetonate complexes. The metals include Pd(II), Hg(II), Cr(III), Fe(III), Rh(III), Ir(III), In(III), Rh(III), and Ni(II). Dark purple \(Fe(dtp)_3\) is unstable in solution (159) and forms Fe(II) and \((EtO)_2(S)P(S)(OEt)_2\) by oxidizing the ligand. The ligand is also reported (315) to act as a unidentate sulfur ligand in some Ag(I) and Hg(II) complexes.
Diethyldiselenophosphate, \((\text{EtO})_2\text{PSe}_2^-\), acts as a bidentate ligand to form inner complexes with the metals Cr(III), Rh(III), Ir(III), Ni(II), Pd(II), Cd(II), and In(III) of the type \(ML_x\). These are also discussed by Jørgensen and Livingstone.

Dialkyldithio- and dialkyldiselenophosphinato groups (\(R_x\text{PX}_2\))

Metal derivatives of phosphinodithioic and phosphinodiselenoic acids, \(R_x\text{P}(X)XH\), are also known. These non-ionic complexes are of the type \((R_x\text{PX}_2)_n\)M. In order for the metal to possess its normal coordination number, it must be assumed that both sulfur or selenium atoms are coordinated to the metal in these complexes.

A brief description of these complexes is appropriate since they have not been reviewed in detail before. Complexes of phosphinodithioic acid are not usually obtained from the free acid (48); however, there are several methods of preparation. These include (1) addition of metal salts to the product of a Grignard reaction with \(\text{PS}_y\) (233, 234, 235); (2) reaction of \(R_x\text{P}(S)\text{SNa}\) with an appropriate metal salt (175, 176, 180, 181, 184); (3) heating a mixture of \(R_x\text{P}(S)\text{P}(S)\text{R}_2\), MS, and S (180, 182, 183); and (4) heating a mixture of \(R_x\text{P}(S)\text{P}(S)\text{R}_2\), M, and 2S (180, 182, 183). Examples of metal complexes are listed in Table 5. A variety of nickel(II) complexes have been prepared and these are given separately in Table 6.
Table 5
Complexes of Phosphinodithioic Acids, \([R_2P(S)S]_x M\)

<table>
<thead>
<tr>
<th>Metal</th>
<th>X</th>
<th>R</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂Al</td>
<td>1</td>
<td>Me</td>
<td>48</td>
</tr>
<tr>
<td>Al</td>
<td>3</td>
<td>Me</td>
<td>48</td>
</tr>
<tr>
<td>Me₂Ga</td>
<td>1</td>
<td>Me</td>
<td>48</td>
</tr>
<tr>
<td>Me₂In</td>
<td>1</td>
<td>Me</td>
<td>48</td>
</tr>
<tr>
<td>MeAl</td>
<td>2</td>
<td>(\emptyset)</td>
<td>48</td>
</tr>
<tr>
<td>In</td>
<td>3</td>
<td>Et</td>
<td>183</td>
</tr>
<tr>
<td>Cr</td>
<td>3</td>
<td>Et</td>
<td>176,181,183</td>
</tr>
<tr>
<td>Co</td>
<td>2</td>
<td>Et</td>
<td>175,176,181</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Me</td>
<td>234,183</td>
</tr>
<tr>
<td>Zn</td>
<td>2</td>
<td>Et</td>
<td>175,181,182,183</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>n-Pr</td>
<td>182,183</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>n-Bu</td>
<td>182,183</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>n-Amyl</td>
<td>182,183,234</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>(\emptyset)</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Me</td>
<td>234</td>
</tr>
<tr>
<td>Cd</td>
<td>2</td>
<td>Et</td>
<td>181,183,236</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>n-Pr</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>n-Bu</td>
<td>182,183</td>
</tr>
<tr>
<td>As</td>
<td>3</td>
<td>n-Pr</td>
<td>182,183</td>
</tr>
</tbody>
</table>
Table 5 (Contd.)

<table>
<thead>
<tr>
<th>Metal</th>
<th>X</th>
<th>R</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>3</td>
<td>n-Pr</td>
<td>181,182,183</td>
</tr>
<tr>
<td>Bi</td>
<td>3</td>
<td>n-Pr</td>
<td>176,181,182,183</td>
</tr>
<tr>
<td>Pb</td>
<td>2</td>
<td>n-Pr</td>
<td>175,181,183</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Et</td>
<td>176,181</td>
</tr>
<tr>
<td>Hg</td>
<td>2</td>
<td>Et</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>n-Pr</td>
<td>182,183</td>
</tr>
<tr>
<td>R₂Sn</td>
<td>2</td>
<td>Et</td>
<td>175,176</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The tin complexes \((\text{Et}_2\text{PS}_2)\text{SnR}_2\) \((R = \text{Cl}, \text{n-Bu}, \text{or } \varnothing)\) possess large dipole moments; therefore it was concluded that these probably have cis-octahedral structure \((175,176)\). Thallium appears to form \(\text{Tl}(\text{Et}_2\text{PS}_2)\) \((183)\), and also the ionic species \([\text{Me}_2\text{Tl}]^+ - [\text{Me}_2\text{PS}_2]^−\), \((48)\). The ionic character of the latter is shown by its 1:1 electrolyte behaviour in aqueous solution and the similarity of its infrared spectrum to that of \(\text{Cs}^+ (\text{Me}_2\text{PS}_2)^−\).

The dithiophosphate group functions \((48)\) as a chelate ligand and gives nonmonomeric Ga, Al, and In complexes of the type \([\text{Me}_2\text{M(S}_2\text{P} \text{Et}_2)]\), whereas, the dimethylphosphinic group, \(\text{Me}_2\text{PO}_2^−\), forms dimeric species of the type \([\text{Me}_2\text{M(O}_2\text{PMe}_2)]_2\), where it was postulated that the phosphinic group behaves as a
Table 6
Nickel(II) Complexes of Phosphinodithioic Acids, \([RR'P(S)S]_2Ni\)

<table>
<thead>
<tr>
<th>(R, R')</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R=R' = \text{iso-Pr})</td>
<td>233, 236</td>
</tr>
<tr>
<td>(R=R' = \text{Et})</td>
<td>175, 176, 181, 234, 235, 236</td>
</tr>
<tr>
<td>(R=R' = \emptyset)</td>
<td>183, 234, 235, 236</td>
</tr>
<tr>
<td>(R=R' = \text{cyclohexyl})</td>
<td>234</td>
</tr>
<tr>
<td>(R=\emptyset, R' = \text{Me})</td>
<td>262</td>
</tr>
<tr>
<td>(R=\emptyset, R' = \text{Et})</td>
<td>262</td>
</tr>
<tr>
<td>(R=\emptyset, R' = \text{iso-Pr})</td>
<td>262</td>
</tr>
<tr>
<td>(R=R' = \text{n-Bu})</td>
<td>262</td>
</tr>
<tr>
<td>(R=R' = \text{iso-Bu})</td>
<td>234</td>
</tr>
<tr>
<td>(R=R' = \text{Me})</td>
<td>234</td>
</tr>
<tr>
<td>(R=R' = \text{n-Bu})</td>
<td>292</td>
</tr>
<tr>
<td>(R=R' = \text{n-C}<em>{18}\text{H}</em>{17})</td>
<td>292</td>
</tr>
<tr>
<td>(R=R' = \text{n-C}<em>{12}\text{H}</em>{25})</td>
<td>292</td>
</tr>
<tr>
<td>(R=R' = \text{PhCH}_2\text{CH}_2^-)</td>
<td>292</td>
</tr>
</tbody>
</table>

three atom bridge (OPO) resulting in an eight-membered ring structure. The fact that dithiophosphinates chelate with tetrahedrally coordinated metals is reasoned (48) to be due to the ease with which sulfur can undergo valency angle deformation relative to oxygen.
The above described work of Coates and Mukherjee (48) is the only one which reports infrared spectra. This is of interest because one can compare the infrared spectra of the salt, \( \text{Cs}^+(\text{Me}_2\text{PS}_2)^- \), with the complexes. This salt exhibits two distinct PS vibrations (48) one at 606 cm\(^{-1}\) \( (v_{\text{P-S}}) \) and the other at 505 cm\(^{-1}\) \( (v_{\text{P=S}}) \). These two PS vibrations may be symmetric and antisymmetric stretching vibrations if extreme delocalization (such as illustrated by XV) occurs.

\[
\begin{array}{c}
\text{S} \\
\text{Me}_2\text{P} \\
\text{S}
\end{array}
\]

XV

The decrease in energy for the 606 cm\(^{-1}\) bond in the complexes is on the order of 5-21 cm\(^{-1}\) compared with the cesium salt whereas the other bond remains unchanged upon complexation.

Infrared data was useful in assigning the structure of the nonmeric complex, MeAl(S\(_2\text{P}\phi_2\)\(_2\)). This could be a five coordinate aluminum species, but it shows a free P=S stretching vibration at 654 cm\(^{-1}\) and therefore was assigned structure XVI (48).

\[
\begin{array}{c}
\phi_2\text{P(S)S} \\
\text{Al} \\
\text{Me}
\end{array}
\]

XVI

In contrast to the zinc compounds, the analogous cadmium and mercury complexes of phosphinodithioic acids are dineric.
(180, 183) and a bridged structure (XVII) has been proposed.

![Diagram of XVII]

The dithiophosphinate transition metal complexes have not been studied by inorganic chemists and the electronic absorption spectra of the nickel(II) and cobalt(II) salts have not been published. A tetrahedral structure has been assigned Co(S$_2$PEt$_2$)$_2$ because it is monomeric in benzene with a magnetic moment of 4.82 B.M. (175). The magnetic moment of Cr(S$_2$PEt$_2$)$_3$ was found to be 3.87 B.M. corresponding to three unpaired electrons (175).

The nickel(II) complexes are intense blue to blue-violet in color. Those of diethyl- and diisopropylphosphinothioic acids have been obtained in two isomeric forms (233). The nickel(II) complex of diethylphosphincdithioic acid is diamagnetic. It undergoes reaction with pyridine and thiophene (C$_4$H$_4$S) to form complexes of the type (Et$_2$PS)$_2$NiL$_2$ and also reacts with ammonia to form Ni(NH$_3$)$_6$(Et$_2$PS$_2$)$_2$ (175).

Kuchen et al. (183) claim that the thermal and chemical stability of the dithioic acid complexes is unusually great and rationalize this fact by suggesting that several resonance forms
are possible (XVIII, XIX, XX) and that this leads to added re-
sonance stability of the chelate ring. Resonance form XIX would corre-
respond to donation of electron density from ligand to empty d-orbitals on the metal. Resonance form XX represents donation of filled d-electron density from metal to empty d-orbitals on sulfur; a contribution not possible in the oxide system.

Kuchen et al. also state (183) that through the positive inductive effect of alkyl groups, the donor ability of the sulfur atoms and, therefore, the basicity of the ligand is raised. Substitution of phenyl for alkyl groups is said to increase the salt-like character of the complexes in line with the negative
inductive effect of the phenyl group which results in lower basicity.

The complexing ability of the diselenium analogs has not been studied to the same extent. The sodium salt of diethylphosphinodiselenoic acid reacts with metal salts to form complexes of Zn(II), Cd(II), Pb(II), Bi(III), In(III), and Th(I) (178,179).

Somewhat similar are the diethylselenothiophosphinate complexes where the ligand contains both sulfur and selenium. These non-electrolytic complexes (Table 7) have been obtained by reacting the sodium salt, Et$_2$P(S)SeNa, with the appropriate metal salts (177,179). Canonical form XXI probably contributes more to the ground state in these complexes than XXII because it

\[
\begin{align*}
[ & \begin{array}{c} S \\
\text{Et}_2\text{PS} \end{array} M]_n \quad [ & \begin{array}{c} S \\
\text{Et}_2\text{PSe} \end{array} M]_n \\
\text{XXI} & \quad \text{XXII}
\end{align*}
\]
was postulated that $\text{Et}_2\text{P(Se)}\cdot\text{S}^-$ is practically the only species present in aqueous solution (177,179); i.e., via XXIII.

$$\text{Et}_2\text{P(S)}\cdot\text{Se}^- \equiv \text{Et}_2\text{P(Se)}\cdot\text{S}^-$$

XXIII

This would be consistent with the fact that the analogous acid, $\text{Et}_2\text{P(S)}\cdot\text{OH}$, occurs in aqueous alcoholic solution almost completely in the thiono form. The idea being that negative charge tends to be localized almost exclusively at the more electronegative atom.

5. **Nature of the chalcogenide atom**

Any comparison of the donor properties of tertiary phosphine and arsine oxides with the analogous sulfide and selenide systems must include a discussion of the differences between oxygen and sulfur (selenium) donors in general.

Generally, the first members of a family in the periodic table exhibit properties differing from succeeding elements which have the same electronic configuration. Thus, boron, nitrogen, and oxygen, as well as compounds of these elements, display properties differing in some respects from those of the heavier members of the same group.

In coordination chemistry, ligands are generally classified according to whether the donor atom is a first row element or a succeeding one. Metals have been classified similarly. Thus, Fajans (81,82) and Bjerrum(23) noted that these can be placed in two categories, according to the type of bases they prefer.
to coordinate with. Schwarzenbach also divided metal ions into
two classes based on the number of outer d-electrons (301).
Ahrland, Chatt, and Davies developed a similar classification
of metal ions based on whether they form their most stable com­
plexes with first row donor atoms or with subsequent members of
each group (1).

Pearson has further developed these ideas (272,273) and
shown that the concept can be expanded to encompass Lewis acids
and bases in general. According to Pearson, class (a) materials,
be they Lewis acids or bases, have certain distinguishing fea­
tures such as small size, high positive oxidation state, are
hard to reduce, show an absence of any outer electrons which
can be easily excited to higher states, and contain empty
orbitals of high energy, which are therefore inaccessible.
These characteristics lead to low polarizability. Class (b)
acids have one or more of the following properties which all
lead to high polarizability: low or zero positive charge, large
size, and/or several easily excited outer electrons (which for
metals are d-orbital electrons). Class (b) bases are those in
which the donor atom is of low electronegativity, contains large
diffuse orbitals (easily polarizable), and is easily oxidized
or associated with empty, low lying orbitals. In general,
oxogen donors are class (a) bases whereas sulfur and selenium
donors exhibit class (b) properties. However, certain sulfur
and selenium donors containing negative charge on these atoms;
e.g., RS\(^-\) and R\(_2\)PS\(^-\), behave both as class (a) and class (b) bases.

Pearson refers to these class (a) materials by the picturesque name of "hard" acids and bases whereas those class (b) acids and bases are termed "soft". He has developed a general principle; hard acids prefer to associate with hard bases and soft acids prefer to associate with soft bases.

This concept can be useful in understanding certain experimental facts (273). It offers an explanation for the stability of Co(NH\(_3\))\(_5\)F\(^2+\) and Co(CN)\(_5\)I\(^3-\) and the unstability of Co(NH\(_3\))\(_5\)I\(^2+\) and Co(CN)\(_5\)F\(^3-\). Thus, [Co(NH\(_3\))\(_5\)]\(^3+\) must be a hard acid whereas [Co(CN)\(_5\)]\(^2-\) is a soft acid. The theory also explains differences in the acceptor properties of BF\(_3\) and BH\(_3\) by assuming the former is a class (a) or hard acid while the latter is a class (b) or soft acid. It also is a rationale for certain metals; e.g., cobalt(II) and nickel(II), forming isothiocyanate (M-NCS) complexes while others; e.g., palladium(II) and platinum(II), form isothiocyanato complexes, (M-SCN).

Pearson's principle can also be applied to Lewis interactions occurring with non-transition metal ions; although usually the rationalization is ipso facto. For example, a thermochemical study of the relative donor strengths of some oxygen and sulfur ligands toward SnCl\(_4\) and SbCl\(_5\) has shown that Et\(_2\)S is coordinated more strongly than Et\(_2\)O (194). Sn(IV) and Sb(V) would normally be expected to exhibit class (a) character. The fact that more stable complexes are formed with a class (b)
donor ligand was interpreted as evidence that these metals should be regarded as borderline in character rather than class (a) (204).

Some of Pearson's postulates are quite reasonable. Hard acids are assumed to bind bases primarily by ionic forces. High positive charge and small size certainly favor such ionic bonding. Soft acids would bind bases primarily by covalent bonds. For good covalent bonding, the two bonded atoms should be of similar size and similar electronegativity. However, he considers the major stabilization factor to be delocalization of filled electrons from soft Lewis acids onto empty, low lying levels of the soft base. Although Pearson's principle is qualitatively useful in explaining a great deal of experimental findings, it is, at present, also subject to criticism (109,244).

The most important feature of class (b) acids, according to the pi-bonding theory of Chatt (37,39), is the presence of loosely held outer d-orbital electrons which can form pi-bonds by donation to ligand orbitals. The latter transition metals in their normal oxidation states are most favorable for this interaction, especially the latter members of the second and third transition series; e.g., Pd(II), Pt(II), and Hg(II). The ligands which form complexes with these class (b) acids; e.g., P, As,S,Se, or I, are those with available empty d-orbitals. Pearson stresses the importance of metal d-electrons for determining class (a) or (b) character by stating that no class (b) metal ion containing less than five d-electrons is known.
However, now there are data which contradict this postulate. Thus, although Ti(IV) is regarded as a class (a) acid and contains no d-electrons, Ti(IV) halides form ill-defined (5) or unstable (300) complexes with dialkylethers, but the compounds TiX₄(R₂S)₂, R equal Me and Et, are stable (5). Molybdenum(V) forms (85) the complexes MoOCl₃(R₂S), R equal Me, Et, and n-Pr. Also, the following complexes of Nb(V) and Ta(V) have been isolated (79,80): MX₅(R₂S) where M = Nb, Ta; X = F, Cl, Br; R = Me, Et; and also TaI₅(R₂S). These are more stable thermally than the corresponding ether complexes. In fact, the ether can be replaced by the corresponding thioether, suggesting that the M-S bond energy is greater.

Vanadium(III) containing one outer d-electron also behaves as a class (b) acid in forming the stable, monomeric VCl₃(R₂S)₂ complexes, where R equal Me and Et (73,88). Vanadium(IV) halides are reduced by dialkylsulfides (73) and by arsenic and phosphorus ligands (26) with formation of coordination compounds of vanadium(III).

Pitzer has suggested that London, or Van der Waals, dispersion forces between atoms or groups in the same molecule may lead to an appreciable stabilization of the molecule. Such London forces are fairly short range and depend on the polarizabilities of the interacting groups. These forces are large when both groups are highly polarizable. However, Pearson suggests (273) that this interaction can only partly account for the affinity of soft acids for soft bases.
Other workers have suggested that polarizability effects may be a major factor in rationalizing stability orders. Fairbrother et al. (79, 80) suggest that the stability order \( S > O \) for the Nb(V) and Ta(V) complexes may be due to a the dipole of the ligands and b the polarizabilities of sulfur and oxygen. The dipole moment of Et<sub>2</sub>S is greater than that of Et<sub>2</sub>O (1.58 D compared to 1.15 D) and the polarizability of sulfur is greater than oxygen. Steric factors were invoked to explain the greater stability of the methyl adducts over the ethyl analogs. Greenwood and Srivastava recently reported (109) that the donor strength, based on thermochemical data, for the complexes \( \text{LGaX}_3 \) \( (L = \text{Et}_2\text{O}, \text{Me}_2\text{S}, \text{or Et}_2\text{S}; X = \text{Cl},\text{Br},\text{I}) \) follows the sequence \( S > C \); they also interpret the data in terms of steric and polarizability effects rather than in terms of pi-bonding.

Greenwood and Srivastava rationalize that, while boron and aluminum trihalides are class (a) or hard acids, gallium and indium trihalides are class (b) or soft acids (or possibly borderline cases). In the pi-bonding theory, gallium and indium have filled \( d_\pi \)-orbitals whereas boron and aluminum have none. Combination of these with empty \( d_\pi \)-orbitals of sulfur could afford stabilization by delocalization and this possibility would be absent when combining with oxygen bases. However, they concluded, that in the absence of specific spectroscopic or other evidence for pi-bonding in the \( (\text{R}_2\text{S})\text{GaX}_3 \) complexes, an interpretation in terms of polarizability of the ligands and acceptors is more satisfactory. Thus, Greenwood and Srivastava continue,
valency-state electron affinities (128,129) show that gallium has a higher value than that of aluminum and boron, and it will, therefore, preferentially bind soft bases such as sulfur. Indium, while having a valency-state electron affinity value intermediate between boron and aluminum, is thought to display soft acid characteristics primarily because of the large, diffuse character of its orbitals.

Greenwood and Srivastava also suggest that other stability sequences of Group III can be interpreted in terms of polarizability (109). For example, borane displays soft acid behavior. Displacement reactions show that it forms a stronger complex with trimethylphosphine than with trimethylamine. In addition, they further postulate that certain stability orders can be interpreted better in terms of the covalent theory of polarizability rather than in terms of pi-bonding. Examples are: The stability sequence Me₂Se > Me₂S for adducts with trimethylgallium (47); the behavior of trimethylboron, gallium, and indium toward trimethylamine and trimethylphosphine (256); the difference between thio- and oxoadducts of tin tetrachloride and antimony pentachloride (194); as well as the differences in complexes of the earlier transition metal halides (i.e., d⁰ systems) in their normal valency state with oxygen and sulfur donors (5,51).

Another possibility is the delocalization of non-bonding electron pairs on sulfur to the empty d-orbitals of these metals. These class (a) acids would have tightly hold outer electrons,
but the empty d-orbitals would be lowered greatly in energy. This ligand-to-metal interaction could provide added stability.

Other workers also question the use of the pi-bonding concept to rationalize experimental facts. Young, McAchran, and Shore reported (336) that the Lewis base strength of trimethylphosphine and trimethylamine, when bonded to oxygen and sulfur substituted boron heterocycles containing terminal B-H bonds, depends on the strength of the acid and not upon supplementary pi-type bonding involving d-orbitals on phosphorus and sulfur ligand atoms. In addition, Fenske (86) cautions that while the modified Wolfsberg and Helnholz approach to molecular orbital theory has had apparent success in recent applications, evaluation of the technique indicates that the results are strongly dependent upon the initial assumptions and that the importance of pi-bonding and appreciable covalent character are automatic consequences.

C. Statement of Problem

In contrast to the oxides, which have been systematically studied, there exists a paucity of data in the literature concerning the donor properties of other tertiary phosphine and arsine chalcogenides. Evidence presented in this introduction (section IB) suggests that tertiary phosphine(arsine) sulfides and selenides might be a better donors than generally believed. The determination of the validity or nonvalidity of this hypothesis is the basis for this dissertation.
D. Review of Synthesis for Potential Ligands

It is appropriate to review some general features concerning the synthesis of potential ligands such as \( \text{R}_3\text{PS} \), \( \text{R}_3\text{PSe} \), \( \text{R}_3\text{AsS} \), and \( \text{R}_3\text{AsSe} \) since their use as such is somewhat novel. This discussion is limited to cases which are not adequately reviewed in the literature or cases where a detailed understanding is necessary to explain the purpose of latter experiments.

1. Tertiary phosphine sulfides

A variety of synthetic routes are available for preparation of tertiary phosphine sulfides. These have recently been reviewed in detail by Maier (275). Reference to certain of these are also listed in Kosolapoff's monograph (169) and other more recent review articles by Maier (223) and by Berlin et al. (19).

Secondary phosphine sulfides, \( \text{R}_2\text{P(S)H} \), may be used (58) to prepare diphosphine disulfides (Eq. 3).

\[
\text{R}_2\text{P(S)H} + \text{R}_2\text{P(S)Cl} \rightarrow \text{R}_2\text{P(S)P(S)R}_2 + \text{HCl}
\]  
(Eq. 3)

These secondary phosphine sulfides can be synthesized by the addition (1:1 mole ratio) of sulfur to the phosphine in inert solvents (274).

The preparation corresponds to that of analogous oxygen compounds. Secondary phosphines are easily oxidized by air but the product usually isolated is the corresponding phosphinic
acid $R_2P(O)OH$. However, by carrying out the reaction in iso-
propyl alcohol, the secondary phosphine oxides have been isolated (291). Other methods for preparation of secondary phosphine
oxides and reactions of these compounds have been described in
a recent review (21). At the start of this investigation, no
selenium species of the type $R_2P(Se)H$ were known.

Two structures are possible for secondary phosphine oxides
and sulfides (XXIV and XXV). Infrared studies indicate that

$$
\begin{align*}
\text{XXIV} & \quad \text{XXV} \\
R_2PXH & \quad R_2PXH
\end{align*}
$$

form XXIV is correct. Bands attributable to P-H and P=S or
P=O are observed along with the absence of a characteristic
hydroxyl absorption. Thus, secondary phosphine oxides show
bands near 1190 (P=O) and 2283 cm$^{-1}$ (P-H) (21). Secondary
phosphine sulfides have a P-H absorption band (227) in the in-
frared at 2320±10 cm$^{-1}$ and a P=S band near 600 cm$^{-1}$ (alkyl)
or 640 cm$^{-1}$ (aryl). Additional evidence for structure XXIV
is obtained from $^{31}$P N.M.R. spectra. Secondary phosphine de-
rivatives show a 1:1 doublet in the phosphorus resonance. The
$J_{P-H}$ coupling constants in these are significantly greater
than in the corresponding secondary phosphines (291). There-
fore, the proton must be directly bonded to the phosphorus,
rather than by a $R_2PXH$ bond.

A second synthesis for diphoshine disulfides is by
addition of sulfur to diphosphines in an inert solvent (144, 265, 303), Eq. 4.

\[ \text{R}_2\text{PPR}_2 + 2\text{S} \rightarrow \text{R}_2\text{P(S)P(S)R}_2 \]  

(Eq. 4)

However, the most convenient preparation of the lower alkyl diphosphine disulfides is by the interaction of excess Grignard reagent with thiophosphoryl chloride \( \text{P(S)Cl}_3 \). This reaction has been termed an "anomalous" Grignard reaction. The reaction is so convenient that it has been used, rather than direct synthesis, to prepare tetraalkyldiphosphines by subsequent removal of sulfur from the corresponding diphosphine disulfides (89).

Phosphoryl chloride, \( \text{P(O)Cl}_3 \), reacts with Grignard reagents by stepwise replacement of the halogen atoms and one can obtain phosphonic and phosphinic acids as well as tertiary phosphine oxides after hydrolysis. This reaction has recently been reviewed (20).

Earlier, it had been reported (309) that tertiary phosphino sulfides are isolated from the reactions of thiophosphoryl chloride, \( \text{P(S)Cl}_3 \), with Grignard reagents in a mole ratio greater than 1:3. However, in 1949 it was reported (161) that methylmagnesium iodide reacts with \( \text{P(S)Cl}_3 \) to give a compound containing a phosphorus-phosphorus bond, \( \text{Me}_2\text{P(S)P(S)Me}_2 \), rather than trimethylphosphine sulfide. This has since been substantiated by a large number of other workers and the synthesis and properties of these compounds have recently been reviewed by Cowley (58).

Employing lower primary alkylmagnesium bromides \( \text{RMeBr} \) (\( \text{R} = \text{Me}, \text{Et}, \text{n-Pr}, \text{n-Bu}, \text{n-Amyl}, \text{and Allyl} \)), the major products isolated
are the tetraalkyldiphosphone disulfides while tertiary phosphine
sulfides, if isolated at all, are only a minor biproduct. In
contrast, long chain aliphatic Grignard reagents result in
formation of tertiary phosphine sulfides in good yields (58)
while aromatic Grignard reagents react with P(S)Cl$_3$ to produce
tertiary phosphine sulfides exclusively (263, 309). Thus, tetra-
aryldiphosphospine disulfides must be prepared by reactions such as expressed by Equations 3 and 4.

The mechanism of this "anomalous" Grignard reaction is not clear at present. Equation 5 is used to describe the reaction

$$6RMgX + 2P(S)Cl_3 \rightarrow R_2P(S)P(S)R_2 + 6MgClX + R-R$$

(Eq. 5)

but it is probably more complicated than this equation depicts. For example, the gaseous products collected during the preparation of Et$_4$P$_2$S$_2$ were ethane and ethylene and not butane as expected (282).

Similar results occur (212) with phosphonothioic di-
chlorides, RP(S)Cl$_2$, and Grignard reagents. Thus, phenyl-
phosphonothioic dichloride, when reacted with methylmagnesium bromide, yields mainly 1,2-dimethyl-1,2-diphenyldiphosphine
disulfide (XXVI). However, tolylmagnesium produces the tertiary

\[
\begin{array}{c}
\phi \\
\phi \\
\hline
\phi \\
\hline
P(S)P(S) \\
\hline
Me \\
\hline
Me \\
\end{array}
\]

XXVI
phosphine sulfide, bis(p-tolyl)phenylphosphine sulfide (254) when reacted with phenylphosphonothioic dichloride. Maier was able (211,212) to separate the meso form of 1,2-dimethyl-1,2-di-phenylphosphine disulfide from the racemic mixture.

The reaction of dialkylphosphiniothioic chlorides or bromides, \( \text{R}_2\text{P(S)X} \), with alkyl and aryl magnesium bromides produces only tertiary phosphine sulfides in high yield (119,283,284). In contrast, however, Russian workers have reported very recently (25) that they find this reaction also leads to the formation of diphosphate disulfides.

In addition, Schmutzler observed (298) that 1,4 or 1,5 di-Grignard reagents react with \( \text{P(S)Cl}_3 \) to yield coupled products (XXVII), whereas Maier found (221) that similar di-Grignard

\[
\begin{align*}
\text{XXVII} & \quad \text{(CH}_2\text{)}_n\text{P-P(}\text{CH}_2\text{)}_n^n = 4,5
\end{align*}
\]

reagents react with \( \text{MeP(S)Br}_2 \) to form cyclic, tertiary phosphines (XXVIII) rather than diphosphate disulfides. Maier also

\[
\begin{align*}
\text{XXVIII} & \quad \text{CH}_3\text{P(}\text{CH}_2\text{)}_n n
\end{align*}
\]

showed that normal replacement occurs with a similar class of compounds (Eq. 6).
\[
\begin{align*}
&\text{Cl}_2\text{P}(S)\text{(CH}_2\text{)}_n\text{P}(S)\text{Cl}_2 + 4\text{EtMgBr} \\
&\quad \rightarrow \\
&\text{Et}_2\text{P}(S)\text{(CH}_2\text{)}_n\text{P}(S)\text{Et}_2 + 4\text{MgBrCl} \\
\end{align*}
\]  
(Eq. 6)

2. Tertiary phosphine selenides

Preparative methods for tertiary phosphine selenides as well as for other organic phosphorus selenide derivatives have not been studied as extensively as their sulfur analogs. Tertiary phosphine selenides have been prepared by either direct fusion of the tertiary phosphine with elemental selenium (340) or by refluxing the phosphine with selenium in an inert solvent (171). The addition of selenium to organic phosphorus halides appears to be a general way to obtain certain phosphorus selenium intermediates (237), (Eq. 7).

\[
\text{R}_2\text{PCl} + \text{Se} \rightarrow \text{R}_2\text{P(Se)Cl} \quad \text{(Eq. 7)}
\]

A catalyst such as aluminum chloride is sometimes required (111). Tetraalkyldiphosphine diselenides are unknown. The reaction of MeP(Se)Br$_2$ with phenylmagnesium bromide produced methyldiphenylphosphine oxide after work up (212). The oxide occurs from the oxidation of the selenide in air, but the point at which this occurs is not clear from the experimental procedure.

3. Tertiary phosphine tellurides

Even less is known about preparative methods for tertiary phosphine tellurides or phosphorus tellurium intermediates. Although it has been reported (169) that tertiary phosphines
add tellurium in a reaction analogous to the addition of sulfur or selenium; Zingaro and Irgolic recently have shown that certain tertiary phosphine tellurides cannot be prepared in this manner (339).

Certain phosphorus esters add tellurium but these tellurides are very unstable and can not be distilled (111). It is not surprising then that no tetraalkyldiphosphine ditellurides have been prepared.

4. Tertiary arsine sulfides

There have been no general reviews published concerning arsine sulfides; only isolated experiments are reported in the literature.

Aliphatic arsine sulfides have been prepared by the reaction of the tertiary arsine with sulfur in a solvent such as ethanol (341,344). It appears that this reaction is not applicable for tertiary aryl arsines. However, the preparation of triphenylarsine sulfide by the reaction expressed by Equation 8 has been reported (345).

\[ \Phi_3\text{AsCl}_2 + \text{H}_2\text{S} \to \Phi_3\text{AsS} + 2 \text{HCl} \]  
(Eq. 8)

The most convenient preparation of triphenylarsine sulfide is the reaction reported by Reichle (293) where sulfur replacement of the oxygen atom in triphenylarsine oxide is accomplished by heating in carbon disulfide. The oxide may be prepared by the hydrogen peroxide oxidation of triphenylarsine (305).
Although Reichle (293) did not investigate the conversion of other tertiary arsine oxides to the corresponding sulfides by this method, he did find that other arsenic-oxygen compounds react with carbon disulfide to produce sulfur derivatives. Thus, dimethylarsenic acid yields trimethylarsine sulfide and cacodyl sulfide, $(\text{Me}_2\text{As})_2\text{S}$, by this method. In addition, phenylarsenous oxide $(\tilde{\text{O}}\text{AsO})_x$ was found to yield red crystals of the tetramer $\text{As}_4\text{S}_4$ by heating in carbon disulfide. The general utility of this reaction for preparation of tertiary arsine sulfides is suggested by Dehn's observation in 1905 (66) that triethylarsine when reacted with carbon disulfide in the presence of ethanol in a sealed tube yields triethylarsine sulfide as the product.

Sulfur replacement of oxygen also occurs (289) when hydrogen sulfide is passed through aqueous solutions of arsonic acids (Eq. 9).

$$\text{RAs}(\tilde{\text{O}})(\text{OH})_2 + 2\text{H}_2\text{S} \rightarrow \text{RAsS}_2 + 3\text{H}_2\text{O} \quad \text{(Eq. 9)}$$

These arsine disulfide products are probably polymeric. The analogous phosphorus materials, $(\text{RPS}_2)_x$ (thionophosphine sulfides), are dimers (217,226) containing a four-membered ring of two sulfur and two phosphorus atoms. In addition, the dimeric methyl- and phenylthionophosphine sulfides have been shown by X-ray diffraction (217,328) to contain a center of symmetry and posses, therefore, the trans configuration XXIX.

$$\begin{array}{ccccc} \text{R} & \text{S} & \text{S} \\ \text{P} & \text{P} & \\ \text{S} & \text{S} & \text{R} \end{array} \quad \text{XXIX}$$
Dehn found (66) that the arsine disulfides produce tertiary arsine sulfides by a disproportionation reaction when heated (Eq. 10).
\[
3R\text{AsS}_2 \xrightarrow{\Delta} R_2\text{AsS} + \text{As}_2\text{S}_5 \quad \text{(Eq. 10)}
\]

Arsenic analogs corresponding to diphosphine disulfides; i.e., \( R_2\text{As(\text{S})As(\text{S})R_2 \) are unknown. A product having the formula \((\text{Me}_2\text{As})_2\text{S}_2 \) was first prepared by Bunsen in 1843 (27) and latter by Dehn and Wilcox (67). Two different methods were employed to prepare this compound. One method involved the reaction of dimethylarsenic acid with hydrogen sulfide in a concentrated alcoholic solution (Eq. 11).
\[
2\text{Me}_2\text{As(OH)} + 3\text{H}_2\text{S} \rightarrow (\text{Me}_2\text{As})_2\text{S}_2 + \text{S} + 4\text{H}_2\text{O} \quad \text{(Eq. 11)}
\]

The other was by the reaction of dimethylarsine with excess sulfur (Eq. 12).
\[
2\text{Me}_2\text{AsH} + 3\text{S} \rightarrow (\text{Me}_2\text{As})_2\text{S}_2 + \text{H}_2\text{S} \quad \text{(Eq. 12)}
\]

An X-ray analysis (35) has shown that this compound is not a structural analog of the diphosphine disulfides but instead contains one trivalent and one pentavalent arsenic atom (XXX).
A series of compounds said to have formulations illustrated by XXXIa and XXXIb have been reported (162). The existence of

\[
\begin{align*}
\text{XXXIa} & : & \begin{array}{c}
\text{S} \ \text{S} \\
\text{RAs=AsR}
\end{array} \\
\text{XXXIb} & : & \begin{array}{c}
\text{S} \ \text{S} \\
\text{RAs=AsR'}
\end{array}
\end{align*}
\]

an arsenic-arsenic double bond is doubtful; phosphobenzene thought to contain a phosphorus-phosphorus double bond but an X-ray analysis of two forms of this compound (63) show that these are five and six membered ring compounds in the solid state. In a paper which discusses the synthesis and insecticide value of compounds such as XXXI (164), Kary states that the methyl analog, arseno As-1,2-disulfide, had a molecular weight of 242 in close agreement with a theoretical value of 244, although he did not report the method employed. A total analysis showed the empirical composition [MeAsS].

Also, Kary stated (163) that arsenonethane As-1,2-disulfide exhibits 1,3-tautomerism (XXXII) as well as dimerization (Eq. 13).

\[
\begin{align*}
\text{XXXII} & : & \begin{array}{c}
\text{S} \ \text{S} \\
\text{SH} \ \text{SH}
\end{array} \\
\text{H}_2\text{C-As=As-CH}_3 & \rightleftharpoons & \text{H}_2\text{C=As=As=CH}_2
\end{align*}
\]

(Eq. 13)
He also claimed that the compound may be chlorinated to yield materials such as XXXIII.

\[
\begin{array}{c}
\text{S} \\
\text{S} \\
\text{Cl-CH}_2\text{As=As-CH}_3 \\
\end{array}
\]

XXXIII

5. Tertiary arsine selenides

Tertiary arsine selenides have been prepared by the direct combination of the tertiary arsine with selenium in a solvent or by a fusion reaction (343).
CHAPTER II

EXPERIMENTAL

A. Purchased Materials

1. Intermediates and other chemicals

The following chemicals were supplied by the companies listed: Engelhard Industries Inc.; palladium metal and sodium tetrachloropalladate(II). Fisher Scientific; selenium powder. A. D. Mackay, New York; tellurium powder. Alpha Inorganics, Inc.; selenium (balls), sodium tetrachloroaurate(III), potassium selenocyanate, zinc(II) iodide (anhydrous), sodium hydride (50% in oil), and palladium(II) nitrate. Platinum Chemicals, Asbury Park, N.J.; sodium tetrachloroplatinate(II). Aldrich Chemicals Co., Inc.; o-dibromobenzene, diphenylchlorophosphine (b.p. 170-172°/10 mm, 132-133°/1 mm), tris(diethylaminoethyl) phosphine, phenyldichlorophosphine (b.p. 96-97°/10 mm), and 2-bromopyridine. Stauffer Chemical Co.; thiophosphorylchloride (b.p. 122-123°). M & T Chemicals, Inc.; triphenylphosphine and tri(n-butyl)phosphine. V-C Chemicals; trimethyl phosphite (b.p. 46-47°/80-81 mm). Arapahoe Chemicals, Inc.; Boulder, Colorado; phenyl and methyl magnesium bromide. Foote Mineral Co.; 1-butyllithium (1.6 M in n-hexane). K & K Laboratories; diethylphosphinothioic chloride (b.p. 83-84°/2 mm, lit.)
values - 99°/10 mm, ref. 218, and 117-120°/15 mm, ref. 170). Carlisle Chemical Co.; tri(n-octyl)phosphine. Metal Hydrides, Inc.; lithium aluminum hydride and calcium hydride. Matheson Coleman and Bell; tert butyl chloride (b.p. 50-51°), 2,2'-azobis(2-methylpropionitrile), and allyl bromide (b.p. 70.0-70.5°). Pierce Chemical Co.; Rockford, Illinois; o-bromoaniline. Columbia Organic Chemicals Co., Inc.; o-bromochlorobenzene. Eastman Organic Chemicals; triphenylarsine oxide and 1-bromo-2-nitrobenzene. Michigan Chemical Corp., Saint Louis, Michigan; gamma-dimethylaminopropylchloride hydrochloride and beta-dimethylaminocetylchloride hydrochloride. Other materials used were reagent grade. The preparation of hexaaquozinc(II) perchlorate and potassium tetranitropalladate(II) is described in the appendix.

2. Ligands

N,N,N',N'-tetramethylethylenediamine was procured from Matheson Coleman and Bell; it was dried over barium oxide and distilled from sodium, b.p. 121° (lit. value 120°, ref. 103). Tetramethyl- and tetraethylidiphosphine disulfide were originally prepared as described in the experimental section and latter they were commercially available from Orgmet, Hampstead, N.H. Tetra(n-propyl)diphosphine disulfide was prepared and supplied
by Miss Susan Mckendry. Strem Chemicals supplied 1,2-bis-(diphenylarsino)ethane.

3. Solvents

Spectral grade dichloromethane was used for the solution spectra. Tetrahydrofuran was distilled from lithium aluminum hydride before use (b.p. 65-66°). Diethyl ether employed in the Grignard syntheses was stored over sodium wire and was pipetted from the storage vessel to the reaction flask. Toluene and benzene were distilled from sodium. Acetonitrile was purified according to the method of Muney and Coetzee (261). Dimethylformamide was dried several days over anhydrous barium oxide and then distilled from fresh barium oxide (b.p. 56-57°/20 mm). Nitromethane was washed with 5% aqueous sodium bicarbonate, dried over anhydrous sodium sulphate, and then fractionated (b.p. 100-101°). Acetone was dried with potassium carbonate and distilled from \( P_4O_{10} \). All distillations were accomplished employing a heated column containing glass helices. Other solvents used were reagent grade and were not further purified.

E. Preparation of Intermediates

\textbf{Dimethylphosphinothiocarbonyl bromide, Me_2P(S)Br (120).} To a cooled suspension of tetramethyldiphosphine disulfide (37.0 g., 0.198 mole) in 200 ml. of carbon tetrachloride was added drop-wise with stirring, under nitrogen, a solution of 10.8 ml. of
bromine (31.6 g., 0.198 mole) in 300 ml. of carbon tetrachloride

\[ \text{Me}_2\text{P(S)P(S)Me}_2 + \text{Br}_2 \rightarrow 2 \text{Me}_2\text{P(S)Br} \quad (\text{Eq. 14}) \]

over a period of two hours. The resulting yellow solution was stirred for an additional 2 hr.; subsequently, the solvent was removed under nitrogen. Vacuum distillation of the residual liquid afforded 53.2 g. (77%) of dimethylphosphinothioic bromide (a colorless liquid), b.p. 94-96°/14 mm (lit. value 87-88°/14 mm., ref. 120). The compound solidified upon standing; it fumes in moist air due to hydrolysis of the phosphorus-bromine bond.

**Phenylphosphonothioic dichloride, \( \text{OPCl}_2 \).** Addition of 11.7 g. (0.367 mole) of sulfur to phenyldichlorophosphine (65.7 g., 0.367 mole) in 60 ml. of toluene produced no apparent reaction; however, refluxing the mixture under nitrogen for 90 min. produced a clear yellow solution. The solvent was removed under nitrogen and the residual liquid was vacuum distilled to give 66.7 g. (yield, 87%) of phenylphosphonothioic dichloride, a straw colored liquid, b.p. 154-157°/26 mm (lit. value 150°/26 mm, ref. 100). The PS stretching frequency of this compound could not be determined by comparison with the infrared spectrum of the starting material. Zingaro, who reported the PS stretching frequency of several compounds of this type (337), also could not assign the PS stretching frequency in this compound.

**Diphenylphosphinothioic chloride, \( \text{OP(S)Cl} \).** To 93.9 g. (0.425 mole) of diphenylchlorophosphine in 100 ml. of toluene
was added 13.6 g (0.425 mole) of sulfur and the mixture was refluxed for three hours. The solvent was removed under nitro-

\[ \text{O}_2\text{PCl} + S \rightarrow \text{O}_2\text{P(S)}\text{Cl} \]  

(Eq. 16)
gon and the residual liquid was distilled at reduced pressure to yield the light yellow product in 96% of theory (102.8 g.), b.p. 183-184°/3 mm (lit. value 160-163°/0.5 mm, ref. 215).

**Phenylphosphonoselenenic dichloride, \( \text{OP(Se)}\text{Cl}_2 \).** Addition of powdered selenium (8.82 g., 0.115 mole) to phenyldichlorophosphine (20.0 g., 0.115 mole) in 75 ml. of toluene was followed by reflux for 12 hr. under nitrogen. The solvent was removed by distillation at atmospheric pressure and the residual red liquid was cooled and filtered through filter paper to remove the unreacted selenium. Subsequently, distillation at reduced pressure afforded 20.2 g. (70%) of phenylphosphonoselenenic dichloride in 70% yield. The straw yellow liquid had a boiling point of 112-119°/mm.

**Diphenylphosphinoselenenic chloride, \( \text{OP(Se)}\text{Cl} \).** Similarly, to 23.9 g. (0.106 mole) of diphenylchlorophosphine in 100 ml. of toluene was added 8.35 g. (0.106 mole) of powdered selenium. The product was isolated as above after refluxing the mixture for 4 hr. under nitrogen. The yield was 24.8 g. (78%) of a light yellow liquid, b.p. 195-197°/1 mm.

**Diphenylphosphoryl chloride, \( \text{OP(O)}\text{Cl} \).** This intermediate was prepared by two different methods. The procedure for
the first was kindly supplied by Stauffer Chemical Co. (142). Chlorine was bubbled through a cooled (to maintain temperature below 65°) slurry of phosphorus pentoxide (34.5 g., 0.242 mole) in 173.3 g. (0.785 mole) of diphenylchlorophosphine until a yellow green solution had formed (45 min.). The chlorine flow was then reduced and the reaction mixture was heated up slowly until the reaction temperature became 140° at which time the chlorine addition was stopped. After cooling, the product was vacuum distilled to yield 159.7 g. (93%) of a colorless liquid, b.p. 175°/1 mm (lit. value 156-160°/1-2 mm, ref. 142).

In the second preparation, air, which had been dried by passing it through a tower containing several drying agents in sequence, was passed through a cooled solution of diphenyl-
\[ \phi_2P(O)Cl \rightarrow \phi_2PCl + \frac{1}{2}O_2 + \phi_2P(O)Cl \] (Eq. 20) chlorophosphine (59.6 g., 0.27 mole) in 100 ml. of toluene for 4 hours. The reaction mixture was vacuum distilled to yield 48.9 g. (76.5%) of product, b.p. 175-177°/1 mm.

**Diphenylphosphine, \( \phi_2PH \).** A modification of a literature method (330) was employed. Triphenylphosphine (159 g., 0.605 mole) in 600 ml. of tetrahydrofuran was treated with 11.3 g.
\[ \phi_3P + 2Li \rightarrow \phi_2PLi + \phiLi \] (Eq. 21) (requires 8.4 g. or 1.21 mole) of freshly cut lithium wire for 3 hr. while stirring under nitrogen. A reflux condenser must be employed because the reaction is exothermic initially; it gradually cools to room temperature. Tert-butyl chloride
(55.7 g, 0.605 mole) was added dropwise to the dark red solution to destroy the phenyl lithium. After refluxing the mixture for 10 min., it was cooled and the excess lithium was removed by filtering the reaction mixture through glass wool into another 3-necked flask under nitrogen. The lithium diphenylphosphide was hydrolyzed by addition of distilled water

\[
\text{C}_6\text{H}_5\text{PLi} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{PH} + \text{LiOH}
\]  
(Eq. 22)

and a 3.8 N hydrochloric acid solution. The cloudy water layer was washed with 100 ml. of ethyl ether and the combined organic phase was washed four times with 50 ml. portions of dilute hydrochloric acid. The organic layer was dried and then it was distilled at reduced pressure to yield 71.9 g. (64%) of diphenylphosphine (a colorless liquid), b.p. 151-155°/10-11 mm (lit. value 150-154°/10 mm, ref. 330).

Diphenylphosphine sulfide, \( \text{C}_6\text{H}_5\text{P(S)H} \) (274). Diphenylphosphine (32.2 g, 0.174 mole) in 80 ml. of toluene was refluxed under nitrogen for 90 min. with 5.55 g. (0.174 mole) of sulfur to

\[
\text{C}_6\text{H}_5\text{PH} + \text{S} \rightarrow \text{C}_6\text{H}_5\text{P(S)H}
\]  
(Eq. 23)

yield a colorless solution. The heating mantle was then replaced with an oil bath and the toluene was removed under nitrogen at atmospheric pressure. The colorless liquid solidified on cooling to yield 36.1 g. of product (97% of theory). The crude material was recrystallized from acetonitrile
to afford 23.6 g. of pure diphenylphosphine sulfide, m.p. 94-96° (lit. value 95-97°, ref. 27).

Anal. Calcd. for C_{12}H_{11}PS:
C, 66.04; H, 5.05%.

Found: C, 66.02; H, 4.99%.

Diphenylphosphine oxide, \( \phi_2P(O)H \) (291). Diphenylphosphine (20.4 g., 0.11 mole) was placed in 75 ml. of iso-propyl alcohol and the solution was cooled with an ice-water bath. Dry air was passed through the solution for one hour. An initial

\[ \phi_2PH + 1/2O_2 \rightarrow \phi_2P(O)H \quad \text{(Eq. 24)} \]
temperature rise was noted; the bath, however, kept the temperature of the reaction from rising above 20°. No further temperature rise was noted during the next four hours. The major part of the solvent was removed at reduced pressure; and, after the addition of 60 ml. of ethyl ether, the solution was cooled with shaking at dry ice/acetone temperature to produce a sticky, white solid. Trituration with ethyl ether formed a semi-powdery material which was filtered, washed with ethyl ether, and dried in vacuo to yield 14.0 g. (63% of theory) of diphenylphosphine oxide, m.p. 47-50° (lit. value 53-56°, ref. 291). The compound could not be prepared pure.

o-Bromo(diphenylarsino)benzene, \( o-BrC_6H_4As\phi_2 \) (50, 151). In a three liter flask equipped with a stirrer and thermometer were added 1000 ml. of glacial acetic acid, 100 ml. of propionic acid, 200 g. of o-bromoaniline, 70 ml. of concentrated sulfuric acid (added quickly), and finally 260 ml. of arsenic
trichloride. The mixture was cooled with an ice bath to 0-5° and maintained at this temperature while sodium nitrate (100 g.) was added in portions over a three hour period. After stirring for an additional 5 hr., the reaction was allowed to warm up slowly overnight to destroy any excess nitrous acid.

Cuprous bromide (7.0 g.) was added and the mixture stirred for 5 hr., while being heated with a boiling water bath, to decompose the diazonium salt. The reaction was cooled and filtered; the residue being washed with glacial acetic acid. One liter of concentrated sulfuric acid and a few potassium iodide crystals were added to the filtrate; and sulfur dioxide was sparged briskly through the solution, with stirring, for two hours. The red oil which had separated was removed and the remaining solution extracted with 1400 ml. of carbon tetrachloride. The oil and carbon tetrachloride extracts were combined and the solvent removed at reduced pressure. The product, o-bromo(dichloroarsino) benzene, was then vacuum distilled to yield a red oil, which solidified upon standing, in 52% of the theoretical yield (176.5 g.), b.p. 120-130°/<1 mm (lit. value 110°/0.51 mm, ref. 151).

The general Grignard procedure employed next is described later. Addition of several drops of 1,2 dibromoethane was used to clean 32.5 g. (1.34 mole) of magnesium in 250 ml. of ethyl ether and initiate reaction. Bromobenzene (212 g., 1.35 mole) in 250 ml. of ethyl ether was added dropwise at a rate sufficient to maintain gentle reflux and stirring was continued for
one hour after complete addition. Then, o-bromo(dichloroarsino) benzene (176 g., 0.581 mole) in 500 ml. of ethyl ether was added very cautiously over 3 hours, with stirring, to the cooled Grignard solution. The reaction mixture, after complete addition, was stirred for another hour, then refluxed for 45 min., and then hydrolyzed with 25% aqueous ammonium chloride after cooling to 0°. The aqueous layer was washed twice with 200 ml. of ether. The combined organic layers were dried over sodium sulphate and the ether was flash distilled under nitrogen. Absolute ethanol (50 ml.) was added to the resulting hot residue; after cooling, filtration afforded a white solid which was washed with a small amount of cold ethanol and dried several days over P₄O₁₀ in vacuo. The compound, 159.2 g. (m.p. 96.5-98°), was recrystallized from absolute ethanol and gave 114.5 g. (52% of theory) of crystalline, pure o-bromo(diphenylarsino)benzene, m.p. 100.5-101.5° (lit. value 101.5-105.5°, ref. 50).

Diphenyl(allyl)phosphine, \( \phi_2P(CH_2CH=CH_2) \). This phosphine was prepared employing the general method of Jones (155) for allyl Grignard reactions with phosphorus and arsenic halides. To a large excess of magnesium (36.5 g., 1.50 mole) in 100 ml. of ethyl ether was added allylbromide (42 ml., 0.485 mole) in 250 ml. of ethyl ether at a sufficient rate to maintain a gentle reflux (2 hr.). The resulting solution was then refluxed for an additional 90 min. After the reaction mixture sat for one hour, it was filtered under nitrogen through glass wool into another 3-necked flask. Diphenylchlorophosphine (88.3 g., 0.40
mole) in 150 ml. of ethyl ether was then added over a 3 hr. period to the Grignard solution which was cooled with an ice bath. The reaction mixture was subsequently refluxed for 30 min., then cooled and hydrolyzed with 20% aqueous ammonium chloride (The ammonium chloride solution was degassed for 1 hr. with a nitrogen sparge). The phases were separated under nitrogen, and the aqueous layer extracted three times with 100 ml. of ether. The organic layer, after drying over sodium sulphate, was vacuum distilled to give 69.8 g. (77% of theory) of diphenyl(allyl)phosphine, a colorless liquid, b.p. 126-129°/2 mm.

The phosphine was characterized by formation of two metal complexes. The reaction of the phosphine with nickel(II) perchlorate (hydrated) in absolute ethanol (4/1 mole ratio) under nitrogen resulted in the formation of a yellow complex (yield, 47%).

\[
\text{Anal. Calcd. for } [\text{NiL}_4](\text{ClO}_4)_2:\ C_{60}H_{60}Cl_4\text{NiO}_6\text{P}_4:
\]

\[
\text{C, 61.98; H, 5.20%}.
\]

\[
\text{Found: C, 60.88; H, 5.12%.}
\]

A white precipitate was isolated from the reaction of 2.08 g. (9.2 mole) of the phosphine with 10 ml. of a saturated solution of mercury(II) chloride in ethanol. The product weighed
4.30 g. (94% based on HgCl₂), m.p. 191° decomp.

Anal. Calcd. for HgCl₂, C₁₅H₁₅Cl₂HgP:
C, 35.19; H, 3.04%.

Found: C, 35.64; H, 3.08%.

2-Chloroethyldimethylamine. Precaution must be employed in handling this material, which was procured as its hydrochloride salt, since it is a type of mustard.

The hydrochloride salt, Me₂NCH₂CH₂Cl·HCl, (50 g., 0.347 mole) was dissolved in 50 ml. of distilled water. The following compounds were added in sequence and the temperature of the solution was kept below 30°: 0.25 g. citric acid, 10 g. of sodium chloride, 150 ml. of ethyl ether, and 56 g. of a cooled, 25% aqueous sodium hydroxide solution. After stirring vigorously for 1 hr., the mixture was transferred to a separatory funnel and allowed to settle for an additional hour. The aqueous layer (lower) was discarded in a hood. The ether layer was partially dried by stirring for 30 min. with 25 g. of a 50% potassium carbonate solution, and then it was dried overnight in the freezer over sodium sulphate. The ether was removed by distillation and the free amine was vacuum distilled to yield 23.1 g. (61%) of 2-chloroethyldimethylamine, b.p. 42°/36 mm.

3-Chloropropyldimethylamine. This compound was also obtained as its hydrochloride salt and the same precautions were observed during its extraction. For instance, gloves were worn, the work was done in the hood, and care was taken when cleaning the equipment. The white, hydrochloride salt, Me₂NCH₂CH₂CH₂Cl·HCl,
(153 g., 1 mole) was dissolved in 158 g. of distilled water and, with external cooling, the following compounds were added: 0.80 g. citric acid, 300 ml. of benzene, and 190 g. of a 25% aqueous sodium hydroxide solution. The separation was performed as above. Distillation of the organic layer afforded, in 60% yield, the desired 3-chloropropylidimethylamine, b.p. 38.5°/22 mm. Workman found (334) that higher yields were obtained if the amine was extracted with ethyl ether in place of benzene. Both this compound and its analog, 2-chloroethyldimethylamine, were used immediately after their isolation.

C. Synthesis of Ligands

1. Tertiary phosphine sulfides

Trimethylphosphine sulfide, Me$_3$PS (119,120). Dimethylphosphinothioic bromide (51.5 g., 0.297 mole) in 100 ml. of ethyl ether was added dropwise, under nitrogen, with vigorous stirring to an ice cooled solution of 3N methylmagnesium bromide (175 ml., 0.525 mole). After stirring for 8 hours at room temperature, the reaction was refluxed for an additional hour, cooled and hydrolyzed with dilute (3.8N) hydrochloric acid. The ether layer was combined with four 200 ml. portions of ether used for extraction of the aqueous layer; and the total volume was evaporated. The resulting white solid was recrystallized from cyclohexane, m.p. 155-157° (lit. value 155-156°, ref. 120). Yield, 11.6 g. (42% of theory).
Triphenylphosphine sulfide, $\text{S}_2\text{PS}$. Sulfur (6.4 g., 0.20 mole) was added portionwise to a cooled solution of triphenylphosphine (42.2 g., 0.161 mole) in 100 ml. of carbon disulfide.

$$\text{S}_2\text{P} + \text{S} \rightarrow \text{S}_2\text{PS}$$

(Eq. 27)

After the addition was completed, the mixture was refluxed for one hour. The resulting insoluble product was isolated by filtration and recrystallized from absolute ethanol. Yield, 19.3 g., 84%. M.p. 158-159° (lit. 157.5°, ref. 248; 158°, ref. 256).

Diphenyl(o-diphenylarsinophenyl)phosphine sulfide, $\text{S}_2\text{P}(\text{O}_{\text{As}}\text{C}_6\text{H}_4)\text{PS}$. To a cooled, stirred solution of $\text{o}$-bromo $\text{S}_2\text{P}(\text{O}_{\text{As}}\text{C}_6\text{H}_4)\text{PS}$, To a cooled, stirred solution of $\text{o}$-bromo (diphenylarsino)benzene (24.8 g., 0.064 mole) in 200 ml. of ethyl ether (nitrogen atmosphere) was added 40 ml. of 1.6N 1-butyllithium (0.064 mole) over a period of 90 min.; the reaction was stirred an additional hour at 0.5°. Diphenylphosphinothioic chloride (16.2 g., 0.064 mole) in 50 ml. ethyl ether was then added over a period of 45 minutes. The reaction was stirred for two hours at room temperature and hyrdolozed with 1/5N hydrochloric acid. The resulting solid was isolated by filtration; washed consecutively with distilled water, abs. ethanol, and ether; and recrystallized from n-butanol to
produce 15.3 g. (yield, 46%) of a white, crystalline compound, m.p. 190-192°.

Anal. Calcd. for C\(_{30}\)H\(_{24}\)AsPS:
C, 68.96; H, 4.63; S, 6.14%.

Found: C, 68.19; H, 4.64; S, 6.22%.

Tetramethyldiphosphine disulfide, Me\(_2\)P(S)P(S)Me\(_2\) (45).

The general procedure described here applies to all the Grignard reactions performed.

A 1-liter, three necked, round bottom flask containing 54.8 g. (2.25 mole, 50% excess) magnesium, glass stirrer, dropping funnel, reflux condenser, and pipettes were all dried in an oven overnight (110°). The apparatus was assembled quickly and flushed with a nitrogen stream which exited through a drying tube, containing P\(_4\)O\(_{10}\), affixed to the open end of the reflux condenser.

The magnesium turnings were covered with 200 ml. of ethyl ether. Methyl iodide (213 g., 1.50 mole) in 200 ml. of ethyl ether was added at a sufficient rate to maintain gentle reflux after initiation of the reaction by the addition of several ml. of methyl iodide. A nitrogen stream was maintained throughout the reaction. The resulting Grignard solution was refluxed one hour, cooled, and filtered through glass wool using a curved adapter (containing two \# 24/40 male joints) into another reaction flask under nitrogen. Then thiophosphoryl chloride,
(65.4 g., 0.386 moles) in 100 ml. ethyl ether was added drop-wise over a period of one hour. The reaction was hydrolyzed with 10% sulfuric acid (cooled to room temperature). The insoluble product was isolated by filtration and dried under partial vacuum at 60° overnight. Recrystallization from toluene/ethanol (3/1) afforded 20.7 g. (yield, 58%) of white needles, m.p. 220-221° (lit. value 215-221°, ref. 45).

Tetraethyldiphosphine disulfide, $\text{Et}_2\text{P}(\text{S})\text{P}(\text{S})\text{Et}_2$ (45).
This compound was prepared in an analogous manner from ethylmagnesium bromide and thiophosphoryl chloride and was recrystallized from ethanol/water. Yield, 46% of theory. M.p. 73-77° (lit. value 75-76, ref. 45).

1,2-Dimethyl,1,2-diphenyldiphosphine disulfide, $\text{MeP}(\text{S})\text{P}(\text{S})\text{Me}$ (212). The interaction of excess methylmagnesium bromide with phenylphosphonothioic dichloride resulted in a product (87% of theory) which was extracted with boiling abs. ethanol to yield, upon cooling, white crystals (m.p. 144-146°). The residue was recrystallized from acetone to give a white
powder, m.p. 202-204°. Maier found (212) these two products melted at 145-146° and 206-208°, respectively.

2. **Tertiary phosphine selenide**

**Tri(n-butly)phosphine selenide, (n-Bu)_3PSe (340).** To 56.5 g. (0.28 mole) of tri(n-butyl)phosphine (weighed in dry box) in 60 ml. of toluene was added, under nitrogen, 22.1 g. (0.28 mole) of selenium powder. The toluene was removed by distillation under nitrogen after two hours of reflux and the remaining liquid was distilled to give 65.3 g. (82% of theory) of a light yellow liquid, b.p. 142-146°/0.40-60 mm. (lit. value 150-151°/0.8 mm, ref. 340).

**Triphenylphosphine selenide, Φ₃PSe.** To potassium selenocyanate (7.2 g., 0.05 mole) in 60 ml. of acetonitrile was added rapidly, with stirring, triphenylphosphine (13.1 g., 0.05 mole) dissolved in 60 ml. of warm acetonitrile. A white, crystalline material began precipitating immediately. The solvent was evaporated after the reaction had been stirred for one hour. The solid residue was transferred to a sintered glass funnel and was washed with 300 ml. of distilled water to remove the potassium cyanide, then with 10 ml. cold abs. ethanol, and finally with ethyl ether. The crude product, after drying for 12 hr. over P₂O₅ in vacuo, melted at 183-186° and weighed 16.4 g. (yield, 96%). Small, white crystals of analytical purity were
obtained after one recrystallization from abs. ethanol, m.p. 187-188° (lit. values - 183-184°, ref. 248; 187-188°, ref. 302).

Anal. Calcd. for \( \text{C}_{18}\text{H}_{15}\text{PSe} \): 
- C, 63.35; H, 4.43; Se, 23.11%.
- Found: C, 63.36; H, 4.45; Se, 23.00%.

The following were prepared in an analogous manner.

**Tri(m-tolyl)phosphine selenide, \((\text{m-C}_7\text{H}_7)_3\text{PSe} \):** White, crystalline compound (yield, 94%) recrystallized from abs. ethanol, m.p. 139-140°.

Anal. Calcd. for \( \text{C}_{21}\text{H}_{21}\text{PSe} \):
- C, 65.80; H, 5.52; Se, 20.60%.
- Found: C, 65.57; H, 5.50; Se, 20.36%.

**Tri(p-tolyl)phosphine selenide, \((\text{p-C}_7\text{H}_7)_3\text{PSe} \):** White needles (yield, 95%) recrystallized from abs. ethanol, m.p. 198-198.5° (lit. value 193°, ref. 247).

Anal. Calcd. for \( \text{C}_{21}\text{H}_{21}\text{PSe} \):
- C, 65.80; H, 5.52; Se, 20.60%.
- Found: C, 65.56; H, 5.45; Se, 20.18%.

**Diphenyl(allyl)phosphine selenide, \( \varphi_2(\text{CH}_2\text{CH}≡\text{CH}_2)\text{PSe} \):** White, crystalline compound (yield, 89%) recrystallized from abs. ethanol, m.p. 78-79°.

Anal. Calcd. for \( \text{C}_{15}\text{H}_{15}\text{PSe} \):
- C, 59.03; H, 4.95; Se, 25.87%.
- Found: C, 58.99; H, 5.13; Se, 25.62%.
1,2-Bis(diphenylphosphino)ethane,
\( \text{O}_2\text{P(Se)}\text{CH}_2\text{CH}_2\text{P(Se)}\text{O}_2 \). White needles, recrystallized from n-butanol (yield, 84%), m.p. 194-195°.

**Anal.** Calcd. for \( \text{C}_{26}\text{H}_{24}\text{P}_2\text{Se}_2 \):
- C, 56.13; H, 4.35; Se, 28.39%.
- Found: C, 56.37; H, 4.42; Se, 28.09%.

Diphenyl(3-dimethylaminopropyl)phosphine selenide,
\( \text{O}_2\text{P(Se)}\text{CH}_2\text{CH}_2\text{CH}_2\text{Me}_2 \). White, crystalline compound (yield, 87%) recrystallized from abs. ethanol, m.p. 90-91°.

**Anal.** Calcd. for \( \text{C}_{17}\text{H}_{22}\text{NPSe} \):
- C, 58.29; H, 6.33; Se, 22.54%.
- Found: C, 58.52; H, 6.50; Se, 22.30%.

3. Synthesis of other ligands

Triphenylarsine sulfide, \( \text{O}_3\text{AsS} \) (293). Triphenylarsine oxide (25 g., 0.078 mole) was refluxed in 100 ml. of carbon disulfide for two hours. The residue, after evaporation of the solvent, was recrystallized from abs. ethanol to produce 25.3 g. (yield, 97%) of white, needle crystals, m.p. 165.5-166.5° (lit. value 163.5-164.5°, ref. 293; 162°, ref. 172).

1,2-Bis(diphenylphosphino)ethane, \( \text{O}_2\text{PCH}_2\text{CH}_2\text{P} \). A modification of Chatt's original method (38) was employed. Under nitrogen, triphenylphosphine (78.7 g., 0.3 mole) in 300 ml. of tetrahydrofuran was stirred for three hours with freshly cut lithium wire (4.16 g., 0.6 mole). To the resulting deep red
solution was slowly added t-butyl chloride (27.6 g., 0.3 mole) followed by refluxing for 15 minutes. The reaction flask was cooled with an ice bath as 1,2 dichloroethane (14.8 g., 0.15 mole) in 50 ml. of tetrahydrofuran was added dropwise during a period of 30 minutes. The reaction was refluxed for an additional hour, cooled, and then 450 ml. of methanol was added. Subsequent addition of distilled water caused the ligand to precipitate, and it was isolated by filtration, washed with distilled water, and dried over \( \text{P}_4\text{O}_{10} \) in vacuo. It was re-crystallized by dissolving in dichloromethane, filtering, and subsequent evaporation of the solvent. Yield, 39.0 g. (65% of theory); m.p. 135-137° (lit. value 143.5-144.0°, ref. 38).

**Diphenyl(2-dimethylaminoethyl)phosphine, \( \text{P}_2\text{PCH}_2\text{CH}_2\text{NMe}_2 \).**

Lithium diphenylphosphide (0.20 mole) in 200 ml. of tetrahydrofuran was prepared as in the previous synthesis and t-butyl chloride (22.3 g., 0.207 mole) was employed to selectively destroy the phenyllithium which was formed in the reaction. To the cooled solution of lithium diphenylphosphide was added, with stirring over an one hour period, a solution of

\[
\text{P}_2\text{P} + \text{CH}_2\text{Cl} \rightarrow \text{P}_2\text{CH} + \text{P} + \text{Cl} \\
\text{P}_2\text{CH} + \text{Cl} \rightarrow \text{P}_2\text{C} + \text{Cl}_2
\]

(Ref. 36)

2-chloroethyl(dimethyl)amine (22.3 g., 0.207 mole) in 50 ml. of
tetrahydrofuran. The reaction was refluxed one hour, cooled, and 25 ml. of methanol followed by 150 ml. of distilled water was added. The aqueous layer was washed with 100 ml. of ethyl ether and this was combined with the organic layer which had separated. The solvent was removed under nitrogen and the product was vacuum distilled after drying over sodium sulphate, b.p. 179-181°/<1 mm. Diphenyl(2-dimethylaminoethyl)phosphine is a yellow liquid. Yield, 13.0 g. (25%).

Diphenyl(3-dimethylaminopropyl)phosphine, \( \phi_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2 \).

This ligand was prepared by two different synthetic routes.

In the first, lithium diphenylphosphide (0.192 mole) in 300 ml. of tetrahydrofuran was prepared by the cleavage of \( \phi_2\text{PPh} + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{ONMe}_2 \) (Eq. 37) triphenylphosphine with lithium. To the cooled, stirred solution was added 3-chloropropyl(dimethylamine) (46.8 g., 0.385 mole) in 50 ml. of tetrahydrofuran over a period of 45 minutes. Addition of 300 ml. of methanol and 400 ml. of distilled water caused separation of a light oil; this was separated and then dried over sodium sulphate. A cloudy distillate was obtained upon distillation, b.p. 160-170/1 mm. Yield, 32.7 g. (63%).

The second method involved the Grignard derivative of the amine. To magnesium turnings (8.7 g., 0.357 mole) covered with 40 ml. of tetrahydrofuran was added, at a sufficient rate to maintain reflux, 3-chloropropyl(dimethylamine) (41.5 g.,
0.34 mole). The reaction had been initiated by the addition of a small amount of 1,2-dibromoethane.

\[
\begin{align*}
\Phi_2\text{PCl} + \text{ClMgCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2 & \rightarrow \\
\Phi_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2 + \text{MgCl}_2
\end{align*}
\] (Eq. 38)

After it had been refluxed for 30 min., the reaction solution was filtered under nitrogen through glass wool into another 3-necked reaction flask. Diphenylchlorophosphine (75.0 g., 0.34 mole) in 75 ml. of tetrahydrofuran was added to the cooled, stirred Grignard solution over a period of 40 minutes. The ivory-brown precipitate, which formed upon refluxing the mixture for one hour, dissolved when the reaction mixture was cooled with an ice/water bath. The cooled solution was hydrolyzed with 3N hydrochloric acid which had been purged with a nitrogen stream for one hour before use. A single, clear yellow phase resulted, and the ethyl ether and excess 25% sodium hydroxide solution were added and the mixture shaken in a separatory flask to effect extraction. The aqueous layer was washed with 100 ml. of ether and the combined organic phase was washed with three 100 ml. portions of dilute sodium hydroxide solution. The organic layer was then dried over sodium sulphate and vacuum distilled, b.p. 175-178°/8 mm. The straw yellow liquid, diphenyl-3-dimethylaminopropyl)phosphine, was obtained in 63% yield (57.8 g.).

The material was characterized for formation of the di-quaternary salt by reacting excess methyl iodide with it in ethyl
ether under nitrogen. Yield, 22% of a hygroscopic white solid.

**Anal.** Calcd. for $\text{C}_{19}\text{H}_{28}\text{NP}_2$:

- C, 41.10; H, 5.08%.
- Found: C, 41.31; H, 5.06%.

**Diphenyl(o-diphenylarsinophenyl)phosphine,**

$\mathcal{C}_2(\mathcal{C}_2\text{AsC}_6\text{H}_4)\mathcal{P}$. To a cooled, stirred solution of o-bromo (diphenylarsino)benzene (24.8 g., 0.064 mole) in 200 ml. of ethyl ether (nitrogen atmosphere) was added 40 ml. of 1.6 N 1-butyllithium (0.064 mole) over a one hour period and the reaction was stirred an additional 90 min. at 0-5°. Diphenylchlorophosphine (14.1 g., 0.064 mole) in 100 ml. of ethyl ether was then added over a period of one hour. The reaction was stirred for three hours at room temperature and then hydrolyzed with 1/5N hydrochloric acid. The resulting solid was isolated by filtration; washed consecutively with distilled water, abs. ethanol, and ether; and recrystallized from n-butanol to produce 15.8 g. (50%) of a white, crystalline compound, m.p. 190.5-192°. Although both this ligand and its phosphine sulfide analog melt at nearly the same temperature, their analyses and infrared spectra are different.

**Anal.** Calcd. for $\text{C}_{30}\text{H}_{24}\text{AsP}$:

- C, 73.47; H, 4.93%.
- Found: C, 72.59; H, 5.13%.
D. Attempted Syntheses

1. Phosphine oxide systems

Tetraphenyldiphosphine dioxide, \( \Phi_2P(O)P(O)\Phi_2 \) (287). To 500 ml. of ethyl ether containing 64.4 g. (0.431 mole) of

\[
2\text{Ar}_2PCl + 2\text{R}_3N + H_2O + 1/2O_2 \rightarrow \text{Ar}_2P(O)P(O)\text{Ar}_2 + 2\text{R}_3N\cdot \text{HCl}
\]

(Eq. 39)

diethylaniline and 0.256 mole of distilled water (.46 g.) was added dropwise at 5-10° a solution of 95.3 g. (0.431 mole) of diphenylchlorophosphine in 400 ml. of ethyl ether. The reaction was allowed to stir overnight open to air and, after filtering, was washed with 1600 ml. of distilled water. A white solid, which weighed 60.6 g., was obtained after drying the material over \( P_4O_{10} \) for 48 hr. in vacuo. The infrared spectrum of this compound agreed with the published spectrum of tetraphenyldiphosphine dioxide (174); however, it melted at 147-153° rather than 167°, the m.p. of tetraphenyldiphosphine dioxide (174, 287). After one recrystallization from acetone/ether the material melted at 147-148°. For comparison, \( \Phi_2P(O)OH \) melts at 191-192° (174) and \( \Phi_3PO \) melts at 153°. The reaction was repeated several times, in each case the experimental results of ref. 287, as expressed by Eq. 39, could not be reproduced.

Other attempts involved tetraphenyldiphosphine as the intermediate. Diphenylchlorophosphine was found not to undergo a Wurtz type coupling with lithium in dry toluene as the
solvent; however, it does if one employs tetrahydrofuran as the solvent. The following reaction describes such a synthesis.

\[ 2\Phi_2PCl + 2Li \rightarrow \Phi_2P\Phi_2 + 2LiCl \]  

(Eq. 40)

The entire reaction was carried out under nitrogen. To 0.70 g. (0.10 mole) of freshly cut lithium wire in 100 ml. of tetrahydrofuran was added, with stirring over a one hour period, a solution of 22 g. (0.10 mole) diphenylchlorophosphine in 100 ml. of tetrahydrofuran. The mixture was then refluxed and a white solid formed as the lithium gradually disappeared. The solution remained colorless but a red color was visible near the unreacted lithium when the stirrer was stopped (i.e., similar to the preparation of \( \Phi_2PLi \) by reacting triphenylphosphine with lithium). All the lithium had completely reacted after two hours and there was a large amount of a white precipitate in the straw yellow solution. Distilled water (75 ml.) was added to dissolve the lithium chloride and the two phases were separated under nitrogen. The organic phase, after drying over sodium sulphate under nitrogen, was evaporated by means of a nitrogen stream. Upon cooling the oil in a dry ice/acetone slush, a white, sticky solid formed. The solid melted on warming to room temperature. Tetraphenyldiphosphine should melt at 120.5° (174). Since the synthesis of tetraphenyldiphosphine dioxide did not require isolation of tetraphenyldiphosphine, it was decided to prepare the latter in situ.
In a reaction similar to the above, the tetrahydrofuran layer was treated with mercury oxide, instead of being evaporated down. A white solid was isolated from this reaction which had a m.p. of 190-193°. This appeared to be diphenyl phosphinic acid, \( \Phi_2P(O)(OH) \), and apparently the mercury oxide resulted in cleavage of the phosphorus-phosphorus bond.

**Anal.** Calcd. for \( \text{C}_{12}\text{H}_{11}\text{PO}_2 \):

\[
\begin{align*}
\text{C, } 66.1; \text{H, } 5.0\%.
\end{align*}
\]

**Found:** C, 65.5; H, 5.02%.

Tetraphenyldiphosphine was again prepared in situ in tetrahydrofuran, but this time no water was added to dissolve the lithium chloride. The passage of dried air through the resulting solution produced an exothermic reaction; it was

\[
\Phi_2\text{PP} \Phi_2 + O_2 \rightarrow \Phi_2\text{P(O)P(O)Φ}_2
\]  
(Eq. 41)

cooled with an ice/water bath while air was passed through the solution until no further temperature rise occurred. Evaporation of the solvent produced an oil which could not be crystallized.

In another reaction, 0.63 g. (0.091 mole) of freshly cut lithium wire was added to 2.5 g. (0.091 mole) of diphenyl-phosphoryl chloride, in 100 ml. of tetrahydrofuran. The lithium dissolved after refluxing the mixture under nitrogen

\[
2\Phi_2\text{P(O)Cl} + 2\text{Li} \rightarrow \Phi_2\text{P(O)P(O)Φ}_2 + 2\text{LiCl}
\]  
(Eq. 42)
for one hour; there was no precipitate in this case. Addition of 300 ml. of distilled water to the resulting yellow solution caused separation of a dense oil which slowly crystallized to a solid mass. The product melted at 140-145°. Again, the melting point is 20° lower than the desired compound although its infrared spectrum also resembled that of tetraphenyldiphosphine dioxide.

2. Phosphine sulfide systems

**Tetraethylldiphosphine disulfide by a different method.** To 23.8 g. (0.015 mole) of diethylphosphinothioic chloride was added 2.25 g. (0.015 mole) of 2,2'-azobis(2-methylpropionitrile). There appeared to be no reaction at room temperature; however, a homogeneous solution resulted at 42° when the reaction was heated with an oil bath. The reaction was then maintained at 85° for one hour. No visible reaction occurred and no precipitate appeared upon cooling.

**Tetrphenyldiphosphine disulfide.** Diphenylphosphinothioic chloride (5.1 g., 0.02 mole) in 50 ml. of tetrahydrofuran was added to 2.4 g. (0.01 mole) of magnesium covered with 50 ml. of tetrahydrofuran. Nitrogen was flushed through the system while it was refluxed for five hours. There was no evidence that a reaction occurred; thus, the Wurtz coupling did not occur in this case.

To 6.3 g. (0.025 mole) of diphenylphosphinothioic chloride was added 4.98 g. (0.025 mole) of mercury. The materials were
heated under nitrogen with an oil bath at 110° for several hours. The only noticeable reaction was that the mercury had darkened.

\[ 2\phi_2P(S)Cl + 2M \rightarrow \phi_2P(S)P(S)\phi_2 + 2MCl \]  
\text{(Eq. 43)}

In another reaction, diphenylphosphine sulfide (10.86 g., 0.05 mole) and diphenylphosphinothioic chloride (12.64 g., 0.05 mole) were heated under nitrogen with an oil bath at 100° for six hours. The material solidified upon cooling; it was re-crystallized from methanol and dried over P4O10. The material weighed 8.7 g. and had a m.p. of approximately 80°. It gave an odor of hydrochloric acid but its infrared spectrum resembled both starting materials. The presence of a phosphorus-hydrogen stretching frequency illustrated that the reaction did not occur. This reaction is reported in the literature (263) but could not be duplicated here.

The same reaction was performed employing dry toluene as the solvent. The addition of pyridine produced no insoluble precipitate of pyridine hydrochloride. A very small amount of white precipitate formed after refluxing for several hours; however, no coupled product could be isolated.

In another attempt 21.9 g. (0.0365 mole) of diphenylphosphinothioic chloride was combined, under nitrogen, with 0.6 g. (0.0365 mole) of freshly cut lithium wire. The reaction
was refluxed for five hours. All the lithium had then reacted,

$$2 \phi_2 P(S)Cl + 2Li \overset{2}{\rightarrow}$$

$$\phi_2 P(S)P(S)\phi_2 + 2LiCl$$

(Eq. 45)

a white solid had formed, and the tetrahydrofuran solution was yellow. Distilled water was then added (100 ml.) and the reaction was allowed to sit overnight. A dense oil separated and from it a solid (0.7 g.) which melted at 157° was obtained. Tetraphenyldiphenyldiphosphine disulfide should have melted at 168.5° (174).

The reaction was repeated and two phases occurred after adding 35 ml. of water to the mixture. The tetrahydrofuran layer was separated and evaporated to a white oil. Addition of hot 95% ethanol, filtration, and cooling the solution gave another oil from which a small amount of solid separated. The solid melted at 120° but its infrared spectrum resembled that of tetraphenyldiphenyldiphosphine disulfide (174). The aqueous phase precipitated silver chloride when treated with a silver nitrate solution. The absence of a dark material indicated that no silver sulfide was formed. Therefore, chloride ion but no $S^{-2}$ was formed during the reaction.

Also, diphenylphosphine sulfide (5.24 g., 0.024 mole) was dissolved in 30 ml. of toluene and the resulting solution was added, under nitrogen, to 8 ml. (0.024 mole) of a 3N methylmagnesium bromide solution in ether. The appearance of bubbles

$$\phi_2 P(S)H + MeMgBr \rightarrow$$

$$\phi_2 P(S)MgBr + CH_4$$

(Eq. 46)
indicated gas evolution and two distinct layers appeared to be present. Diphenylphosphinothioic chloride (6.1 g., 0.024 mole)

\[ \Phi_2\text{P(S)}\text{MgBr} + \Phi_2\text{P(S)}\text{Cl} → \]

\[ \Phi_2\text{P(S)}\text{P(S)}\Phi_2 + \text{MgBrCl} \]

(Eq. 47)
in 20 ml. of toluene was then quickly added. A hazy gray color resulted and, after one hour of reflux, a white solid was obtained on cooling the mixture. Following hydrolysis with 3.8N hydrochloric acid, the organic layer was separated and washed with more of the dilute acid solution. Evaporation of the solvent left a liquid which solidified upon addition of ethanol followed by water. The white material (0.98 g.) melted partially at 96-100° and completely melted at approximately 130°. The infrared spectrum of the compound showed that the material isolated was diphenylphosphine sulfide.

Finally, a white slurry was produced by adding 20 ml. of tetrahydrofuran to 1.0 g. of sodium hydride (50% oil, 0.50 g., 0.021 mole). To this was added, under nitrogen, 4.52 g. (0.021 mole) of diphenylphosphine sulfide in 40 ml. of tetrahydrofuran over a period of one hour. Bubbles were noticed and at the end of the reaction there was a white solid present in a

\[ \Phi_2\text{P(S)}\text{H} + \text{NaH} \xrightarrow{2} \Phi_2\text{P(S)}\text{Na} + \text{H}_2 \]

(Eq. 48)
light green solution. To this mixture was added 5.3 g. (0.012 mole) of diphenylphosphinothioic chloride in 20 ml. of tetrahydrofuran over a period of 45 minutes. The reaction mixture was then refluxed for 30 minutes and, after cooling, was hydrolyzed with water. No violent hydrolysis was evident,
indicating that the sodium hydride had reacted. The organic phase was separated, dried over sodium sulphate, and evaporated to an oil. Absolute ethanol was added and the mixture was heated and filtered. Upon cooling, a small amount of white crystals formed (0.8 g.), m.p. 153-175°. The product was not purified further.

1,1-Diethyl 2,2-diphenyldiphosphine disulfide. Under nitrogen, 8.7 g. (0.04 mole) of diphenylphosphine sulfide and 6.3 g. (0.04 mole) of diethylphosphiniothioic chloride were heated at 90-100° for 6 hours. Upon cooling, a solid mass in a trace of liquid remained. The crude solid showed an infrared spectrum comparable only with diphenylphosphine sulfide and melted at 82-97°.

1,1-Dimethyl 2,2-diphenyldiphosphine disulfide. A solution of diphenylphosphine sulfide (4.36 g., 0.02 mole) in 10 ml. of toluene was added to 3.46 g. (0.02 mole) of dimethylphosphiniothioic bromide in 40 ml. of toluene under nitrogen. No precipitate occurred; however, addition of 1.61 ml. (0.02 mole) of pyridine caused a white precipitate to form. The reaction mixture was filtered, washed with toluene, and the filtrate evaporated to dryness. The resulting solid was recrystallized from ethanol to yield 3.43 g. of a white solid, m.p. 94-96°. Both the melting point and the infrared spectrum, which showed a P-H stretching frequency, indicated that this product was the
starting material, diphenylphosphine sulfide. Further experiments showed that dimethylphosphinothioic bromide itself reacted with pyridine in toluene to form an insoluble, hygroscopic solid.

Also, tetramethyldiphosphine disulfide (0.93 g., 5 mmole) and diphenylphosphine sulfide (1.09 g., 5 mmole) were dissolved in 30 ml. of warm toluene. The white needles which formed upon cooling, after refluxing for one hour, melted at 224.5-225.5°.

$$\text{Me}_2\text{P(S)P(S)Me}_2 + \text{Me}_2\text{P(S)H} \rightarrow \text{Me}_2\text{P(S)P(S)Me}_2 \downarrow + \text{Me}_2\text{P(S)H}$$

(Eq. 50)

The melting point and infrared spectrum of the product isolated indicated that it was one of the starting materials, Me₂P(S)P(S)Me₂, and it was recovered in 81% yield.

Diphenyl(allyl)phosphine sulfide. The first attempt to prepare this compound was direct combination of the phosphine with sulfur. Under nitrogen, to diphenyl(allyl)phoshine (5.2 g., 0.023 mole) in 40 ml. of benzene was added 0.74 g. (0.023 mole) of sulfur; heat was evolved. The reaction was refluxed for one hour but no crystals formed on cooling; evaporation of the solvent left an oil which could not be crystallized.

The method of Screttas and Isbell (302) was also tried. To 2.99 g. (6 mmole) of the mercury chloride salt of the phosphine was added 50 ml. of 95% ethanol and 25 ml. of ammonium polysulfide. After refluxing the mixture for one hour, it was filtered and the black residue of mercury sulfide was washed with 50 ml. of warm 95% ethanol. Evaporation of the solvent left an oil which could not be crystallized.
Diphenyl(3-dimethylaminopropyl)phosphine sulfide. In 50 ml. of benzene, under nitrogen, was placed 2.0 g. (7.4 mmole) of diphenyl(3-dimethylaminopropyl)phosphine. Sulfur (0.26 g., 8.1 mmole) dissolved in an exothermic reaction when added to the phosphine solution. The reaction was refluxed for one hour and allowed to cool overnight; no crystals formed and evaporation of the solvent left a yellow oil which could not be crystallized.

Triphenylphosphine sulfide by the interaction of triphenylphosphine with potassium thiocyanate. To triphenylphosphine (0.79 g., 3 mmole) dissolved in 10 ml. of warm acetonitrile was added potassium thiocyanate (0.29 g., 3 mmole) in 10 ml. of acetonitrile. Only unreacted triphenylphosphine was recovered

\[ \text{OP} + \text{KCN} \rightarrow \text{OPS} + \text{KCN} \]  
(Eq. 51)

after evaporation of the solvent and washing the residue with distilled water.

Alpha-(diphenylphosphino sulfide)acetic acid, \( \text{OP(S)}\text{CH}_2\text{C(O)}\text{OH} \). Diphenylphosphine sulfide, (4.52 g., 0.021 mole) and monochloroacetic acid (1.97 g., 0.021 mole) were dissolved in 50 ml. of chloroform and refluxed under nitrogen for four hr. The solvent was evaporated and the residue recrystallized from hot abs. ethanol; only unreacted diphenylphosphine sulfide could be isolated (m.p. 95-97.5°). The reaction apparently did not proceed under these conditions.
2-(Diphenylphosphino)pyridine. Lithium diphenyl phosphide was prepared in situ (0.1 mole) in tetrahydrofuran by the usual procedure. To this solution was added 2-bromopyridine in 20 ml.

\[ 2\text{-BrC}_5\text{H}_5\text{N} + \text{LiBr} \xrightarrow{2\text{OH}} 2\text{-}2\text{-}(\text{O}_2\text{P})\text{C}_5\text{H}_5\text{N} + \text{LiBr} \]  
(Eq. 53)

of tetrahydrofuran over a one hour period at reflux. The resulting deep brown solution was cooled and hydrolyzed with distilled water. The organic phase, upon evaporation, yielded only an intractable brown residue which was not further characterized.

2-(Diphenylphosphino Sulfide)pyridine. To a solution of 1.14 g. (0.01 mole) of 2-chloropyridine in 10 ml. of ethyl ether was added 2.18 g. (0.01 mole) of diphenylphosphine sulfide in 50 ml. of a 2:3 toluene/ether solution. No precipitate occurred either upon mixing the solutions or upon addition of 2 ml. of pyridine to the mixture. If reaction occurred hydrochloric acid would have been produced and pyridine hydrochloride would have precipitated.

In another reaction, diphenylphosphine sulfide (l.74 g., 8 mmole) was dissolved in 30 ml. of a 1:1 toluene/ether solution and cooled. 1-Butyllithium (5ml. of a 1.6N hexane solution, 8 mmole) was then added with stirring under nitrogen. To the
resulting light yellow solution which contained a white solid was added 0.91 g. (8 mmole) of 2-chloropyridine in 5 ml. of ether. Methanol (200 ml.) was then added and the addition of 500 ml. of distilled water produced two layers. After drying over sodium sulphate, the organic phase yielded a gummy orange residue which was not studied further.

3. Phosphine selenides and tellurides

To 9.05 g. (0.144 mole) of powdered selenium and 0.31 g. (2.3 mmoles) of aluminum trichloride was added 10 ml. (15.74 g., 0.114 mole) of phosphorus trichloride. There was no evidence of reaction after refluxing for four hours. The unreacted phosphorus trichloride was recovered (b.p. 75.0-75.5°) in 64% yield. No higher boiling liquids were present.

Diphenylphosphinothioselenic chloride by the interaction of diphenylchlorophosphine with potassium selenocyanate. Addition of potassium selenocyanate in acetonitrile to diphenylchlorophosphine resulted in immediate deposition of red, elemental selenium.

Diphenylphosphine selenide, \( \Phi_2P(Se)H \). In the first attempt, a reaction similar to the above was employed. Diphenylphosphine (2.2 g., 0.012 mole) in 10 ml. of acetonitrile was
mixed with 1.7 g. (0.012 mole) of potassium selenocyanate in 15 ml. of acetonitrile. No selenium deposition occurred at first but the solution became cloudy; however, evaporation of the solvent gave a white solid together with red selenium.

Next, a reaction analogous to the preparation of diphenylphosphine sulfide was employed. To 5.1 g. (0.027 mole) of di-

\[ \Phi_2PH + Se \rightarrow \Phi_2P(Se)H \]  

(Eq. 60)

phenylphosphine in 75 ml. of toluene was added, under nitrogen, 2.21 g. (0.027 mole) of powdered selenium. After three hours of reflux only a trace amount of unreacted selenium remained. The toluene was removed under nitrogen, while heating with an oil bath. The resulting gray solid was dissolved in 40 ml. of hot acetonitrile and filtered. Upon cooling and concentrating the yellow filtrate, 4.03 g. (57%) of a white, crystalline material was obtained. The infrared spectrum of the product showed three strong peaks in the 510-600 cm\(^{-1}\) region; i.e., the phosphorus-selenium stretching region and it melted at 106-108\(^\circ\). The product melted at 100-111.5\(^\circ\) after a second recrystallization from acetonitrile. However, a third recrystallization produced a product which became yellow at about 165\(^\circ\) and melted to an orange liquid at 185-188\(^\circ\). The infrared spectrum of this compound showed two peaks in the phosphorus-selenium stretching region. This sample was submitted for analysis.
Anal. Calcd. for C_{12}H_{11}PSe:

C, 54.36; H, 4.18; P, 11.68%.

Found: C, 53.17; H, 3.86; P, 15.77%.

The product decomposed upon standing.

**Diphenylphosphinetelluride, \( \phi_2P(Te)H \).** To 5.1 g. (0.027 mole) of diphenylphosphine in 80 ml. of toluene was added, under nitrogen, 3.45 g. (0.027 mole) of powdered tellurium. The tellurium was unreacted after refluxing the mixture for eight hours and only tellurium was left after vacuum distillation of the solvent and diphenylphosphine. Evidently, no reaction occurred.

**Tributylphosphine selenide by reaction of the phosphine with potassium selenocyanate in acetonitrile.** The reactants were weighed and solutions prepared in a dry box. The reaction was carried out under nitrogen in a closed system. Tri(n-butyl)phosphine (9.6 g., 0.046 mole) and potassium selenocyanate (6.56 g., 0.465 mole) in 30 ml. of degassed acetonitrile were mixed. A gelatinous precipitate occurred as the liquid phase became yellow. The reaction was stirred for one hour and allowed to stand for an additional two hours. No heat was evolved when the reaction was opened to the atmosphere. The solvent was evaporated under nitrogen to yield a liquid phase together with a gelatinous solid. Addition of 50 ml. of distilled water resulted in two clear phases; these were separated and the aqueous
layer was discarded. The other phase was fractionally distilled to yield a product which came over at 190-195°/1 mm (lit. value 150-151°/0.80 mm, ref. 340). Although the infrared spectrum of this compound agreed with a sample of tri(n-butyl)phosphine selenide which was prepared by fusion of the phosphine with selenium, its b.p. was too high.

Tri(n-octyl)phosphine selenide. Tri(n-octyl)phosphine (7.7 g., 0.021 mole) formed a dense, oily phase which was immiscible with acetonitrile. Potassium selenocyanate (2.88 g., 0.021 mole) in 25 ml. of acetonitrile was added to the reaction mixture. The solution color became yellow but the oil was still present. The reaction mixture was stirred under nitrogen for three hours and a gelatinous precipitate was present. Evaporation of the solvent produced a small amount of a solid material together with an oil. The products were not studied further; the insolubility of the phosphine in acetonitrile was probably responsible for its apparent non-reaction.

Triphenylarsine selenide. The interaction of triphenylarsine (0.92 g., 3 mmole) in 10 ml. of acetonitrile with 0.43 g.

\[ \text{As} + \text{KCNSe} \rightarrow \text{AsSe} + \text{KCN} \]  
(Eq. 62)

(3 mmole) of potassium selenocyanate in 10 ml. of acetonitrile produced no precipitate. Evaporation of the solvent, followed by washing with distilled water, resulted only, in recovery of triphenylarsine. Both the m.p. (58.5°) and infrared spectrum confirmed this conclusion.
Diphenyl(o-diphenylarsinophenyl)phosphine selenide by the interaction of potassium selenocyanate with diphenyl(o-diphenylarsinophenyl)phosphine. Since the mixed tertiary arsine-phosphine was not very soluble in hot acetonitrile, it (2.45 g., 5 mmole) was dissolved in 65 ml. of boiling n-butanol and to

\[ \Phi_2(\sigma-\Phi_2\text{AsC}_6\text{H}_4)\text{P} + \text{KCNSe} \rightarrow \Phi_2(\sigma-\Phi_2\text{AsC}_6\text{H}_4)\text{PSe} + \text{KCN} \]  

(Eq. 63)

this solution was added 0.72 g. (5 mmole) of potassium selenocyanate in 5 ml. of acetonitrile. The reaction was stirred for one hour and the product, which had precipitated as the solution cooled, was isolated by filtration. Recrystallization from dichloromethane/ether afforded 1.30 g. of a white, crystalline material, m.p. 189-189.5° (clear liquid). The product melted close to the starting material (190-191°) and its infrared spectrum lacked the characteristic PSe stretching vibration.

Tris(diethylaminomethyl)phosphine selenide, \((\text{Et}_2\text{NCH}_2)_3\text{PSe}\). Tris(diethylaminomethyl)phosphine (5.5 g., 0.019 mole) was weighed under nitrogen, added to 10 ml. of acetonitrile, and combined with potassium selenocyanate (2.74 g., 0.019 mole) in 30 ml. of acetonitrile. The resulting solution was hazy after stirring for one hour and evaporation of the solvent resulted in the presence of a solid material together with a liquid phase. No elemental selenium was present. Addition of water dissolved the solid and left an oil. This selenide is probably a liquid and was not characterized further.
1,2-Bis(diphenylphosphino)ethane monoselenide, \( \Phi_2P(Se)CH_2CH_2P\Phi_2 \). To 1.99 g. (5 mmole) of 1,2 bis(diphenylphosphino)ethane dissolved in 100 ml. of warm acetonitrile was added potassium selenocyanate (0.72 g., 5 mmole) in 25 ml. of acetonitrile. An immediate cloudiness and flocculent precipitate occurred. The solvent was evaporated after stirring one hour, and the product was worked up in the usual manner to yield 3.80 g. of a white compound; m.p. 130-160°. The product was recrystallized from n-butanol to yield 1.83 g. of a white, crystalline material; m.p. 170-175°.

Anal. Calcd. for \( C_{26}H_{24}P_2Se \):

\[
\begin{align*}
C &\text{, 65.41; H, 5.07%} \\
\text{Found: C, 60.59; H, 5.04%}
\end{align*}
\]

Diphenyl(2-dimethylaminoethyl)phosphine selenide, \( \Phi_2P(Se)CH_2CH2NMe_2 \). The interaction of diphenyl(2-dimethylaminoethyl)phosphine with potassium selenocyanate in a 1:1 molar ratio in acetonitrile, under a nitrogen atmosphere, followed by work up according to the usual procedure produced a taffy like material. Recrystallization from acetonitrile produced a small amount of waxy material.
Anal. Calcd. for C$_{16}$H$_{20}$NPSe:
C, 57.15; H, 6.00%.
Found: C, 63.09; H, 4.78%.

Tetramethyldiphosphine diselenide by interaction of the disulfide with potassium selenocyanate. Tetramethyldiphosphine disulfide (0.28 g., 1.5 mmole) in 20 ml. of warm acetonitrile

$$\text{Me}_2\text{P}(\text{S})\text{P(Se)Me}_2 + 2\text{KNCS} \rightarrow$$

was reacted with potassium selenocyanate (0.43 g., 3 mmole) in 10 ml. of acetonitrile. Upon work up of the reaction mixture, unreacted tetramethyldiphosphine disulfide was obtained (evidence, infrared spectrum).

4. Mixed sulfide-selenides

Tetramethyldiphosphine monosulfide monoselenide,

$$\text{Me}_2\text{P}(\text{S})\text{P(Se)Me}_2.$$ Tetramethyldiphosphine disulfide (3.72 g., 0.02 mole) and triphenylphosphine (5.25 g, 0.02 mole) were refluxed in 100 ml. of deoxygenated acetonitrile for one hour

$$\text{Me}_2\text{P}(\text{S})\text{P} + \text{OP} \rightarrow$$

under nitrogen. Potassium selenocyanate (2.88 g., 0.02 mole) in 30 ml. of acetonitrile was added to the resulting yellow

$$\text{Me}_2\text{P}(\text{Se})\text{PMe}_2 + \text{KNCSe} \rightarrow$$

(eq. 65, 66, 67)
solution. The solvent was evaporated after stirring for one hour, and the residue washed with distilled water. It was found that 9.1 g. of a white solid was obtained after drying over $P_4O_{10}$ in vacuo. The infrared spectrum of this material clearly showed that no triphenylphosphine sulfide was present. This indicated that Equation 55 did not proceed and the product isolated contained triphenylphosphine selenide and unreacted tetramethyldiphosphinedisulfide.

5. Other intermediates

Sodium diphenylphosphide, $\Phi_2PNa$. To a stirred slurry of 0.96 g. of a 50% sodium hydride oil (0.48 g. of NaH, 0.02 mole) in 10 ml. of tetrahydrofuran was added 5.25 g. (0.02 mole) of triphenylphosphine in 50 ml. of tetrahydrofuran. The reaction was carried out under nitrogen. No initial reaction occurred; however, refluxing the mixture for one hour produced an orange-yellow solution together with what appeared to be a light-green solid. Addition of 1,2 dichloroethane, which would react with a nucleophile, caused the solution to become colorless. Slow addition of water produced strong bubbling which indicated that all the sodium hydride had not been consumed. The reaction appears to have gone to only a small extent.

Another attempt was made by adding, under nitrogen, a solution of 3.70 g. (0.02 mole) of diphenylphosphine in 20 ml. of

$$\Phi_2PH + NaH \rightarrow \Phi_2PNa + H_2$$  \hspace{1cm} (Eq. 69)
tetrahydrofuran to a stirred slurry of 0.96 g. of 50% sodium hydride oil (0.02 mole) in 10 ml. of tetrahydrofuran. A fizzing reaction occurred and the mixture was stirred for fifteen minutes. The resulting yellow solution which contained a light yellow solid was hydrolyzed with water after cooling. Again, vigorous gas evolution indicated that a large amount of sodium hydride had been unreacted.

The reaction of 2-chloroethyl(dimethyl)amine with magnesium. The reaction was undertaken employing the usual Grignard procedure; tetrahydrofuran, however, was employed as a solvent in place of diethylether. Magnesium (5.1 g., 0.21 mole) was covered with 50 ml. of tetrahydrofuran. Addition of a few ml. of the amine did not initiate the reaction; neither did an iodine crystal or heating. The amine (22.6 g., 0.21 mole) in 100 ml. of tetrahydrofuran was then added at reflux over a period of forty-five minutes. Still there was no visible reaction; however, after several hours of reflux, the typical dark Grignard color was obtained and only a few splinters of unreacted magnesium remained. Upon cooling, hydrolysis with aqueous ammonium chloride produced a violent reaction which also indicated that the Grignard had formed.

\[
\text{Me}_2\text{NCH}_2\text{CH}_2\text{Cl} + \text{Mg} \rightarrow \text{Me}_2\text{NCH}_2\text{CH}_2\text{MgCl}
\]

(Eq. 70)
tetrahydrofuran and this solution was added over a period of

\[ \phi_2 \text{PLi} + o^-\text{BrC}_6\text{H}_4\text{I} \rightarrow o^-\text{BrC}_6\text{H}_4\text{P\phi}_2 + \text{LiI} \]  

(Eq. 71)
ninety minutes to cooled solution of o-bromoiodobenzene

(25.0 g., 0.088 mole) in 100 ml. of tetrahydrofuran. The resulting solution was refluxed 15 minutes, cooled, and hydrolyzed with distilled water. A concentrated solution of lithium iodide had to be added to obtain phase separation. The water layer was washed with 100 ml. of diethyl ether and the combined organic phases were dried over sodium sulphate. To the dark solution resulting from flash distillation of this resulting solution under nitrogen was added 20 ml. of abs. ethanol. A white, crystalline material which weighed about 2 g. when dried resulted after cooling in the freezer overnight. The crude material melted at 176-180° and upon recrystallization from n-butanol, 0.88 g. of white needles were obtained, m.p. 181-182°.

The melting point corresponded closely to that of o-bis(diphenyolphosphino)benzene (117), m.p. 186.5-187.5°. Elemental analysis for this compound also confirmed that it was o-bis(diphenyolphosphino)benzene.

\[ \phi_2 \text{PLi} + o^-\text{BrC}_6\text{H}_4\text{I} \rightarrow \]

\[ 1/2 o^-\phi_2 \text{PC}_6\text{H}_4\text{P\phi}_2 + \]  

(Eq. 72)

+ 1/2 o^-\text{BrC}_6\text{H}_4\text{I} + 1/2 \text{LiBr} + 1/2 \text{LiI} \]
Anal. Calcd. for C₁₈H₁₄BrP (o-BrC₆H₄PØ₂):
C, 63.36; H, 4.13%.

Calcd. for C₃₀H₂₄P₂ (o-P₂C₆H₄PØ₂):
C, 80.71; H, 5.42%.

Found: C, 80.76; H, 5.41%.

Since the reaction of lithium diphenylphosphide with o-bromoiodobenzene in a 1:1 mole ratio produced the dissubstituted product in small yield, the same reaction was next carried out with a 2:1 ratio of lithium diphenylphosphide to o-bromoiodobenzene. This led to a 15% yield of crude o-(diphenylphosphino) benzene, m.p. 175-179°C.

o-Bromophenyl(diphenylarsine sulfide), o-BrC₆H₄As(S)Ø₂.
Sulfur (0.17 g., 5.2 mmole) was added to a solution of o-bromophenyl(diphenylarsine) (2.0 g., 5.2 mmole) in 15 ml. of carbon disulfide. No apparent heat was given off and the sulfur did not go into solution after refluxing for two hours.

o-Chloro(diphenylphosphino)benzene, o-ClC₆H₄PØ₂. The reaction of lithium diphenylphosphide (0.10 mole) and o-dichlorobenzene (0.05 mole) in tetrahydrofuran failed to dissipate the dark red color of the diphenylphosphide solution, and it was assumed that little if any reaction occurred.
o-Nitro(diphenylphosphino)benzene, \( \text{o-NO}_2\text{C}_6\text{H}_4\text{PF}_2 \). The reaction of lithium diphenylphosphide with o-bromonitrobenzene in tetrahydrofuran produced a dark solution from which only a trace amount of red oil could be isolated.

\[
\text{PH}_2\text{Li} + \text{o-BrC}_6\text{H}_4\text{NO}_2 \rightarrow \text{o-P}_2\text{C}_6\text{H}_4\text{NO}_2 + \text{LiCl}
\]  
(Eq. 75)

The initial reaction of o-bromonitrobenzene with 1-butyl-lithium followed by subsequent reaction with diphenylchlorobenzene produced a brown tar.

E. Synthesis Of Coordination Compounds

1. Complexes of monodentate tertiary phosphine sulfides

Trimethylphosphine sulfide

\[ \text{Di-iodobis(trimethylphosphine sulfide)zinc(II)}, [\text{Zn(Me}_3\text{PS})_2\text{I}_2] \]. The solution resulting from the addition of trimethylphosphine sulfide (0.43 g., 4 mmole) in 5 ml. of abs. ethanol to anhydrous zinc(II) iodide (0.32 g., 1 mmole) in 5 ml. of abs. ethanol was cooled in the freezer overnight. The white, crystalline precipitate was isolated by filtration, washed with several ml. of cold abs. ethanol and then with ether, and dried in vacuo for 12 hours. Henceforth, unless mentioned otherwise, all samples were dried for at least 12 hours. Yield, 0.41 g., 75% of theory. M.p. 171-173°

\[ \text{Anal. Calcd. for C}_8\text{H}_18\text{I}_2\text{P}_2\text{S}_2\text{Zn:} \]
\[ \text{C}, 13.46; \text{H}, 3.39; \text{I}, 47.40\% . \]
\[ \text{Found: C}, 13.69; \text{H}, 3.37; \text{I}, 47.37\% . \]
Tetrakis(trimethylphosphine sulfide)zinc(II) perchlorate, \[ \text{[Zn(Me}_2\text{PS})_4]^{2-}(\text{ClO}_4)_2 \]. To 0.37 g. (1 mmole) of zinc(II) perchlorate hexahydrate in 5 ml. of abs. ethanol was added an ethanolic solution of trimethylphosphine sulfide (0.43 g., 4 mmole). The white crystals which formed were filtered, washed with ether, and dried in vacuo. Yield, 0.46 g., 66% of theory. M.p. 217° decomp.

**Anal.** Calcd. for \( C_{12}H_{36}Cl_2O_8P_4S_4Zn \):
- C, 20.68; H, 5.21; Cl, 10.18%.
- Found: C, 20.93; H, 5.25; Cl, 10.43%.

The following complexes were prepared similarly.

**Di-iodobis(trimethylphosphine sulfide)cadmium(II),** \[ \text{[Cd(Me}_2\text{PS})_2I}_2 \]. White, crystalline compound, m.p. 155-156°. Yield, 90%.

**Anal.** Calcd. for \( C_{18}I_2P_2S_2 \):
- C, 12.37; H, 3.11; I, 43.57%.
- Found: C, 12.58; H, 3.11; I, 43.47%.

**Dichlorobis(trimethylphosphine sulfide)mercury(II),** \[ \text{[Hg(Me}_2\text{PS})_2Cl}_2 \]. White powder, m.p. 140° decomp. Yield, 99%.

**Anal.** Calcd. for \( C_{18}H_{18}Cl_2HgP_2S_2 \):
- C, 14.77; H, 3.72; Cl, 14.54%.
- Found: C, 14.69; H, 3.72; Cl, 14.24%.
Dibromobis(trimethylphosphine sulfide)mercury(II), 
\[ \text{[Hg(Me}_3\text{PS)}_2\text{Br}^+]} \]. White powder, m.p. 131-132°. Yield, 86%

**Anal.** Calcd. for \( \text{C}_6\text{H}_{18}\text{Br}_2\text{HgP}_2\text{S}_2 \):
\[
\begin{align*}
\text{C}, & \quad 12.50; \\
\text{H}, & \quad 3.14; \\
\text{Br}, & \quad 27.71%.
\end{align*}
\]

**Found:** C, 12.47; H, 3.17; Br, 26.94%.

Di-iodobis(trimethylphosphine sulfide)mercury(II), 
\[ \text{[Hg(Me}_3\text{PS)}_2\text{I}^-]} \]. White, crystalline compound, m.p. 167-168°. Yield, 82%

**Anal.** Calcd. for \( \text{C}_6\text{H}_{18}\text{Hg}_2\text{P}_2\text{S}_2 \):
\[
\begin{align*}
\text{C}, & \quad 10.74; \\
\text{H}, & \quad 2.70; \\
\text{I}, & \quad 37.84%.
\end{align*}
\]

**Found:** C, 10.56; H, 2.72; I, 37.67%.

Dichlorobis(trimethylphosphine sulfide)palladium(II), 
\[ \text{[Pd(Me}_3\text{PS)}_2\text{Cl}^-]} \]. To a stirred, filtered solution of sodium tetrachloropalladate(II) (0.88 g., 3 mmole) in 75 ml. abs. ethanol was added trimethylphosphine sulfide (0.65 g., 6 mmole) dissolved in 25 ml. of abs. ethanol. The precipitate, which formed immediately, was isolated by filtration, and washed with abs. ethanol followed by ether. The crude material (1.20 g.) was recrystallized by dissolution in 250 ml. of dichloromethane, filtration, and reprecipitation by the addition of n-hexane. Yield, 0.53 g. (40% of theory) of a dark brown powder.

**Anal.** Calcd. for \( \text{C}_6\text{H}_{18}\text{Cl}_2\text{PdS}_2 \):
\[
\begin{align*}
\text{C}, & \quad 17.90; \\
\text{H}, & \quad 4.51; \\
\text{Cl}, & \quad 17.61; \\
\text{S}, & \quad 15.93%.
\end{align*}
\]

**Found:** C, 17.67; H, 4.54; Cl, 17.43; S, 16.03%.
Dibromobis(trimethylphosphine sulfide)palladium(II), 
\([\text{Pd}(\text{Me}_3\text{PS})_2\text{Br}_2]\). A solution of tetrabromopalladate(II) was prepared in situ by the addition of excess lithium bromide (2.22 g., 25 mmole) in 50 ml. of abs. ethanol to 0.74 g. (2.5 mmole) of sodium tetrachloropalladate(II) in 75 ml. of abs. ethanol. The resulting solution was filtered and to it was added, with stirring, a solution of 0.54 g. (5 mmole) trimethylphosphine sulfide in 25 ml. of abs. ethanol. The complex, which precipitated immediately, was isolated as above (1.02 g.) and recrystallized from dichloromethane/n-hexane to yield 0.85 g. (70% of theory) of a dark brown powder; m.p. 195-196°.

**Anal.** Calcd. for C_{6}H_{18}Br_{2}P_{2}P_{2}S_{2}:

- C, 14.93; H, 3.76; Br, 33.12; P, 12.84%.
- Found: C, 15.15; H, 4.08; Br, 32.78; P, 12.66%.

Dichlorobis(trimethylphosphine sulfide)platinum(II), 
\([\text{Pt}(\text{Me}_3\text{PS})_2\text{Cl}_2]\). To a stirred, filtered solution of sodium tetrachloroplatinate(II) (0.76 g., 2 mmole) in 100 ml. of abs. ethanol was added trimethylphosphine sulfide (0.43 g., 4 mmole) in 25 ml. of abs. ethanol. After stirring the mixture for one hour and cooling in the freezer, the precipitate was isolated and washed as above to produce 0.49 g. of a tan powder. Recrystallization from dichloromethane/n-hexane afforded 0.37 g. (39% of theory) of a light orange powder, m.p. 163.5°.

**Anal.** Calcd. for C_{6}H_{18}Cl_{2}P_{2}PtS_{2}:

- C, 14.94; H, 3.76; Cl, 14.70%.
- Found: C, 14.71; H, 3.72; Cl, 13.81%.
To a stirred solution of copper(II) perchlorate hexahydrate (0.55 g., 1.5 mmole) in 20 ml. of abs. ethanol was added trimethylphosphine sulfide (0.65 g., 6 mmole) in 20 ml. of abs. ethanol. The white needles, which formed from the resulting colorless solution, were isolated by filtration, washed with abs. ethanol and ether, and dried in vacuo. Yield, 0.70 g., 72% of theory. M.p. 197° decomp.

**Anal.** Calcd. for \( \text{CuH}_3\text{ClCuO}_2\text{P}_3\text{S}_3 \):

- C, 22.18; H, 5.59; Cl, 7.27;
- Cu, 13.04; O, 13.11; P, 19.07; S, 19.72%.

**Found:** C, 22.09; H, 5.63; Cl, 7.12;
- Cu, 12.98; O, 10.51; P, 19.13; S, 19.96%.

Triphenylphosphine sulfide

Dichloro(triphenylphosphine sulfide)mercury(II), \( \Phi_2\text{PS-HgCl}_2 \).

The white platlets which formed upon mixing anhydrous mercury(II) chloride (0.27 g., 1 mmole) in 20 ml. abs. ethanol with triphenylphosphine sulfide (0.59 g., 2 mmole) in 25 ml. of boiling abs. ethanol (25 ml.) were isolated by filtration, washed with dichloromethane and ether, and then dried in vacuo. Yield, 0.54 g., 95% of theory.

**Anal.** Calcd. for \( \text{C}_{18}\text{H}_{15}\text{Cl}_2\text{HgPS} \):

- C, 38.21; H, 2.67; Cl, 12.53%.

**Found:** C, 38.31; H, 2.94; Cl, 12.20%.

The following complexes were prepared similarly.
Dibromo(triphenylphosphine sulfide)mercury(II), $\text{HgBr}_2\text{PS}$.  
White platlets, m.p. 228-232° decomp. Yield, 90%

Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{Br}_2\text{HgPS}$:

$\text{C}$, 33.01; $\text{H}$, 2.31; $\text{Br}$, 24.41%.

Found: $\text{C}$, 32.97; $\text{H}$, 2.63; $\text{Br}$, 24.61%.

Di-iodo(triphenylphosphine sulfide)mercury(II), $\text{HgI}_2\text{PS}$.  
Light yellow feather needles, m.p. 167-168°. Yield, 68%.

Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{HgI}_2\text{PS}$:

$\text{C}$, 28.87; $\text{H}$, 2.02; $\text{I}$, 33.89%.

Found: $\text{C}$, 28.95; $\text{H}$, 2.17; $\text{I}$, 33.87%.

Dichlorobis(triphenylphosphine sulfide)palladium(II), $\text{Pd(PS)_2Cl}_2$.  
To a stirred, filtered solution of 0.53 g. (1.8 mmole) of sodium tetrachloropalladate(II) in 50 ml. of abs. ethanol was added triphenylphosphine sulfide (.06 g., 3.6 mmole) in 75 ml. of boiling abs. ethanol. The precipitate, which formed immediately, was isolated by filtration and washed with distilled water followed by abs. ethanol and ether. An analytical sample was obtained from the light yellow-brown powder (1.34 g., 98% of theory) by recrystallizing a small portion from a large quantity of dichloromethane by the addition of n-hexane, m.p. 225° decomp.

Anal. Calcd. for $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{PdS}_2$:

$\text{C}$, 56.44; $\text{H}$, 3.95; $\text{Cl}$, 9.26%.

Found: $\text{C}$, 56.28; $\text{H}$, 4.19; $\text{Cl}$, 9.56%.
Dichlorobis(triphenylphosphine)palladium(II), \([\text{Pd}(\text{Ph}_3\text{P})_2\text{Cl}_2]\). Light yellow complex prepared in a similar manner with triphenylphosphine.

**Anal. Calcd. for C_{36}H_{30}Cl_2P_2Pd:**

- C, 61.60; H, 4.34; Cl, 10.13%.
- Found: C, 61.48; H, 4.37; Cl, 9.95%.

Dibromobis(triphenylphosphine sulfide)palladium(II), \([\text{Pd}(\text{Ph}_3\text{PS})_2\text{Br}_2]\). Tetrabromopalladate(II) was prepared in situ by the addition of excess lithium bromide (1.78 g., 20 mmole) in 25 ml. of abs. ethanol to 0.59 g. (2 mmole) of sodium tetra-chloropalladate(II) in 50 ml. of abs. ethanol. To this stirred solution was added triphenylphosphine sulfide (1.18 g., 4 mmole) in 100 ml. of boiling abs. ethanol. The precipitate, which formed immediately, was isolated by filtration after stirring for one hour and washed in sequence with distilled water, abs. ethanol, and ether. The product was dried for 24 hrs. over \(\text{P}_4\text{O}_{10}\) in vacuo to yield a light orange-brown powder. Yield, 1.51 g., 88% of theory.

**Anal. Calcd. for C_{36}H_{30}Br_2P_2PdS_2:**

- C, 50.57; H, 3.54; Br, 18.69; S, 7.50%.
- Found: C, 50.41; H, 3.56; Br, 18.46; S, 7.26%.

Dichlorobis(triphenylphosphine sulfide)platinum(II), \([\text{Pt}(\text{Ph}_3\text{PS})_2\text{Cl}_2]\). To a stirred, filtered solution of sodium tetrachloroplatinate(II) (0.42 g., 1.1 mmole) in 50 ml. of abs. ethanol was added a boiling solution of triphenylphosphine sulfide (0.65 g., 2.2 mmole) in 50 ml of ethanol. After stirring
the mixture for one hour and cooling overnight in the freezer, the precipitate was isolated by filtration and washed with abs. ethanol and ether. The flesh colored powder (0.77 g.) was recrystallized from dichloromethane/n-hexane; yield, 0.15 g. (16% of theory). M.p. 182-183°.

Anal. Calcd. for C_{36}H_{30}Cl_{2}P_{2}PtCl_{2}:  
C, 50.59; H, 3.54; Cl, 8.30%.

Found: C, 48.90; H, 3.66; Cl, 8.36%.

Tetrakis(triphenylphosphine sulfide)copper(I) perchlorate, \([\text{Cu}(\phi\text{PS})_{4}]\text{ClO}_{4}\). To 0.74 g. (2 mmole) of \(\text{Cu(ClO}_4\)\text{)}_2\cdot6\text{H}_2\text{O} in 25 ml. of abs. ethanol was added 2.35 g. (8 mmole) of triphenylphosphine sulfide in 125 ml. of boiling abs. ethanol; sulfur dioxide was sparged briskly through the solution for fifteen minutes and the reaction vessel was stoppered. A white precipitate formed quickly from the light green solution. After placing the reaction vessel in the freezer for two days, the precipitate was isolated by filtration from a colorless solution. The complex was washed with abs. ethanol and ether, and dried over \(\text{P}_4\text{O}_{10}\) in vacuo. Yield, 2.18 g. (84%); m.p. 205° detonates.

Anal. Calcd. for CuL_{4}\text{ClO}_4, C_{72}H_{60}ClCuO_{4}P_{S}S_{4}:  
C, 64.52; H, 4.51; Cl, 2.64%.

Calcd. for CuL_{3}\text{ClO}_4, C_{54}H_{45}ClCuO_{4}P_{S}S_{3}:  
C, 62.01; H, 4.44; Cl, 3.19%.

Found: C, 63.57; H, 4.53; Cl, 2.93%.

Attempted syntheses

Although trimethylphosphine sulfide forms complexes with zinc(II) and cadmium(II), no evidence of reaction was noted
when triphenylphosphine sulfide was mixed with ethanolic solutions of Zn(ClO$_4$)$_2$·6H$_2$O, Cd(NO)$_3$·4H$_2$O, CdCl$_2$·2H$_2$O, ZnI$_2$, or CdI$_2$. For example, colorless needles form upon cooling a mixture of cadmium(II) iodide (0.40 g., 1.1 mmole) in 10 ml. of abs. ethanol and triphenylphosphine sulfide (0.65 g., 2.2 mmole) in 30 ml. of boiling abs. ethanol. The crystals are unreacted ligand (74% recovery) as evidenced by infrared spectra and melting point (161-162°).

The same stoichiometry for the zinc(II), cadmium(II), and mercury(II) complexes was obtained regardless of the ligand/metal ratio. For example, mixing triphenylphosphine sulfide with mercury(II) iodide in a 6:1 mole ratio produces the complex $\phi_3\text{PS} \cdot \text{HgI}_2$ as evidenced by its melting point (166-167°) and infrared spectral comparison with an authentic sample.

Attempts to prepare HgL$_4$(ClO$_4$)$_2$ complexes were unsuccessful. Thus, mixing trimethylphosphine sulfide with Hg(ClO$_4$)$_2$·6H$_2$O in abs. ethanol (4:1 mole ratio) led to disproportionation as evidenced by the formation of a dark product which was probably colloidal mercury. No perchlorate bands were detected in the infrared spectrum of the product which precipitated when triphenylphosphine sulfide (0.94 g., 3.2 mmole) in 50 ml. of boiling abs. ethanol was added to a solution of mercury(II) bromide (0.29 g. 0.8 mmole) and lithium perchlorate (0.17 g., 1.6 mmole) in 20 ml. of abs. ethanol. The complex isolated melted at 227-230° and, thus, appeared to be $\phi_3\text{PS} \cdot \text{HgBr}_2$ rather than [Hg($\phi_3\text{PS}$)$_4$](ClO$_4$)$_2$. 
The use of sulfur dioxide in the preparation of 
\[ \text{[Cu(\(\phi_3\text{PS})_4\)](ClO}_4\text{)}_2 \] is necessary because without it no color change occurs and the unreacted ligand precipitates from solution. Also, triphenylphosphine sulfide does not reduce an ethanolic copper(II) bromide solution without addition of sulfur dioxide. Sulfur dioxide sparged through a solution of just ethanolic copper(II) perchlorate produces a color change from light blue to light green but does not result in a colorless solution.

Although trimethylphosphine sulfide and triphenylphosphine sulfide displace chloride and bromide ions from PdX\(_4\)\(^-\) species in ethanol to form complexes of the type [PdL\(_2\)X\(_2\)], no reaction occurs when X is iodide, thiocyanate, or selenocyanate.

No more than two phosphine sulfide ligands could be placed around palladium. Thus, by mixing PdCl\(_4\)\(^-\) with 4 mole equivalents of triphenylphosphine sulfide, one still isolates [Pd(\(\phi_3\text{PS})_2\text{Br}_2\)]. Excess triphenylphosphine sulfide produces no color change or precipitate when reacted with a dichloromethane solution of [Pd(\(\phi_3\text{PS})_2\text{Br}_2\)]. In addition, the reaction of 4 mole equivalents of triphenylphosphine sulfide with an ethanolic solution of Na\(_2\)PdCl\(_4\) (1 mole equivalent) and LiClO\(_4\) (2 mole equivalents) yields [Pd(\(\phi_3\text{PS})_2\text{Cl}_2\)], not the expected [Pd(\(\phi_3\text{PS})_4\)](ClO\(_4\))\(_2\).

Color changes occur when the phosphine sulfide ligands are reacted with Pd(NO\(_3\))\(_2\) (4:1 mole ratio) in either DMF or acetonitrile. However, a crystalline complex could not be isolated. Addition of ether to the DMF solutions of PdL\(_4\)(NO\(_3\))\(_2\)
produces tarry materials; evaporation of acetonitrile solutions produces similar products.

The reaction, in ethanolic solution, between NaAuCl₄ and trimethylphosphine sulfide in a 1:1 mole ratio initially produces a color change from yellow to orange, together with an orange precipitate. However, the precipitate then turns brown and on filtration only a trace of brown residue can be collected. The filtrate then deposits a metallic mirror on the glass container (metallic gold).

A yellow solid is obtained when triphenylphosphine sulfide (0.41 g., 1.38 mmole) in 20 ml. of boiling abs. ethanol is reacted with a stirred solution of sodium tetra-chlorosulfate(III) (0.50 g., 1.38 mmole) in 20 ml. of abs. ethanol. A yellow, crystalline material is produced by dissolving the compound in dichloromethane, filtering, and re-precipitating with n-hexane.

Analytical data:

Calcd. for $\text{C}_5\text{H}_{15}\text{AuCl}_3\text{PS}$:
\begin{align*}
C & : 36.17; \\
H & : 2.53; \\
Cl & : 17.80; \\
P & : 5.18; \\
S & : 5.36%.
\end{align*}

Calcd. for $(\text{C}_3\text{PS})_3\text{AuCl}_7$:
\begin{align*}
C & : 37.66; \\
H & : 2.63; \\
Cl & : 14.41; \\
P & : 5.40; \\
S & : 5.59%.
\end{align*}

Found:
\begin{align*}
C & : 38.10; \\
H & : 2.75; \\
Cl & : 14.00; \\
P & : 5.54; \\
S & : 5.82%.
\end{align*}

These tertiary phosphine sulfides produce no color changes or colored precipitates when ethanolic solutions of the ligands
are mixed with ethanolic solutions of cobalt(II) and nickel(II) salts.

2. Complexes of bidentate tertiary phosphine sulfides

1,2-Bis(diphenylphosphino sulfide)ethane

Dichloro[1,2-bis(diphenylphosphino sulfide)ethane]palladium(II). To a filtered solution of 0.59 g. (2 mmole) of sodium tetrachloropalladate(II) in 50 ml. of abs. ethanol was added 1,2-bis(diphenylphosphino sulfide)ethane (0.93 g., 2 mmole) in a boiling solution of 150 ml. abs. ethanol and 90 ml. acetonitrile. After the mixture stood overnight, the orange product was collected by filtration. It was washed consecutively with distilled water, abs. ethanol, and ether and subsequently dried over P4O10 in vacuo for 24 hrs. to produce 1.28 g. (yield, 100%) of product.

Anal. Calcd. for C26H24Cl2P2PdS2:
C, 48.80; H, 3.78; Cl, 11.08%.

Found: C, 48.89; H, 3.99; Cl, 10.52%.

Diphenyl(o-diphenylarsino-phenyl)phosphine sulfide

The abbreviation APS shall be used for the ligand diphenyl-(o-diphenylarsinophenyl)phosphine sulfide, O2(o-o-ArC6H4)PS.

[Pd(APS)Cl2]. To a filtered, stirred solution of sodium tetrachloropalladate(II) (0.88 g., 3 mmole) in 75 ml. abs. ethanol was added APS (1.57 g., 3 mmole) in 75 ml. of hot
n-butanol. The product precipitated immediately but the reaction was stirred an additional hour, filtered, and washed with abs. ethanol followed by ethyl ether. The complex was re-crystallized by dissolution in 20 ml. hot DMF, filtration, and subsequent addition of ethanol to afford 1.45 g. of a crystalline yellow compound (yield, 69%).

**Anal.** Calcd. for C$_{30}$H$_{24}$AsCl$_2$PPdS:

C, 51.49; H, 3.46; Cl, 10.13; S, 4.58%.

Found: C, 51.38; H, 3.60; Cl, 9.98; S, 4.73%.

[[Pd(APS)Br$_2$]]. Tetrabromopalladate(II) was prepared in situ by the addition of lithium bromide (2.67 g., 30 mmole) to sodium tetrachloropalladate(II) in 75 ml. of abs. ethanol. The resulting solution was filtered and 1.57 g. (3 mmole) of APS in 75 ml. of hot n-butanol was added. After stirring for one hour, the precipitate was filtered and washed with abs. ethanol and ether. The product was recrystallized from DMF/ethanol to afford 2.00 g. (yield, 85%) of an orange, crystalline complex.

**Anal.** Calcd. for C$_{30}$H$_{24}$AsBr$_2$PPdS:

C, 46.68; H, 3.07; Br, 20.26; S, 4.07%.

Found: C, 46.63; H, 3.23; Br, 20.07; S, 4.22%.

[[Pd(APS)I$_2$]]. Lithium iodide (3.99 g., 30 mmole) in 25 ml. of abs. ethanol was added to a solution of sodium tetrachloropalladate(II) (0.88 g., 3 mmole) in 75 ml. of abs. ethanol. The resulting solution was filtered and 1.57 g. (3 mmole) of APS in 75 ml. of hot n-butanol was added. The precipitate was then isolated and dried as in the preceding syntheses. Likewise,
it was recrystallized from DMF/ethanol to yield 2.38 g. (90%) of a purple, crystalline complex.

Anal. Calcd. for $C_{30}H_{24}AsI_2PPdS$:

$C$, 40.82; $H$, 2.74; $I$, 28.76; $S$, 3.63%.

Found: $C$, 41.00; $H$, 2.95; $I$, 28.48; $S$, 3.30%.

$[\text{Pd}(\text{APS})(\text{SCN})_2]$. To sodium tetrachloropalladate(II) (0.88 g., 3 mmole) in 75 ml. abs. ethanol was added sodium thiocyanate (2.43 g., 30 mmole) in 25 ml. of abs. ethanol. This solution was filtered and to it was added APS (1.57 g., 3 mmole) in 75 ml. of hot n-butanol. The precipitate was isolated and recrystallized as the other $[\text{Pd}(\text{APS})X_2]$ complexes to produce 1.76 g. of orange needle crystals (79% of theory).

Anal. Calcd. for $C_{32}H_{24}AsN_2PPdS_3$:

$C$, 51.59; $H$, 3.24; $N$, 3.76; $S$, 12.89%.

Found: $C$, 51.64; $H$, 3.40; $N$, 3.55; $S$, 13.00%.

$[\text{Pd}(\text{APS})(\text{SeCN})_2]$. The ligand (APS), 0.78 g., 1.5 mmole, in 50 ml. of hot n-butanol was added to a stirred, filtered solution which had been obtained by mixing 0.44 g. (1.5 mmole) of sodium tetrachloropalladate(II) in 50 ml. of abs. ethanol with 0.87 g. (6 mmole) of potassium selenocyanate in 30 ml. of abs. ethanol. The precipitate was isolated and recrystallized as the other $[\text{Pd}(\text{APS})X_2]$ complexes to yield 1.00 g. (79%) of a crystalline red-orange compound, m.p. 233° decomp.

Anal. Calcd. for $C_{32}H_{24}AsN_2PPdSSe_2$:

$C$, 45.82; $H$, 2.88; $N$, 3.34%.

Found: $C$, 45.65; $H$, 3.00; $N$, 3.20%.
The dark orange color of 0.345 g. (1.5 mmole) of palladium(II) nitrate in 30 ml. of DMF was converted to a lemon yellow upon addition of APS (1.57 g., 3 mmole) in 20 ml. of DMF. The addition of ethyl ether caused a lemon yellow precipitate which was collected by filtration and re-crystallized from DMF/ether to yield 1.25 g. (66%) of complex.

Anal. Calcd. for $C_{60}H_{48}As_2N_2O_6P_2PdS_2$:  
C, 56.34; H, 3.90; N, 1.97; S, 3.90%.

Found: C, 56.51; H, 3.79; N, 2.19; S, 5.03%.

$[{\text{Pt(APS)Cl}}_2]$. To a filtered, stirred solution of 0.67 g., 1.74 mole, of sodium tetrachloroplatinate(II) in 75 ml. of abs. ethanol was added a solution of APS (0.91 g., 1.74 mole) in 50 ml. of hot n-butanol. The reaction was stirred one hour, cooled, and the product filtered and washed with abs. ethanol and ether. This compound, as initially isolated, was insoluble in dichloromethane but could be re-crystallized from dichloromethane/n-hexane after first being re-crystallized from DMF/ethanol. A yellow, crystalline complex weighing 0.46 g. (yield, 34%) was obtained by this method.

Anal. Calcd. for $C_{30}H_{24}AsCl_2PtS$:  
C, 45.70; H, 3.07; Cl, 8.99; S, 4.07%.

Found: C, 45.54; H, 3.07; Cl, 9.20; S, 3.95%.

$[{\text{Pt(APS)Br}}_2]$. Lithium bromide (1.34 g., 15 mmole) in 20 ml. of abs. ethanol was added to 0.57 g. (1.5 mmole) of sodium tetrabromoplatinate(II) in 75 ml. of abs. ethanol and the resulting solution filtered. To this was added 0.79 g.
(1.5 mmole) of APS in 50 ml. of hot n-butanol. The resulting complex was isolated and recrystallized in a similar manner to its chlorine analog to yield 0.35 g. (27%) of a yellow crystalline compound.

**[Au(APS)Cl]**. To 0.25 g. (0.692 mmoles) of sodium tetrachloraurate(III) in 5 ml. of abs. ethanol was added, with stirring, 0.73 g. (1.4 mmole) of APS in 25 ml. of hot n-butanol. An immediate orange precipitate formed but redissolved to yield a colorless solution from which a white product precipitated. The product was isolated by filtration and recrystallized from dichloromethane/n-hexane to afford 0.15 g. (yield, 29%) of white crystals, m.p. 202-203° decomp.

**[Cu(APS)Cl]**. To 0.56 g. (1.5 mmole) of Cu(ClO$_4$)$_2$·6H$_2$O in 15 ml. of abs. ethanol was added 1.57 g. (3 mmole) of APS in 50 ml. of hot n-butanol. The solution became a light green color and a very pale green complex precipitated upon cooling. It was isolated by filtration and, after washing with ethanol and ether, dried over P$_2$O$_5$ in vacuo. Yield, 1.43 g. (79%); m.p. 227-230° decomp.
Anal. Calcd. for $C_{60}H_{48}As_2ClCuO_4P_2S_2$:

C, 59.66; H, 4.01; Cl, 2.93; S, 5.31%.

Found: C, 59.53; H, 4.07; Cl, 3.18; S, 5.08%.

Attempted syntheses

No complexes of diphenyl(o-diphenylarsinophenyl)phosphine sulfide could be isolated from the reactions of anhydrous or hydrated cobalt(II) and nickel(II) halides or manganese(II), iron(II), cobalt(II), and nickel(II) perchlorate with the ligand in several non-aqueous solvents. Slight color changes can be observed in solution, but all attempts to isolate a complex result in crystallization of free ligand.

3. Complexes of tetraalkyldiphosphine disulfides

Cadmium(II)

Di-iodo(tetramethyldiphosphine disulfide)cadmium(II), $[Cd(Me_4P_2S_2)_2]$. Addition of a solution of tetramethyldiphosphine disulfide (0.37 g., 2 mmole) in 50 ml. of hot methanol to 0.73 g. (2 mmole) of anhydrous cadmium(II) iodide in 15 ml. of warm methanol produced a white crystalline product upon cooling. The complex was collected on a sintered glass funnel, washed with ether, and dried over $P_4O_{10}$ in vacuo. Yield, 0.68 g. (62%); m.p. 255-261° (yellow liquid). An analytical sample was recrystallized from hot acetonitrile.

Anal. Calcd. for $C_{4}H_{12}CdI_{2}P_{2}S_{2}$:

C, 8.70; H, 2.19; I, 45.94%.

Found: C, 8.91; H, 2.15; I, 45.79%.
Di-iodo(tetraethylidiphosphine disulfide)cadmium(II), 
\[\text{[Cd(Et}_4\text{P}_2\text{S}_2)\text{I}_2]\]. This white complex was prepared in a manner 
similar to the above employing abs. ethanol as solvent; yield, 
83%. M.p. 174-177°.

Anal. Calcd. for \(\text{C}_9\text{H}_{20}\text{CdI}_2\text{P}_2\text{S}_2\):

- C, 15.79; H, 3.31; I, 41.71%.

- Found: C, 15.77; H, 3.11; I, 41.90%.

Mercury(II)

The following complexes were prepared in the same manner 
as their cadmium(II) analogs.

Di-iodo(tetramethyldiphosphine disulfide)mercury(II), 
\[\text{[Hg(Me}_4\text{P}_2\text{S}_2)\text{I}_2]\]. Light yellow powder; yield, 86%. M.p. 218-220° 
(oranges liquid).

Anal. Calcd. for \(\text{C}_8\text{H}_{12}\text{H}_2\text{I}_2\text{P}_2\text{S}_2\):

- C, 7.50; H, 1.89; I, 39.62%.

- Found: C, 7.56; H, 2.00; I, 39.38%.

Employing a mole ratio of \(\text{HgI}_2/\text{Me}_4\text{P}_2\text{S}_2\) of 2:1 produces a 
light yellow green complex whose infrared spectrum is similar 
to that of the above and which melts at 204-212° (orange liquid). 
This is probably the same complex.

Di-iodo(tetraethylidiphosphine disulfide)mercury(II), 
\[\text{[Hg(Et}_4\text{P}_2\text{S}_2)\text{I}_2]\]. Light yellow powder; yield, 72%. M.p. 145-146° 
(yellow liquid).
Anal. Calcd. for $C_8H_{20}HgI_2P_2S_2$:  

C, 15.79; H, 2.89; I, 36.43%.

Found: C, 13.61; H, 2.83; I, 36.65%.

**Silver(I)**

**Bis(tetramethyldiphosphine disulfide)silver(I) perchlorate**, $[\text{Ag(Me}_4\text{P}_2\text{S}_2]_2\text{ClO}_4$. A solution of tetramethyldiphosphine disulfide (0.74 g., 4 mmole) in 100 ml. boiling abs. ethanol was added, with stirring, to 0.41 g. (2 mmole) of anhydrous silver(I) perchlorate in 25 ml. of ethanol. The complex precipitated immediately and, after cooling the reaction mixture, it was collected on a sintered glass funnel and washed with ethanol and ether. A white, crystalline material (0.53 g.; yield, 46%) was obtained by recrystallization from hot acetonitrile. Carrying out the reaction in a 1:1 mole ratio led to the formation of a black precipitate which was not characterized.

Anal. Calcd. for $C_8H_{24}AgClO_4P_4S_4$:  

C, 16.58; H, 4.17; Cl, 6.11%.

Found: C, 16.57; H, 4.16; Cl, 6.22%.

The material slowly decomposes on standing.

**Reaction of silver(I) nitrate with Me$_4$P$_2$S$_2$.** A solution of 0.37 g. (2 mmole) of tetramethyldiphosphine disulfide in 40 ml. of warm acetonitrile was added to a solution of anhydrous silver(I) nitrate (0.11 g., 0.67 mmole) in 5 ml. of acetonitrile. A white precipitate formed immediately; it became grayish-white after stirring overnight. Isolation afforded 0.1 g. of a gray
material. The product from this reaction was recrystallized from hot pyridine to afford a trace amount of a crystalline white material; the infrared spectrum of which showed that no nitrate was present. Chocolate-brown precipitates resulted when a ligand:metal mole ratio of 1:1 or 2:1 was employed.

**Anal. Calcd. for C$_2$H$_6$AgPS$_2$:**

C, 10.31; H, 2.60; P, 13.29%.

**Found:** C, 10.26; H, 2.48; P, 13.23%.

**Bis(tetraethyldiphosphine disulfide)silver(I) perchlorate**, [Ag(ET$_2$P$_2$S$_2$)$_2$]ClO$_4$. A solution of tetraethyldiphosphine disulfide (0.97 g., 4 mmole) in 25 ml. abs. ethanol was added, with stirring, to 0.41 g. (2 mmole) of anhydrous silver(I) perchlorate in 25 ml. abs. ethanol. The product which formed immediately was isolated as the preceding complex and 1.08 g. (yield, 84%) of white needles were obtained by dissolving the crude material in 20 ml. of dichloromethane, filtering, and reprecipitation with n-hexane. Carrying out the reaction in a 1:1 mole ratio led to the formation of a black precipitate which was not characterized.

**Anal. Calcd. for C$_{16}$H$_{40}$AgClO$_4$P$_4$S$_4$:**

C, 27.77; H, 5.83; Cl, 5.12%.

**Found:** C, 28.34; H, 6.15; Cl, 4.24%.

**Copper(I)**

**Bis(tetramethyldiphosphine disulfide)copper(I) perchlorate**, [Cu(Me$_4$P$_2$S$_2$)$_2$]ClO$_4$. To Cu(ClO$_4$)$_2$·6H$_2$O (1.48 g., 4 mmole) in 10 ml. methanol was added, with stirring, 1.49 g. (8 mmole) of
tetramethyldiphosphine disulfide in 225 ml. of boiling methanol. A transient light green color developed along with a white precipitate. After stirring overnight, the crystalline material that deposited was separated from the almost colorless solution, washed with methanol and ether, and dried over P$_4$O$_{10}$ in vacuo. Yield, 1.66 g. (78%). An analytical sample was recrystallized from hot acetonitrile. The complex detonates at 175°.

Anal. Calcd. for C$_8$H$_{24}$ClCuO$_4$P$_4$S$_4^-$:

C, 17.94; H, 4.49; Cl, 6.62; P, 23.5%.

Found: C, 17.56; H, 4.34; Cl, 6.59; P, 23.11%.

The same complex can be prepared, as evidenced by similar infrared spectra and melting point (175°), by the reaction expressed in Equation 76.

\[
\text{CuBr}_2 + 2\text{Me}_2\text{P(S)P(S)Me}_2 + \text{LiClO}_4^-> \quad [\text{CuL}_2^+]\text{ClO}_4^-
\]  

(Eq. 76)

The addition of a solution of 0.37 g. of tetramethyldiphosphine disulfide (2 mmole) in 50 ml. boiling ethanol to a stirred solution of 0.22 g. (1 mmole) anhydrous copper(II) bromide and 0.11 g. (1 mmole) of lithium perchlorate in 25 ml. methanol produced a colorless solution and a white, crystalline complex after cooling which was isolated as above (0.27 g.; yield, 50%).

In addition, the same complex was also made using a different mole ratio (Eq. 77).

\[
2\text{CuBr}_2 + \text{LiClO}_4^-> 2\text{Me}_2\text{P(S)P(S)Me}_2 + [\text{CuL}_2^+]\text{ClO}_4^- + \text{Li}^+ + \text{CuBr}_2^{-}
\]  

(Eq. 77)
To a stirred solution of anhydrous copper(II) bromide (0.13 g, 1 mmole) and lithium perchlorate (0.07 g, 0.66 mmole) in 25 ml. of methanol was added a solution of tetramethyldiphosphine disulfide (0.19 g, 1 mmole) in 25 ml. of boiling methanol. After stirring overnight, the white, crystalline material was separated from the light green solution by filtration. It was washed with methanol and ether and subsequently dried in vacuo. Yield, 0.19 g (70%). The sample was recrystallized from acetonitrile.

**Anal.** Found: C, 17.58; H, 4.20%.

**Bis(tetraethyldiphosphine disulfide)copper(I) perchlorate,**

\[
\text{[Cu(\text{Et}_4\text{P}_2\text{S}_2)_2]ClO}_4. \]

Tetraethyldiphosphinedisulfide (2.42 g, 10 mmole) in 20 ml. of warm abs. ethanol was added with stirring to a solution of \(\text{Cu(ClO}_4)_2\cdot6\text{H}_2\text{O}\) (1.85 g, 5 mmole) in 10 ml. of absolute ethanol. A light yellow solution resulted immediately upon mixing the two solutions and a white compound crystallized from the cooled solution. The crystals were collected on a sintered glass funnel, washed with ethanol and ether, and dried over \(\text{P}_4\text{O}_{10}\) in vacuo; yield, 2.70 g (83%). The complex was prepared several times and the detonation temperature of the complexes ranged between 188-196°.

**Anal.** Calcd. for \(\text{C}_{8}\text{H}_{24}\text{ClCuO}_4\text{P}_4\text{S}_4:\)

\[
\text{C}, 29.67; \text{H}, 6.23; \text{Cl}, 5.47; \text{S}, 19.80%. \\
\text{Found: C}, 29.55; \text{H}, 6.28; \text{Cl}, 5.69; \text{S}, 20.09%. \\
\]

The same complex can be prepared (59% yield), as evidenced
by similar infrared spectrum and detonation point (192°), by the reaction expressed by Equation 78.

\[
\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{Et}_2\text{P(S)P(S)Et}_2 + \text{LiClO}_4 \rightarrow \quad [\text{CuL}_2]\text{ClO}_4
\]

\text{(Eq. 78)}

Tetraethyldiphosphine disulfide (1.21 g., 5 mmole) in 25 ml. of warm abs. ethanol was added, with stirring, to \text{CuCl}_2 \cdot 2\text{H}_2\text{O} (0.43 g., 2.5 mmole) in 25 ml. of abs. ethanol. A yellow solution resulted with no precipitate and lithium perchlorate (0.27 g., 2.5 mmole) in 25 ml. of warm abs. ethanol was added. A white, crystalline material formed (0.98 g.) which was isolated as above.

Displacement of \text{Et}_4\text{P}_2\text{S}_2 from its [\text{CuL}_2]\text{ClO}_4 complex. To 1.0 g. (1.55 mmole) of \text{[Cu(Et}_4\text{P}_2\text{S}_2)_2]\text{ClO}_4 was added 50 ml. of ammonium polysulfide and the slurry was allowed to stand overnight. The reaction mixture was extracted with three-50 ml. portions of ether and the ether was evaporated to leave 0.63 g. of a white, crystalline solid (84% yield, based on \text{Et}_4\text{P}_2\text{S}_2), m.p. 81-82.5°.

\text{Anal. Calcd. for C}_8\text{H}_{20}\text{P}_2\text{S}_2:}

\text{C, 39.65; H, 8.32%}.

\text{Found: C, 37.84; H, 8.02%}.

The melting point of tetraethyldiphosphine disulfide is 75-76°. The infrared spectrum of the material isolated in this reaction corresponds exactly to that of authentic tetraethyldiphosphine disulfide.
Bis[tetra(n-propyl)diphosphine disulfide] copper(I) perchlorate, \([Cu(P_{4}P_{2}S_{2})ClO_{4}]\). Tetra(n-propyl)diphosphine disulfide (1.19 g., 4 mmole) in 35 ml. of warm abs. ethanol was added, with stirring, to a solution of \(Cu(ClO_{4})_{2} \cdot 6H_{2}O\) (0.74 g., 2 mmole) in 10 ml. of abs. ethanol. A fleeting dark red color which immediately became light yellow resulted and white needles formed upon cooling; these were isolated by filtration, washed with ethanol and ether, and subsequently dried over \(P_{4}O_{10}\) in vacuo; yield, 0.91 g. (60%). M.p. 176-177° (followed by detonation).

Anal. Calcd. for \(C_{24}H_{56}ClCu_{4}P_{4}S_{4}\):
- C, 37.96; H, 7.43; Cl, 4.66%.
- Found: C, 37.75; H, 7.45; Cl, 4.90%.

\([Cu(Me_{4}P_{2}S_{2})_{2}][CuBr_{2}]\). To a stirred, boiling solution of tetramethyldiphosphine disulfide (0.37 g., 2 mmole) in 150 ml. of methanol was added copper(II) bromide (0.22 g., 1 mmole) in 30 ml. of methanol. A white precipitate began forming and the color of the solution lightened to become almost colorless as the reaction mixture was allowed to cool slowly to room temperature. The precipitate was isolated by filtration, washed with methanol and ether, and then dried in vacuo. Recrystallization from acetonitrile afforded 0.29 g. (88% of theory) of the white, crystalline complex.

Anal. Calcd. for \(C_{8}H_{24}Cu_{2}Br_{2}P_{4}S_{4}\):
- C, 14.57; H, 3.67; Br, 24.24%.
- Found: C, 15.40; H, 4.26; Br, 24.70%.
**[Cu(Me₂P₂S₂)₂][CuBrCl]**. To a stirred solution of anhydrous copper(II) chloride (0.27 g, 2 mmole) and lithium bromide (0.18 g, 2 mmole) in 25 ml. of methanol was added a boiling solution of tetramethyldiphosphine disulfide (0.74 g, 4 mmole) in 75 ml. of methanol. After stirring overnight, the white precipitate was isolated from the colorless solution and recrystallized from acetonitrile. Yield, 0.54 g. (88%).

**Anal.** Calcd. for C₇H₂₄BrClCu₂P₄S₄:

C, 15.62; H, 3.93; P, 20.15%.

Found: C, 15.60; H, 4.01; P, 20.34%.

**[Cu(Me₂P₂S₂)₂][CuI₂]**. Cuprous iodide (1.47 g, 3.78 mmole) was dissolved in 100 ml. of methanol containing 26 g. of sodium iodide. The resulting solution was added with stirring to 1.41 g. (7.56 mmole) of tetramethyldiphosphine disulfide in 150 ml. of boiling methanol. After stirring overnight, the white precipitate which had formed was isolated by filtration, washed with methanol and ether, and dried in vacuo. Yield, 2.41 g., (85%). An analytical sample was recrystallized from acetonitrile.

**Anal.** Calcd. for C₈H₂₄Cu₂I₂P₄S₄:

C, 12.75; H, 3.21; I, 33.69%.

Found: C, 12.65; H, 3.36; I, 33.97%.

**[Cu(Et₂P₂S₂)₂][CuCl₂]**. A solution of tetraethylidiphosphine disulfide (2.42 g, 10 mmole) in 10 ml. of abs. ethanol was added to 0.85 g. (5 mmole) of CuCl₂·2H₂O in 10 ml. of abs.
ethanol. After stirring for 20 min., addition of ether to the yellow solution induced crystallization. The white platlets which formed were collected on a sintered glass funnel, washed with ether (in which the ligand is very soluble), and dried over P₄O₁₀ in vacuo. Yield, 1.65 g. (96%). M.p. 121-122° decom. The complex decomposes upon standing.

**Anal.** Calc. for C₁₆H₄₀Cl₂Cu₂P₂S₄:

C, 28.15; H, 5.91; Cl, 10.39; P, 18.15%.

Found: C, 28.28; H, 5.91; Cl, 10.32; P, 18.06%.

The same complex was prepared in a similar reaction of tetraethyldiposphine disulfide and CuCl₂·2H₂O; only a 1:1 mole ratio was employed. (Eq. 81).

\[
\text{CuCl₂·2H₂O + Et₂P(S)P(S)Et₂} \rightarrow \frac{1}{2}[\text{CuL₂}][\text{CuCl₂}]
\]

(Eq. 81)

The product was isolated by cooling the reaction mixture in a freezer and not by the addition of ether; yield, 62%. M.p. 119-120° decom.

**Anal.** Found: C, 27.91; H, 5.83; Cl, 10.52%.

\[
[\text{Cu(Et₄P₂S₂)₂}][\text{CuBr₂}]. \text{ This complex was prepared and isolated as its chloride analog by the reaction of anhydrous copper(II) bromide with tetraethyldiposphine disulfide in abs. ethanol except that crystallization was induced by cooling the reaction mixture in a freezer; yield, 92%. This complex slowly decomposes upon standing.} \]
Anal. Calcd. for $\text{C}_{16}\text{H}_{40}\text{Cu}_2\text{Br}_2\text{P}_4\text{S}_4$:

C, 24.91; H, 5.22; Br, 20.71; Cu, 16.47%.

Found: C, 24.99; H, 5.11; Br, 20.93; Cu, 16.23%.

Attempted syntheses

Neither tetramethyldiphosphine disulfide, tetraethyldiphosphine disulfide, nor racemic or meso 1,2-diphenyl, 1,2-dimethyldiphosphine disulfide undergo any reaction with a variety of first row transition metal ions (mole ratios of 2:1 and 3:1) such as the perchlorates of chromium(III), manganese(II), cobalt(II), nickel(II), or zinc(II); halides (hydrated and anhydrous) of cobalt(II), nickel(II), or zinc(II); nor with Na$_3$[Co(CO$_3$)$_5$]$\text{3H}_2\text{O}$. A variety of non-aqueous solvents were employed in these attempted reactions. No color changes were found to occur; the ligands, usually dissolved in hot solvent, precipitate when the reaction solutions are cooled. Thallous nitrate also failed to yield a complex with tetramethyldiphosphine disulfide.

The tetramethyldiphosphine disulfide complex, $\text{[Cu(\text{Et}_4\text{P}_2\text{S}_2)_2]}\text{CuCl}_2$, was prepared in a manner similar to the bromide; this complex is very unstable and begins darkening immediately.

The interaction of 0.50 g. (1.38 mmole) of NaAuCl$_4$ in 25 ml. of abs. ethanol with a solution of tetramethyldiphosphine disulfide (0.26 g., 1.38 mmole) in 50 ml. of warm abs. ethanol
leads to the formation of a trace amount of brown precipitate; the filtrate deposits a metallic mirror upon standing.

4. Complexes of triphenylarsine sulfide

**Di-iodo(triphenylarsine sulfide)cadmium(II), \( \text{CdI}_2\text{AsS} \).**

A solution of triphenylarsine sulfide (0.34 g., 1 mmole) in 15 ml. of boiling abs. ethanol was mixed with cadmium(II) iodide (0.37 g., 1 mmole) in 10 ml. of warm abs. ethanol and the resulting solution was cooled in the freezer overnight. The precipitate was isolated by filtration, washed with 5 ml. of cold abs. ethanol, and dried. Recrystallization was achieved by dissolving the compound in dichloromethane (10 ml.) followed by filtering and the addition of n-hexane (30 ml.) to produce three-tenths of one gram (43%) of a white crystalline complex.

**Anal. Calcd. for \( C_{16}H_{15}AsCdI_2S \):**

- C, 30.68; H, 2.15; I, 36.03; S, 4.55%.
- Found: C, 30.45; H, 1.98; I, 36.20; S, 4.40%.

**Dichloro(triphenylarsine sulfide)mercury(II), \( \text{HgCl}_2\text{AsS} \).**

To a solution of mercury(II) chloride (0.27 g., 1 mmole) in 20 ml. of abs. ethanol was added 0.68 g. (2 mmole) of triphenylarsine sulfide in 25 ml. of boiling abs. ethanol. A white precipitate formed immediately, but redissolved to give a milky solution which deposited white needles upon cooling. These were collected, washed with ether and then 10 ml. of dichloromethane, and dried in vacuo. Yield, 0.43 g. (69%).
Anal. Calcd. for C\textsubscript{18}H\textsubscript{15}AsCl\textsubscript{2}HgS:

C, 35.45; H, 2.48; Cl, 11.63; S, 5.26%.

Found: C, 35.48; H, 2.62; Cl, 11.91; S, 5.21%.

Dibromo(triphenylarsine sulfide)mercury(II), \( \mathcal{O}_{\text{2As}} \text{HgBr}_{2} \).

White crystals formed upon mixing mercury(II) bromide (0.36 g., 1 mmole) in 10 ml. of abs. ethanol with 0.68 g. (2 mmole) of triphenylarsine sulfide in 25 ml. of boiling abs. ethanol. After cooling, these were isolated by filtration, washed with ethanol and ether followed by 10 ml. of dichloromethane, and then dried in vacuo. Yield, 0.54 g. (78%).

Anal. Calcd. for C\textsubscript{18}H\textsubscript{15}AsBr\textsubscript{2}HgS:

C, 30.94; H, 2.16; Br, 22.86%.

Found: C, 31.56; H, 2.36; Br, 22.83%.

Di-iodo(triphenylarsine sulfide)mercury(II), \( \mathcal{O}_{\text{2As}} \text{HgI}_{2} \).

Triphenylarsine sulfide (0.34 g., 1 mmole) in 25 ml. of boiling methanol was added to mercury(II) iodide (0.23 g., 0.5 mmoles) dissolved in 25 ml. of boiling methanol. The light yellow crystalline product, which precipitated upon cooling, was isolated by filtration, washed with ether and 10 ml. of dichloromethane, and dried in vacuo. Yield, 0.27 g. (68%).

Anal. Calcd. for C\textsubscript{18}H\textsubscript{15}AsHgI\textsubscript{2}S:

C, 27.27; H, 1.91; I, 32.02%.

Found: C, 26.70; H, 1.68; I, 31.92%.

Bis(triphenylarsine sulfide)silver(I) perchlorate, 

\[ \text{[Ag(\mathcal{O}_{\text{2As}})\text{ClO}_{4}]}. \] 

To a solution of silver(I) perchlorate (0.21g. 1 mmole) in 25 ml. of abs. ethanol was added 0.68 g. (2 mmole) of
triphenylarsine sulfide in 25 ml. of boiling abs. ethanol. The product, which formed upon cooling, was isolated by filtration, washed with ether, and air dried. This compound was recrystal-
ilized from dichloromethane/n-hexane. Yield, 0.73 g. (83%); m.p. 223-224° decomp.

**Anal.** Calcd. for C_{36}H_{30}As_{2}ClO_{4}S_{2}:

C, 48.91; H, 3.42; Cl, 4.01; S, 7.25%.

Found: C, 48.88; H, 3.49; Cl, 4.23; S, 7.20%.

Tetrakis(triphenylarsine sulfide)copper(I) perchlorate, C_{72}H_{60}As_{4}Cl_{4}Cu_{2}O_{4}S_{4}·CH_{2}Cl_{2}. The addition of 1.35 g. (4 mmole) of triphenylarsine sulfide in 50 ml. of warm abs. ethanol to 0.37 g. (1 mmole) of copper(II) perchlorate hexahydrate in 25 ml. of abs. ethanol initially produced a dark blue color; the solution color then lightened as white needle crystals formed. The precipitate was isolated, after cooling, and subsequently washed with ethanol and ether. The dried product was recrystallized from dichloromethane/n-hexane. Yield, 59% (0.95 g.); m.p. 192-193°.

**Anal.** Calcd. for [CuL_{4}]ClO_{4}, C_{72}H_{60}As_{4}ClCuO_{4}S_{4}:

C, 57.03; H, 3.99; Cl, 2.34; S, 8.46%.

Calcd. for [CuL_{4}]ClO_{4}·CH_{2}Cl_{2}, C_{72}H_{62}As_{4}Cl_{3}Cu_{2}O_{4}S_{4}:

C, 54.76; H, 3.90; Cl, 6.64; S, 8.02%.

Found: C, 53.84; H, 4.30; Cl, 7.23; S, 8.28%.

Bromo(triphenylarsine sulfide)copper(I), As_{2}Br·CuBr. To a solution of 0.22 g. (1 mmole) of copper(II) bromide in 50 ml. of boiling abs. ethanol was added 1.35 g. (4 mmole) of
triphenylarsine sulfide in 50 ml. of boiling ethanol. The resulting opaque white solution was cooled overnight in the freezer and the white product was isolated and recrystallized as above to yield 0.37 g. (77%) of white needles.

Anal. Calcd. for $C_{18}H_{15}AsBrCuS$:

<table>
<thead>
<tr>
<th>Element</th>
<th>Calcd. (%)</th>
<th>Found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>44.88</td>
<td>45.37</td>
</tr>
<tr>
<td>H</td>
<td>3.14</td>
<td>3.61</td>
</tr>
<tr>
<td>Br</td>
<td>16.59</td>
<td>16.37</td>
</tr>
<tr>
<td>S</td>
<td>6.65</td>
<td>6.74</td>
</tr>
</tbody>
</table>

Dichlorobis(triphenylarsine sulfide)palladium(II), $[\text{Pd(O}_2\text{As}S)_2\text{Cl}_2]$.

To a stirred, filtered solution of 0.59 g. (2 mmole) of sodium tetrachloropalladate(II) in 50 ml. of abs. ethanol was added 1.33 g. (4 mmole) of triphenylarsine sulfide in 50 ml. of boiling abs. ethanol. The reaction was stirred for 1 hour and the precipitate, which had come down immediately, was isolated by filtration. The material was air dried after washing in sequence with distilled water, ethanol, and ether. Recrystallization from DMF/Ethanol afforded 0.50 g. (29% of theory) of an orange brown solid.

Anal. Calcd. for $C_{36}H_{30}As_2Cl_2PdS_2$:

<table>
<thead>
<tr>
<th>Element</th>
<th>Calcd. (%)</th>
<th>Found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>50.63</td>
<td>50.62</td>
</tr>
<tr>
<td>H</td>
<td>3.53</td>
<td>3.52</td>
</tr>
<tr>
<td>Cl</td>
<td>8.30</td>
<td>8.30</td>
</tr>
<tr>
<td>S</td>
<td>7.51</td>
<td>7.51</td>
</tr>
</tbody>
</table>

Dichlorobis(triphenylarsine)palladium(II), $[\text{Pd(O}_2\text{As})_2\text{Cl}_2]$. Yellow complex prepared in a manner similar to the above employing triphenylarsine.

Anal. Calcd. for $C_{36}H_{30}As_2Cl_2Pd$:

<table>
<thead>
<tr>
<th>Element</th>
<th>Calcd. (%)</th>
<th>Found (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>54.75</td>
<td>54.54</td>
</tr>
<tr>
<td>H</td>
<td>3.83</td>
<td>3.62</td>
</tr>
<tr>
<td>Cl</td>
<td>8.98</td>
<td>8.76</td>
</tr>
</tbody>
</table>

Found:  C, 54.54; H, 3.62; Cl, 8.76%.
Dibromobis(triphenylarsine sulfide) palladium(II), \([\text{Pd}(\text{Ar}_2\text{AsS})_2\text{Br}_2]\). Tetrabromaopalladate(II) was prepared in situ by the reaction of 0.44 g. (1.5 mmole) sodium tetrachloropalladate (II) in 50 ml. of abs. ethanol with 1.53 g. (15 mmole) of lithium bromide in 25 ml. of abs. ethanol. The mixture was filtered and to it was added a solution of 1.01 g. (5 mmole) of triphenylarsine sulfide in 50 ml. of boiling abs. ethanol. The precipitate was isolated by the same procedure as the chloride analog and recrystallization from dichloromethane/n-hexane resulted in 0.45 g. (32% of theory) of the brown complex.

**Anal. Calcd.** for \(\text{C}_{36}\text{H}_{30}\text{As}_2\text{Br}_2\text{PdS}_2\):
- C, 45.86; H, 3.21; Br, 16.95; S, 6.80%.
- Found: C, 46.97; H, 3.50; Br, 17.16; S, 6.43%.

Di-iodobis(triphenylarsine sulfide) palladium(II), \([\text{Pd}(\text{Ar}_2\text{AsS})_2\text{I}_2]\). This brown complex was prepared in a manner analogous to the di-bromide with the exception that sodium iodide (2.25 g.) was employed. Yield, 0.30 g. (19% of theory).

**Anal. Calcd.** for \(\text{C}_{36}\text{H}_{30}\text{As}_2\text{I}_2\text{PdS}_2\):
- C, 41.70; H, 2.92; As, 14.45; I, 24.48%.
- Found: C, 41.47; H, 2.70; As, 14.48; I, 24.21%.

No complexes of triphenylarsine sulfide could be isolated from the reactions of anhydrous or hydrated cobalt(II), nickel(II), and zinc(II) halides or perchlorates. The unreacted ligand being recovered unchanged as evidenced by its melting point and infrared.

Triphenylarsine sulfide reacts with NaAuCl₄ (1:1 mole
ratio) in abs. ethanol or acetonitrile and also with Pd(NO$_3$)$_2$
 in DMF (4:1 mole ratio); but work up of these reactions yielded
only intractable residues which could not be recrystallized.

5. Complexes of tertiary phosphine selenide

Tri(n-butyl)phosphine selenide

Di-iodobis[Tri(n-butyl)phosphine selenide] cadmium(II)
[Cd(C$_{12}$H$_{26}$PSe)$_2$I$_2$]. To 0.73 g. (2 mmole) of anhydrous cadmium(II)
iodide in 20 ml. of abs. ethanol was added 21.2 ml. (8 mmole) of
a 0.376 M. ethanolic tri(n-butyl)phosphine selenide solution. The
reaction mixture was cooled overnight in a freezer after the ad­
dition of a small quantity of ether to produce large colorless
crystals. Yield, 0.70 g. (38%).

**Anal.** Calcd. for C$_{24}$H$_{54}$CdI$_2$P$_2$Se$_2$:
- C, 31.04; H, 5.86; I, 27.32; P, 6.67%.
- Found: C, 30.77; H, 5.73; I, 27.15; P, 6.63%.

Dibromobis[tri(n-butyl)phosphine selenide]mercury(II),
[Hg(C$_{12}$H$_{26}$PSe)$_2$Br$_2$]. An ethanolic solution of a 0.376 M. tri-
(n-butyl)phosphine selenide (10 ml., 3.76 mmole) was added to a
warm solution of 0.68 g. (1.88 mmole) anhydrous mercury(II) bro­
mide in 10 ml. abs. ethanol. A white precipitate formed upon
cooling and it was isolated by filtration, dried, and recrystal­
lized from dichloromethane/n-hexane. The resulting crystalline
material weighed 0.93 g. (53% of theory).
Anal. Calcd. for C_{24}H_{54}Br_{2}HgP_{2}Se_{2}:
C, 31.23; H, 5.90; Br, 17.32; Se, 17.11%.

Found: C, 31.27; H, 6.08; Br, 16.53; Se, 16.90%.

Triphenylphosphine selenide

Dichloro(triphenylphosphine selenide)mercury(II),
\( \Phi_{2}PSe \cdot HgCl_{2} \). White platlets formed when a solution of mercury(II) chloride (0.43 g., 1.6 mmole) in 5 ml. of abs. ethanol was mixed with a warm solution of triphenylphosphine selenide (0.68 g., 2 mmole) in 50 ml. of abs. ethanol. After cooling, these were collected by filtration and washed with ethanol, dichloromethane, and ether. The yield of compound, after drying in vacuo, was 0.90 g. (92% of theory).

Anal. Calcd. for C_{18}H_{15}Cl_{2}HgPSe:
C, 35.28; H, 2.47; Cl, 11.57%.

Found: C, 35.35; H, 2.70; Cl, 11.92%.

Dibromo(triphenylphosphine selenide)mercury(II),
\( \Phi_{2}PSe \cdot HgBr_{2} \). To a solution of 0.36 g. (1 mmole) of mercury(II) bromide in 10 ml. of warm abs. ethanol was added 0.68 g. (2 mmole) of triphenylphosphine selenide in 50 ml. of warm abs. ethanol. After cooling, the white crystalline material was isolated, washed, and dried in the same manner as for the chlorine analog. Yield, 0.67 g. (95%).

Anal. Calcd. for C_{18}H_{15}Br_{2}HgPSe:
C, 30.81; H, 2.15; Br, 22.78%.

Found: C, 31.35; H, 2.31; Br, 23.01%. 
Di-iodo(triphenylphosphine selenide)mercury(II), $\text{C}_2\text{PSe}_2\text{HgI}_2$.

A solution of triphenylphosphine selenide (0.68 g., 2 mmole) in 50 ml. of warm abs. ethanol was added to mercury(II) iodide (0.45 g., 1 mmole) in 25 ml. of abs. ethanol. A light yellow precipitate formed upon cooling and it was collected and worked up as in the preceding syntheses to yield 0.69 g. of compound (86% of theory).

**Anal. Calcd. for $\text{C}_{18}\text{H}_{19}\text{HgI}_2\text{PSe}$:**

C, 27.17; H, 1.90; I, 31.90%.

**Found:** C, 27.66; H, 2.09; I, 31.95%.

Bis(triphenylphosphine selenide)silver(I) perchlorate, \([\text{Ag}(\text{C}_2\text{PSe})_2]\text{ClO}_4\). To 0.21 g. (1 mmole) of anhydrous silver(I) perchlorate in 25 ml. of abs. ethanol was added 0.68 g. (2 mmole) of triphenylphosphine selenide in 50 ml. of warm abs. ethanol. The white precipitate was isolated and then washed with ethanol and ether; recrystallization from dichloromethane/n-hexane afforded 0.65 g. (yield, 83%) of small, white needle crystals.

**Anal. Calcd. for $\text{C}_{32}\text{H}_{30}\text{AgClO}_4\text{P}_2\text{Se}_2$:**

C, 48.59; H, 3.40; Cl, 3.98%.

**Found:** C, 48.36; H, 3.46; Cl, 3.83%.

Dichlorobis(triphenylphosphine selenide)palladium(II), $[\text{Pd}(\text{C}_2\text{PSe})_2\text{Cl}_2]$. Triphenylphosphine selenide (1.36 g., 4 mmole) in 100 ml. of warm abs. ethanol was added to a stirred, filtered solution of 0.59 g. (2 mmole) of sodium tetrachloropalladate(II)
in 50 ml. of abs. ethanol. The light orange-brown precipitate was collected after stirring for 1 hr. It was washed with distilled water, ethanol, and ether (followed by a small quantity of dichloromethane) and subsequently dried for 24 hr. over P_{4}O_{10} in vacuo to afford 1.50 g. (yield, 75\%) of complex. M.p. 208\° decomp.

Anal. Calcd. for C_{32}H_{30}Cl_{2}P_{2}PdSe_{2}:

- C, 50.29; H, 3.52; Cl, 8.25\%.
- Found: C, 48.95; H, 3.57; Cl, 8.25\%.

Dibromobis(triphenylphosphine selenide) palladium(II), [Pd(\text{\textsuperscript{3}PSe})_{2}Br_{2}]. To a stirred, filtered solution, which had been made by mixing 0.44 g. (1.5 mmole) of sodium tetrachloropalladate(II) in 30 ml. of abs. ethanol with 1.33 g. (15 mmole) of lithium bromide in 50 ml. of abs. ethanol, was added a warm solution of triphenylphosphine selenide (1.02 g., 3 mmole) in 100 ml. of abs. ethanol. The light brown-orange precipitate was collected and washed in the same manner as its chloride analog. Yield, 1.15 g. (81\%); m.p. 222° decomp.

Anal. Calcd. for C_{32}H_{30}Br_{2}P_{2}PdSe_{2}:

- C, 45.57; H, 3.19; Br, 16.85\%.
- Found: C, 44.66; H, 3.24; Br, 16.74\%.

Dichlorobis(triphenylphosphine selenide) platinum(II), [Pt(\text{\textsuperscript{3}PSe})_{2}Cl_{2}]. To a stirred, filtered solution of 0.38 g. (1 mmole) of sodium tetrachloroplatinate(II) in 50 ml. of abs. ethanol was added 0.68 g. (2 mmole) of triphenylphosphine selenide in 50 ml. of warm abs. ethanol. The reaction was
stirred one hour and the precipitate was then isolated. It was washed with distilled water, ethanol, and ether and a small quantity of dichloromethane. The flesh colored product, after drying for 24 hr. over P_4O_{10} in vacuo, weighed 0.50 g. (yield, 53%).

**Anal.** Calcd. for C_{32}H_{30}Cl_2P_2PtSe_2:

C, 45.58; H, 3.19; Cl, 7.47%.

Found: C, 45.35; H, 3.15; Cl, 7.31%.

Other

The following compounds were prepared and isolated in a manner analogous to the preparation of [Pd(O_3PSe)_2Cl_2].

**Dichlorobis[tri(m-tolyl)phosphine selenide]palladium(II),**

[Pd(C_{21}H_{21}PSe)_2Cl_2]. Red-orange powder. Yield, 75%; m.p. 262° decomp.

**Anal.** Calcd. for C_{42}H_{42}Cl_2P_2PdSe_2:

C, 53.44; H, 4.48; Cl, 7.51%.

Found: C, 53.18; H, 4.60; Cl, 7.74%.

**Dichlorobis[tri(p-tolyl)phosphine selenide]palladium(II),**

[Pd(C_{21}H_{21}PSe)_2Cl_2]. Orange powder. Yield, 54%; m.p. 182° decomp.

**Anal.** Calcd. for C_{42}H_{42}Cl_2P_2PdSe_2:

C, 53.44; H, 4.48; Cl, 7.51%.

Found: C, 53.43; H, 4.49; Cl, 7.93%.

**Dichlorobis[diphenyl(allyl)phosphine selenide]palladium(II),**

[Pd(C_{15}H_{15}PSe)_2Cl_2]. Red brown powder which was recrystallized
from dichloromethane/n-hexane to afford 0.53 g. of product (yield, 45%).

**Anal.** Calcd. for \( \text{C}_{30}\text{H}_{30}\text{Cl}_{2}\text{P}_{2}\text{PdSe}_{2} \):

\[
\begin{align*}
\text{C} & \text{, 45.74; } \text{H} \text{, 3.84; } \text{Cl} \text{, 9.00%}. \\
\text{Found: } \text{C} & \text{, 44.85; } \text{H} \text{, 3.83; } \text{Cl} \text{, 9.46%}.
\end{align*}
\]

**Attempted syntheses**

The reaction of ethanolic solutions of tri(n-butyl)phosphine selenide or triphenylphosphine selenide in boiling ethanol with zinc(II) iodide or perchlorate in abs. ethanol produces no complexes; for example, unreacted triphenylphosphine selenide precipitates when the reaction solutions are cooled. These ligands also produce no color changes when they are mixed with ethanolic solutions of cobalt(II) halides or perchlorates or nickel(II) halides, perchlorate, or nitrate.

Unlike tertiary phosphine sulfides, these selenides do not form copper(I) complexes when reacted with copper(II) chloride, bromide, or perchlorate in ethanol. Reduction occurs as evidenced by resulting colorless solutions, but elemental selenium is also formed; i.e., tertiary phosphine selenides decompose in the presence of copper(II).

Although an immediate white precipitate occurs upon mixing ethanolic solutions of triphenylphosphine selenide and silver(I) perchlorate, no precipitate forms in a similar reaction with tri(n-butyl)phosphine selenide.

Analogous to tertiary phosphine sulfides,
triphenylphosphine selenide does not displace iodide or thiocyanate from \( \text{PdX}_4^- \) species to form complexes of the type 
\[ \text{[Pd(Ø}_3 \text{PSe)}_2 \text{X}_2] \]
containing these anions; nor can the species, 
\[ \text{[Pd(Ø}_3 \text{PSe)}_4] \text{(NO}_3)_2 \], be isolated although color changes occur when 
a DMF solution of \( \text{Pd(NO}_3)_2 \) is reacted with one of triphenyl-
phosphine selenide.

Tri(n-butyl)phosphine selenide reacts with palladium(II) 
and platinum(II) salts in ethanol to produce dark colored solu-
tions but no crystalline complexes can be isolated.

These tertiary phosphine selenides produce trace amounts 
of dark colored precipitates when reacted in a 1:1 mole ratio 
with \( \text{NaAuCl}_4 \). Initially, the color of these precipitates is 
red-orange but they darken very quickly. The infrared spectra 
of these residues show little organic material present.

6. Complexes synthesized for 
thiocyanate study

Diphenyl(o-diphenylarsinophenyl) 
phosphine complexes

The abbreviation AP shall be used to designate the ligand 
diphenyl(o-diphenylarsinophenyl)phosphine, \( Ø_2 (o-Ø_2 \text{AsC}_6 \text{H}_4) \text{P} \).

General procedure. The first preparation illustrates the 
general procedure. In the preparation of the other halide and 
pseudohalide derivatives, the tetrahalopalladate(II) species 
were prepared in situ by mixing an ethanolic solution of sodium 
tetrachloropalladate(II) with a ten fold excess of the appropriate 
lithium or sodium halide or pseudohalide except where potassium
selenocyanate was used in a 4:1 mole ratio excess. The same procedure was employed in the preparation of the platinum(II) complexes using sodium tetrachloroplatinate(II).

$[\text{Pd}(\text{AP})\text{Cl}_2]$. To a stirred, filtered solution of 1.18 g. (4 mmole) of sodium tetrachloropalladate(II) in 100 ml. of abs. ethanol was added a warm solution of AP (1.96 g., 4 mmole) in 90 ml. of n-butanol. The reaction was stirred for one hour. The precipitate, which had formed immediately, was filtered and washed with ethanol and ether. The complex was recrystallized from hot DMT to yield 0.67 g. of a very light yellow crystalline product (yield, 24%).

**Anal. Calcd. for $\text{C}_{30}\text{H}_{24}\text{AsCl}_2\text{PPd}$:**

- C, 53.96; H, 3.62; Cl, 10.62%.
- Found: C, 53.88; H, 3.80; Cl, 10.55%.

$[\text{Pd}(\text{AP})\text{Br}_2]$. Light lemon yellow complex which was re-crystallized by dissolution in minimum amount of dichloromethane followed by filtration and reprecipitation with n-hexane (yield, 43%).

**Anal. Calcd. for $\text{C}_{30}\text{H}_{24}\text{AsBr}_2\text{PPd}$:**

- C, 47.62; H, 3.20; Br, 21.12%.
- Found: C, 47.82; H, 3.48; Br, 20.84%.

$[\text{Pd}(\text{AP})\text{I}_2]$. Light orange, crystalline compound recrystallized from dichloromethane/n-hexane (yield, 75%).

**Anal. Calcd. for $\text{C}_{30}\text{H}_{24}\text{AsI}_2\text{PPd}$:**

- C, 42.36; H, 2.84; I, 29.84%.
- Found: C, 42.55; H, 3.03; I, 29.56%. 
[Pd(AP)₂][Pd(SCN)₄]. This orange complex was the product of reaction between Pd(SCN)₄⁻ and AP. It was isolated by washing with distilled water followed by ethanol and ether and was subsequently dried for 24 hr. over P₂O₅ in vacuo in a yield of 77%. This complex converts to a yellow form at approximately 190-200° and then melts at 253.5-254°.

Anal. Calcd. for C₆₄AsNH₄₂P₂₂Pd₂S₄:
C, 53.91; H, 3.39; N, 3.93; S, 8.99%.
Found: C, 54.10; H, 3.49; N, 3.91; S, 8.79%.

[Pd(AP)(NCS)(SCN)]. This complex, a crystalline, bright yellow material, was prepared by recrystallizing the above orange isomer from DMF/ethanol with an additional recrystallization from dichloromethane/n-hexane. Yield, 45%; m.p. 253-253.5°.

Anal. Calcd. for C₃₂H₂₄AsNH₂₂PdS₂:
C, 53.91; H, 3.39; N, 3.93; S, 8.99%.
Found: C, 53.61; H, 3.20; N, 3.74; S, 8.72%.

[Pd(AP)(SeCN)₂]. Red-orange, crystalline material which was recrystallized from DMF/ethanol; yield, 79%.

Anal. Calcd. for C₃₂H₂₄AsNH₂₂PdSe₂:
C, 45.82; H, 2.88; N, 3.34%.
Found: C, 45.65; H, 3.00; N, 3.20%.

[Pt(AP)Cl₂]. White, crystalline material which was recrystallized from DMF/ethanol; yield, 34%.

Anal. Calcd. for C₃₀H₂₄AsCl₂Pt:
C, 47.63; H, 3.20; Cl, 9.37%.
Found: C, 47.71; H, 3.40; Cl, 9.58%.
To 0.46 g. (2 mmole) of palladium(II) nitrate in 20 ml. of DMF was added, with stirring, a solution of 1.96 g. (4 mmole) of AP in 20 ml. of warm DMF. The complex was precipitated from solution by addition of ether. Recrystallization from DMF/ether afforded 1.26 g. of a pale yellow, crystalline material. Yield, 52%; m.p. 224°.

Anal. Calcd. for C₆₀H₄₈As₂N₂O₂P₂Pd:

C, 59.51; H, 3.99; N, 2.31%.

Found: C, 59.58; H, 4.12; N, 2.50%.

1,2-Bis(diphenylarsino)ethane complexes

The abbreviation AA shall be used to designate the ligand 1,2-bis(diphenylarsino)ethane, \( \phi_2\text{AsCH}_2\text{CH}_2\text{As}\phi_2 \).

General procedure. The first preparation is illustrative of the general procedure employed in preparing these complexes. In the preparation of the other halide or pseudohalide derivatives, the tetrahalopalladate(II) species were prepared in situ by the addition of a 10 fold excess of the corresponding lithium or sodium halide or thiocyanate to an ethanolic solution of sodium tetrachloropalladate(II) except for the selenocyanate derivative where a 4:1 mole excess of potassium selenocyanate was employed.

Dichloro[1,2-bis(diphenylarsino)ethane]palladium(II), \([\text{Pd(AA)}\text{Cl}_2]\). To a filtered, stirred solution of sodium tetrachloropalladate(II) (0.59 g., 2 mmole) in 75 ml. of abs. ethanol was added a solution of 1,2-bis(diphenylarsino)ethane (0.97 g.,
2 mmol) in 15 ml. of dichloromethane. The reaction mixture was allowed to stand overnight and the precipitate was isolated by filtration, washed with ethanol and ether, and recrystallized from dichloromethane/n-hexane to afford 0.90 g. of a light yellow, crystalline compound (68% of theory).

**Dibromo[1,2-bis(diphenylarsino)ethane]palladium(II),**

[\(\text{Pd(\text{AA})Br}_2\)]. Yellow, crystalline compound which was recrystallized from dichloromethane/n-hexane in 40% yield.

**Dibromo[1,2-bis(diphenylarsino)ethane]palladium(II),**

[\(\text{Pd(\text{AA})Br}_2\)]. Yellow, crystalline compound which was recrystallized from dichloromethane/n-hexane in 40% yield.

**Dibromo[1,2-bis(diphenylarsino)ethane]palladium(II),**

[\(\text{Pd(\text{AA})Br}_2\)]. Yellow, crystalline compound which was recrystallized from dichloromethane/n-hexane in 40% yield.

**Dibromo[1,2-bis(diphenylarsino)ethane]palladium(II),**

[\(\text{Pd(\text{AA})Br}_2\)]. Yellow, crystalline compound which was recrystallized from dichloromethane/n-hexane in 40% yield.

**Dibromo[1,2-bis(diphenylarsino)ethane]palladium(II),**

[\(\text{Pd(\text{AA})Br}_2\)]. Yellow, crystalline compound which was recrystallized from dichloromethane/n-hexane in 40% yield.

**Dibromo[1,2-bis(diphenylarsino)ethane]palladium(II),**

[\(\text{Pd(\text{AA})Br}_2\)]. Yellow, crystalline compound which was recrystallized from dichloromethane/n-hexane in 40% yield.

**Dibromo[1,2-bis(diphenylarsino)ethane]palladium(II),**

[\(\text{Pd(\text{AA})Br}_2\)]. Yellow, crystalline compound which was recrystallized from dichloromethane/n-hexane in 40% yield.
A yellow complex showing an identical infrared spectrum to the above complex was prepared by adding 1,2-bis(diphenylarsino)ethane in boiling n-butanol to a boiling solution of Pd(SCN)$_4^{2-}$ in abs. ethanol with immediate quenching in a ice-water bath.

Diselenocyanato[1,2-bis(diphenylarsino)ethane]palladium(II), [Pd(AA)(SeCN)$_2$]. Yellow orange, crystalline compound which was recrystallized from dichloromethane/n-hexane in 42% yield.

1,2-Bis(diphenylphosphino)ethane complexes

The abbreviation PP shall be used to designate the ligand 1,2-bis(diphenylphosphino)ethane, $\Phi_2$PCH$_2$CH$_2$P$\Phi_2$.

General procedure. The general procedure for the preparation of these complexes is the same as that employed in the preparation of 1,2-bis(diphenylarsino)ethane complexes.

Dichloro[1,2-bis(diphenylphosphino)ethane]palladium(II), [Pd(PP)Cl$_2$]. Light yellow compound which was recrystallized from dichloromethane/n-hexane (yield, 17%).
Anal. Calcd. for $C_{26}H_{24}Cl_2Pd$:  
\[ C, 54.24; H, 4.20; Cl, 12.32\% . \]

Found: $C, 54.03; H, 4.34; Cl, 12.35\%$.

**Dibromo[1,2-bis(diphenylphosphino)ethane]palladium(II),**  
$[\text{Pd}(\text{PP})\text{Br}_2]$. Yellow, crystalline compound which was recrystallized from dichloromethane/n-hexane (yield, 72\%).  

Anal. Calcd. for $C_{26}H_{24}Br_2Pd$:  
\[ C, 46.98; H, 3.64; Br, 24.05\% . \]

Found: $C, 47.69; H, 3.86; Br, 22.94\%$.

**Di-iodo[1,2-bis(diphenylphosphino)ethane]palladium(II),**  
$[\text{Pd}(\text{PP})\text{I}_2]$. Rich yellow, crystalline complex which was recrystallized from dichloromethane/n-hexane (yield, 81\%).  

Anal. Calcd. for $C_{26}H_{24}I_2Pd$:  
\[ C, 41.16; H, 3.19; I, 33.46\% . \]

Found: $C, 40.92; H, 3.37; I, 33.86\%$.

$[\text{Pd}(\text{PP})(\text{NCS})(\text{SCN})]$. Light yellow compound which was recrystallized from dichloromethane/n-hexane (yield, 59\%). A light orange product initially formed during the reaction but it converted to the yellow form after stirring overnight.

Anal. Calcd. for $C_{28}H_{24}As_2N_2PdS_2$:  
\[ C, 54.15; H, 3.89; N, 4.51; S, 10.33\% . \]

Found: $C, 54.01; H, 3.85; N, 4.32; S, 10.58\%$.

A light yellow complex exhibiting an infrared spectrum identical with the above complex was prepared by adding 1,2-bis(diphenylphosphino)ethane in boiling n-butanol to a
boiling solution of Pd(SCN)$_4^{2-}$ in abs. ethanol with immediate quenching in an ice-water bath.

$[^\text{Pd(PP)}_2][\text{Pd(SCN)}_4]$. This light orange complex was isolated by carrying out the reaction with both the ethanolic solution of Pd(SCN)$_4^{2-}$ and the dichloromethane solution of the ligand cooled to zero degrees. The product, after stirring for 15 min. at 0°, was isolated by filtration; washed with distilled water, ethanol, and ether; and then dried over $P_2O_5$ for 48 hr. in vacuo. Yield, 73%.

Anal. Calcd. for C$_{56}$H$_{48}$N$_4$P$_4$Pd$_2$S$_4$:

C, 54.15; H, 3.90; N, 4.51; S, 10.33%.

Found: C, 53.92 H, 4.06; N, 4.29; S, 10.40%.

$[^\text{Pd(PP)}_2][\text{Pd(SeCN)}_4]$. The complex, diselenocyanato $[1,2$-bis(diphenylphosphino)ethane] palladium(II) - Pd(PP)(SeCN)$_2$, could not be prepared by the general procedure. The light orange Magnus type complex, $[^\text{Pd(PP)}_2][\text{Pd(SeCN)}_4]$, was obtained, however, by reacting an ethanolic solution of Pd(SeCN)$_4^{2-}$ with the ligand in boiling n-butanol. The precipitate was isolated by filtration; washed with distilled water, ethanol, and ether; and subsequently dried for 48 hr. over $P_2O_5$ in vacuo. Yield, 70%.
Tetramethylethylene diamine complexes

The abbreviation TMEN shall be used to designate the ligand tetramethylethylene diamine, Me₂NCH₂CH₂NMe₂.

Dichloro(tetramethylethylene diamine)palladium(II), [Pd(TMEN)Cl₂]. This complex was supplied by Dr. Mock and its preparation is in the literature (242).

Dibromo (tetramethylethylene diamine) palladium(II), [Pd(TMEN)Br₂]. To a stirred solution of 2 mmole of PdBr₄⁻ (which had been prepared in the usual fashion) in 115 ml. of abs. ethanol was added a solution containing 1 ml. of the diamine (1.58 g., 7.3 mmole - in excess) in 25 ml. of abs. ethanol. The precipitate was collected after stirring for one hour, washed with ethanol and ether, and then air dried. It was recrystallized from DMF/ethanol to afford 0.54 g. of a crystalline yellow compound (yield, 47%).

Anal. Calcd. for C₆H₁₆Br₂N₂Pd:
C, 18.84; H, 4.22; N, 7.33; Br, 41.79%.
Found: C, 18.94; H, 4.30; N, 7.41; Br, 41.91%.

Di-iodo(tetramethylethylene diamine)palladium(II), [Pd(TMEN)I₂]. An analogous reaction carried out with 2 mmole of PdI₄²⁻ in abs. ethanol and 1 ml. of the ligand resulted in
0.56 g. of a rod compound after recrystallization from dichloromethane/n-hexane (yield, 59%).

Anal. Calcd. for C₂₆H₁₆I₂N₂Pd:
C, 15.13; H, 3.39; I, 53.23%.

Found: C, 15.26; H, 3.39; I, 53.08%.

Di-isothiocyanato(tetramethylethylene diamine)palladium(II), [Pd(TMEN)(NCS)₂]. The analogous interaction of 1 ml. of tetramethylethylene diamine in 25 ml. of abs. ethanol with an ethanolic solution of 5 mmole of Pd(SCN)₄⁺ was used to prepare this complex. It was recrystallized from DMF/ethanol to yield 1.20 g. (71%) of a yellow powder.

Anal. Calcd. for C₂₆H₁₆N₄PdS₂:
C, 28.36; H, 4.76; N, 16.54; S, 18.93%.

Found: C, 28.40; H, 4.91; N, 16.34; S, 18.71%.

The selenocyanate analog could not be prepared in a similar manner.

Diphenyl(2-dimethylaminoethyl)phosphine complexes

The abbreviation PN shall be used to designate the ligand diphenyl(2-dimethylaminoethyl)phosphine, C₆H₄P(CH₂CH₂NMe₂). The density of this ligand was approximately 1 g./ml.

General procedure. To a stirred, ethanolic solution of the appropriate PdX₄⁺ salt (3 mmole), prepared as previously described, was added a solution of 0.67 ml. (3 mmole) of the ligand in 10 ml. of abs. ethanol. The precipitates which formed were allowed to stir for one hour and then were isolated.
by filtration. The products were subsequently washed with distilled water, ethanol, and ether followed by drying for 48 hr. over $P_4O_{10}$ in vacuo.

Dichloro[diphenyl(2-dimethylaminoethyl)phosphine]palladium(II), $[\text{Pd(PN)Cl}_2]$. Light orange complex; yield, 38%.

In this case, an analytical sample was recrystallized by dissolving in the minimum amount of dichloromethane, filtering, and adding $n$-hexane to cause precipitation. The analyses found for this complex were not good.

**Anal. Calcd. for $C_{16}H_{20}Cl_2NPPd$:**

\[
\begin{align*}
C & : 44.21; H, 4.64; Cl, 16.32\%.
\end{align*}
\]

**Found:** $C, 40.53; H, 4.73; Cl, 17.65\%.$

Dibromo[diphenyl(2-dimethylaminoethyl)phosphine]palladium(II), $[\text{Pd(PN)Br}_2]$. Yellow-brown complex; yield, 36%.

**Anal. Calcd. for $C_{16}H_{20}Br_2NPPd$:**

\[
\begin{align*}
C & : 36.70; H, 3.85; Br, 30.53.
\end{align*}
\]

**Found:** $C, 36.52; H, 4.01; Br, 30.28\%.$

Di-iodo[diphenyl(2-dimethylaminoethyl)phosphine]palladium(II), $[\text{Pd(PN)I}_2]$. Red-brown complex; yield, 50%.

**Anal. Calcd. for $C_{16}H_{20}I_2NPPd$:**

\[
\begin{align*}
C & : 31.12; H, 3.26; I, 41.10\%.
\end{align*}
\]

**Found:** $C, 31.06; H, 3.10; I, 41.27\%.$

$[\text{Pd(PN)(NCS)(SCN)}]$. Yellow, crystalline complex which was recrystallized from dichloromethane/$n$-hexane; yield, 45%. 
Anal. Calcd. for C_{18}H_{20}N_{3}PPdS_{2}:
C, 45.05; H, 4.20; N, 8.76; S, 13.36%.
Found: C, 45.26; H, 4.22; N, 8.66; S, 13.59%.

A selenocyanate complex could be prepared by the general procedure.

F. Instrumentation

1. Conductivity measurements

Molar conductance measurements were carried out employing an Industrial Instruments Model RC-16B conductivity bridge (cell, K = 1.47). The measurements were taken on approximately 10^{-3} molar solutions of acetonitrile, acetone, or nitromethane in a room thermostated for constant temperature.

2. Spectral measurements

Infrared spectra were obtained routinely on a Perkin-Elmer Mode; 337 grating spectrophotometer with samples mounted as potassium bromide pellets or as Nujol mulls between crystalline potassium bromide disks. The polystyrene spectrum was used for calibration. Accurate peak determinations were ascertained by use of a Beckman IR-9 high resolution spectrophotometer, the position being read directly from the optical dial with an accuracy of ± 0.5 cm^{-1} in the 500-700 cm^{-1} region and ± 1 cm^{-1} in the 2100 cm^{-1} region.

Raman spectra

Raman spectra were recorded and supplied by the Perkin-Elmer Corp. employing a Model LR-1 Laser excited Raman
Spectrometer. Prof. Stuart Tobias of the University of Minnesota also supplied some Raman spectra.

Electronic absorption spectra

**Reflectance spectra.** Reflectance spectra were determined on a Cary Model 14 recording spectrophotometer. The samples were mounted as Mujol mulls on Whatman #1 filter paper employing the basic procedure of Lee, Griswold, and Kleinberg (185) and is described in detail by Pavokovid (271).

**Solution spectra.** Solution spectra of the complexes were obtained with a Cary Model 14 recording spectrophotometer using matched one cm. quartz cells in the region 700 μm-300μm. The solutions were prepared by dissolving known quantities of the complexes in the respective solvents. The corrected absorbance of a peak was determined by running the pure solvent over the same region and subtracting its absorbance from that of the peak. Extinction coefficients (ε) were calculated from the equation $A = εbc$; where $A$ equals the absorbance at a particular wavelength, $b$ equals 1 cm., and $c$ equals the molar concentration (moles/liter).

3. **Differential thermal analysis**

The differential thermal analysis experiment was performed by C. S. Springer, Jr. with the co-operation of Dr. R. Sievers.
at the Wright-Patterson Airforce Base, Dayton, Ohio.

4. **X-ray diffraction work**

    The X-ray parameter data was supplied by Dr. P. J. Wheatley of Monsanto Research, S.A., in Zurich, Switzerland.

5. **Molecular weight determinations**

    Molecular weights were performed by Galbraith Laboratories, Knoxville, Tenn.

6. **Elemental analyses**

    Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. and by Dr. A. Bernhardt at the Mikroanalytisches Laboratorium in Max-Planck-Institut für Kohlenforschung, Mulheim (Ruhr), Hohenweg 17, Germany.
CHAPTER III

DISCUSSION

A. Synthesis of Ligands

1. Phosphine and arsine sulfides

Simple tertiary phosphine and arsine sulfides; e.g., trimethylphosphine sulfide, triphenylphosphine sulfide, and triphenylarsine sulfide, were prepared employing standard procedures. Elimination reactions of the general type shown in Equation 82 were used in order to prepare certain more complicated phosphine sulfide ligands. These attempts were unsuccessful.

Although the organolithium reaction has been used only once before by Screttas and Isbell (302) to prepare tertiary phosphine sulfides by reaction with thiophosphoryl compounds, the use of this type reaction to produce diphenyl(o-diphenylarsinophenyl)phosphine sulfide, XXXIV, (Eq. 29) shows the general utility of the reaction.

\[ \text{XXXIV} \]

\[ \text{XXXV} \]

It would have been advantageous to prepare diphenyl(o-diphenylphosphinophenyl)arsine sulfide (XXXV), the arsine sulfide
analog of diphenyl(o-diphenylarsinophenyl)phosphine sulfide. The intermediates which would be necessary for the synthesis of XXXV are XXXVI and XXXVII. Compound XXXVI, o-bromophenyl(diphenyl-

\[
\begin{align*}
XXXVI & \quad XXXVII \\
\text{Br} & \quad \text{P}\phi_2 \\
\end{align*}
\]

phosphine) is reported to be very difficult to prepare in good yield (75); attempts to prepare this species are described in Section IIIA5. In addition, compounds such as XXXVII, analogous to the phosphorus compounds, are unknown. These limitation prevent the preparation of XXXV by an organolithium route similar to Equations 28 and 29.

Addition of sulfur to the tertiary arsine intermediate failed to produce o-bromophenyl(diphenylarsine sulfide) (Eq. 75). Alternatively, this compound would have permitted XXXV to be prepared possibly as shown in Equations 83 and 84.

\[
\begin{align*}
\text{o-BrC}_6\text{H}_4\text{As}(S)\phi_2 + \text{1-BuLi} & \to \\
\text{o-LiC}_6\text{H}_4\text{As}(S)\phi_2 + \text{n-BuBr} & \to \\
\text{o-LiC}_6\text{H}_4\text{As}(S)\phi_2 + \phi_2\text{PCl} & \to \\
\phi_2\text{PC}_6\text{H}_4\text{As}(S)\phi_2 + \text{LiCl} & \to
\end{align*}
\]

(Eq. 83) (Eq. 84)

2. Phosphine selenides

Investigations by this author indicate that potassium selenocyanate, KNCSe, probably is capable of producing elemental selenium in a reactive form. For instance, the selenocyanate
ion decomposes to yield red, elemental selenium, instead of forming \( \text{Cu(NCSe)}_2 \), during a metathetical reaction between hydrated copper(II) chloride and potassium selenocyanate in ethanol. Also, Russian workers report (3) that \( \text{Cd(SeCN)}_2 \) is unstable and yields \( \text{CdSe} \) as one of its decomposition products. They also found that \( \text{KNCSe} \) decomposes reversibly at 158° to yield \( \text{KCN} \) and \( \text{Se} \).

An equilibrium of the type expressed by XXXVIII may occur

\[
\text{KNCSe} \rightleftharpoons \text{KCN} + \text{Se}
\]

XXXVIII

at temperatures lower than the decomposition point of \( \text{KNCSe} \); the atomic selenium formed should be very reactive. Thus it was reasoned that \( \text{KNCSe} \) might react with tertiary phosphines to produce tertiary phosphine selenides. The removal of selenium should then drive the dissociation of \( \text{KNCSe} \) to completion.

The reaction was first tried with triphenylphosphine employing acetonitrile as solvent. A product was isolated which had a melting point differing from the starting phosphine and a band at 512 cm\(^{-1}\) in its infrared spectrum together with other bands consistent with triphenylphosphine. The properties of the isolated compound suggested that it was triphenylphosphine selenide; elemental analysis (including selenium) confirmed this. It appears then that the overall reaction expressed by Equation 85 occurs. This is the first example of a tertiary phosphine reacting with an inorganic species to produce a selenide derivative. Tertiary phosphines abstract sulfur from
a variety of organic compounds to form tertiary phosphine sul-
fides (65) and triphenylphosphine abstracts sulfur from the
inorganic species $S_4N_4$ to form the sulfide (87), but no examples
of tertiary phosphines abstracting selenium from organic com-
pounds are known to this author.

A similar reaction of triphenylphosphine with KNCS was
attempted with the phosphine being recovered unreacted after
work up similar to the preparation of triphenylphosphine
selenide. It has been noted in the literature (11) that this
reaction does not occur nor does $\Phi_3PS$ exchange with KCN.

The reaction of potassium selenocyanate with triphenyl-
arsine failed to produce triphenylarsine selenide; triphenyl-
arsine was recovered unreacted. Although triphenylarsine
selenide has been reported (343), it was not characterized.
Recently, Zingaro and Merijanian failed to prepare $\Phi_3AsSe$
by the reported procedure (343), owing probably to the inherent
instability of the compound.

The reaction was used to prepare other tertiary aromatic
and mixed aromatic-aliphatic phosphine selenides as listed in
Table 8. The melting points are uncorrected and $v_{P-Se}$ was
determined by comparison with the unreacted phosphine.

The reaction was submitted to Inorganic Syntheses and
independently checked by F. A. Cotton (259). S. C. Cummings,
of Ohio State University, has used the reaction to prepare
diphenylethylphosphine selenide (61). However, she noted that
benzene should be used to extract this phosphine selenide rather
Table 8
Tertiary Phosphine Selenides Prepared by the KCNSe Reaction

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield, %</th>
<th>n.p. °</th>
<th>$\nu_{P-Se}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p-CH$_3$C$_6$H$_4$)$_3$PSe</td>
<td>95</td>
<td>198-198.5</td>
<td>544</td>
</tr>
<tr>
<td>(n-CH$_3$C$_6$H$_4$)$_3$PSe</td>
<td>94</td>
<td>139-140</td>
<td>574</td>
</tr>
<tr>
<td>Me$_2$NCH$_2$CH$_2$P(Se)CH$_2$</td>
<td>87</td>
<td>90-91</td>
<td>532</td>
</tr>
<tr>
<td>$\phi_2P(Se)CH_2P(Se)CH_2$</td>
<td>84</td>
<td>194-195</td>
<td>539</td>
</tr>
<tr>
<td>$\phi_2P(Se)CH_2CH=CH_2$</td>
<td>89</td>
<td>78-79</td>
<td>$^\dag$</td>
</tr>
</tbody>
</table>

$^\dag$ indeterminate

than employ the separation procedure developed in the experimental section.

The reaction appears to be a general one and should work with tertiary aliphatic phosphines also. Thus, tri(n-butyl)-phosphine selenide appears to be formed by this reaction because the infrared spectrum of the product is identical with that of the selenide prepared by addition of elemental selenium to tri(n-butyl)phosphine; however, the boiling point of the liquid obtained by the KCNSe reaction was 40° higher. An attempt to prepare tri(n-octyl)phosphine selenide was unsuccessful because the phosphine is insoluble in acetonitrile and forms a separate oily layer which does not react with KCNSe.

The diselenide, $\phi_2P(Se)CH_2P(Se)CH_2$, is easily prepared by employing a 2:1 ratio of KCNSe to phosphine. The monoselenide
derivative could not be prepared by employing a 1:1 mole ratio of reactants.

Tris(diethylaminomethyl)phosphine, \((\text{Et}_2\text{NCH}_2)_3\text{P}\), reacts with KNCSe to yield an oil upon work up. This selenide, \((\text{Et}_2\text{NCH}_2)_3\text{PSe}\), is probably a liquid but was not characterized.

The potassium selenocyanate reaction is particularly advantageous in preparation of solid phosphine selenide derivatives. No particular advantage is gained from this reaction in the preparation of liquid phosphine selenides since these can be prepared by either direct fusion of the tertiary phosphine with elemental selenium (171) or by refluxing the phosphine with selenium in an inert solvent (340). These can be easily separated from unreacted selenium by fractional distillation as in the preparation of tri(n-butyl)phosphine selenide by the latter method. The advantage of the KNCSe reaction is in preparing solid derivatives in near quantitative yields with high purity and the ease with which the reaction is accomplished. The melting points of the crude solid selenides prepared were just slightly below the melting points of the recrystallized products. In addition, there is no unreacted selenium which can be a problem to separate in the alternate syntheses of solid selenides.

There exists another possible rationalization to explain the reaction of tertiary phosphines with potassium selenocyanate which does not depend on an equilibrium such as XXXVIII. Since tertiary phosphines act as nucleophilic agents in displacement reactions at the sulfur atom in organosulfur compounds (65), it
is reasonable that a nucleophilic displacement might also occur at the selenium atom of NCSe\textsuperscript{−} in this reaction (Eq. 86).

\[
\text{L: } + \text{NCSe}^\text{−} \rightarrow [\text{L...SeCN}]^\text{−} \rightarrow \text{LSe} + \text{CN}^\text{−} \quad \text{(Eq. 86)}
\]

This would be consistent with the finding that diphenyl(o-diphenylarsinophenyl)phosphine, \(\text{o-(AsPh}_2\text{)}\text{C}_6\text{H}_4\text{(PPh}_2\text{)}\), does not react with KNCSe, the large arsenic atom in an ortho-position would decrease the nucleophilicity of the phosphine.

The following argument for such a possible mechanism has been suggested by Dr. Meek (243). Edwards and Pearson postulated (76) that polarizability becomes more important than basicity for nucleophilic attack on bivalent oxygen and sulfur. In the case of nucleophilic reactions on selenium, polarizability, or soft base character, will be even more important than in analogous sulfur or oxygen compounds. The following canonical forms illustrate one plausible explanation as to why triphenylphosphine reacts with SeCN\textsuperscript{−} and not with SCN\textsuperscript{−} or OCN\textsuperscript{−}. Canonical form XLI would be relatively unimportant in the NCO\textsuperscript{−} case, but

\[
\text{XXXIX} \quad \text{XL} \quad \text{XLI}
\]

its contribution would increase in NCS\textsuperscript{−} and especially in the NCSe\textsuperscript{−} case due to decreasing electronegativity of the chalcogenide atom. Indeed, it has been postulated that selenium can be positively polarized by induction through negative substituents attached to it (294). The relative importance of form XL compared with form XXXIX also should increase through the series NCO\textsuperscript{−}, NCS\textsuperscript{−}, NCSe\textsuperscript{−}. 
Since the C-N bond order should decrease as the contribution of forms XL and XLI increases, the C-N bond distances and the C-N stretching frequency should reflect the relative importance of the resonance structures in the series NCO$^-$, NCS$^-$, NCSe$^-$. The C-N stretching frequency of NCS$^-$ (2053 cm$^{-1}$, refs. 152 and 153) is smaller than for either NCO$^-$ (2160 cm$^{-1}$, ref. 108) or NCSe$^-$ (2070 cm$^{-1}$, ref. 108). This is not the order (NCSe$^- <$ NCS$^- <$ NCO$^-$) expected from electronegativity arguments. Whenever accurate force constants become available for all the ions, the change in bond order may be in the expected direction. Jones has calculated from force constants that the C-S bond in NCS$^-$ exhibits considerable multiple bond character. The C-N bond distance in all the ions is about 1.16 Å, the normal value for triple C-N bonds. However, the Se-C distance of 1.829 ± 0.025 Å is shorter than the normal single bond length, indicating some multiple bond character (312). The net result of these considerations is that the increasing relative importance of forms XL and XLI in the selenocyanate ion, due to the low energy empty d-orbitals on selenium, provides a favorable charge distribution for nucleophilic attack by tertiary phosphines.

3. Phosphine tellurides

An attempt to prepare the unknown diphenylphosphine telluride, $\Phi_2P(\text{Te})H$, was unsuccessful. This result is consistent with the findings of Zingaro and Irgolic (339) that the ease of
tollurium addition to tertiary phosphines decreases as phenyl substitution increases. For example, they found that triphenylphosphine telluride can not be prepared by fusion of triphenylphosphine with elemental tellurium powder.

4. Diphosphine dichalcogenides

The tetraalkyldiphosphine disulfides were prepared by the Grignard syntheses described in the review section. Diethylphosphinothioic chloride, Et₂P(S)Cl, was heated with a free radical initiator to see if these diphosphine disulfides could be prepared by a free radical radical reaction. There was no evidence of reaction.

Attempted preparation of tetraphenyldiphosphine disulfide by a literature method was unsuccessful. This involved the attempted coupling of \( \overset{\circ}{\overset{\circ}{P}}(S)Cl \) and \( \overset{\circ}{\overset{\circ}{P}}(S)H \) with elimination of HCl. A disadvantage of this synthetic route is that whereas this coupling is apparently rapid for trivalent phosphorus compounds; e.g., \( R_2PH + R_2PCl \), it appears to be slower with pentavalent phosphorus compounds.

Other attempts to prepare tetraphenyldiphosphine disulfide via coupling reactions of diphenylphosphinothioic chloride, \( \overset{\circ}{\overset{\circ}{P}}(S)Cl \), with the metals magnesium, mercury, and lithium were unsuccessful. No reaction occurred with magnesium. Mercury probably desulfurizes the phosphorus compound instead of coupling it. The lithium reaction produced a compound whose infrared
spectrum resembled the published spectrum of \( \phi_2\text{P}(S)\text{P}(S)\phi_2 \), although it had a lower melting point.

Diphosphine disulfides of the type \( R_2\text{P}(S)\text{P}(S)R_2 \) or \( RR'\text{P}(S)\text{P}(S)RR' \) exhibit one infrared active phosphorus-sulfur stretching frequency because of their trans confirmation. It was desired to prepare one of these which, although it contained trans phosphine sulfide groups, would exhibit two infrared stretching vibrations. A compound of type \( R_2\text{P}(S)\text{P}(S)R' \) should show this feature because the different inductive effects of the two \( R \)-groups acting on individual phosphorus atoms should give rise to two stretching vibrations of different frequency (I.R.). Diphosphine disulfides of this type have not been prepared since the usual Grignard synthesis will not work for the preparation of these unsymmetrical diphosphine disulfides. Attempts to prepare 1,1-dimethyl-2,2-diphenyldiphosphine disulfide are illustrative of the syntheses tried. No apparent reaction occurs when dimethylphosphinothioic bromide and diphenylphosphine sulfide (\( \text{Me}_2\text{P}(S)\text{Br} + \phi_2\text{P}(S)\text{H} \)) are mixed in toluene. Addition of pyridine to this solution results in a white precipitate; originally this was thought to be pyridine hydrobromide. However, only unreacted diphenylphosphine sulfide could be isolated. A subsequent experiment showed that dimethylphosphinothioic bromide reacts with pyridine in toluene to form an insoluble, hygroscopic solid. The nature of this material was not investigated further.

Next, the reaction of a phosphorus species analogous to
an organic Grignard material was attempted with dimethylphosphinothioic bromide (Eq. 47). The phosphorus Grignard material, \( \Phi_2 P(S)MgBr \), was prepared by the exchange reaction depicted in Equation 46. This species has never been reported, although \( \Phi_2 PMgBr \) and \( \Phi P(MgBr)_2 \) have been prepared by this type of reaction (148, 238). Gas evolution during the exchange reaction indicated that the reaction proceeded. Only diphenylphosphine sulfide was isolated after reaction of this intermediate with \( Mo_2 P(S)Br \). Diphenylphosphine sulfide could have been regenerated during the hydrolysis step (Eq. 87).

\[
\Phi_2 P(S)MgBr + H_2O \rightarrow \Phi_2 P(S)H + Mg(OH)Br \quad \text{(Eq. 87)}
\]

The unsuccessful reaction of diphenylphosphine with tetramethyldiphosphine disulfide (Eq. 50) was attempted because halogens will react with a P-H bond as shown in Equation 88 and

\[
\Phi_2 P(S)H + Me_2 P(S)P(S)Me_2 \rightleftharpoons \Phi_2 P(S)P(S)Me_2 + Me_2 P(S)H
\]

\[ \rightleftharpoons \text{PH} + X_2 \rightarrow \text{PX} + HX \quad \text{(Eq. 88)}
\]

general chemical reactions of tetraalkyldiphosphine disulfides suggest that they behave as pseudohalogens (29). For instance, tetramethyldiphosphine disulfide adds to ethylene as expressed by Equation 89 (269).

\[
Me_2 P(S)P(S)Me_2 + CH_2=CH_2 \rightarrow Me_2 P(S)CH_2CH_2 P(S)Me_2
\]

Further attempts to prepare compounds of the type \( R_2 P(S)P(S)R_2 \) were abandoned.
It was also of interest to attempt preparation of the un­
known tetraalkylphosphine diselenides, \( R_2P(Se)P(Se)R_2 \). It
appeared reasonable that a Grignard reaction (Eq. 5) similar to
that used for preparation of diphosphine disulfides might be
useful (Eq. 90), however \( P(Se)Cl_3 \) has never been reported.

\[
2P(Se)Cl_3 + 6RMgX \rightarrow R_2P(Se)P(Se)R_2 + 3MgXCl + R_2
\]

(Eq. 90)

Attempts to prepare \( P(Se)Cl_3 \) by a reaction similar to the syn­
thesis of \( P(S)Cl_3 \) (252) were unsuccessful. Selenium does add
to diphenylchlorophosphine and also phenyldichlorophosphine to
form the selenium derivatives in good yield simply by refluxing
in toluene without a catalyst. The phenyl group appears similar
to chlorine in inductive effects from infrared measurements of
these compounds (337). It is surprising then that \( PCl_3 \) does not
form the selenide derivative.

The Grignard reaction (Eq. 90) could not be carried out
because of the failure to prepare \( P(Se)Cl_3 \). Maier has shown
that methylphosphonoselenoic dibromide, \( MeP(Se)Br_2 \), does not
form a diphosphine diselenide derivative when reacted with
methyl and phenyl Grignard reagents (212).

Another possible scheme would be the reaction exemplified
by Equation 91.

\[
R_2P(Se)H + R_2P(Se)Cl \rightarrow R_2P(Se)P(Se)R_2 + HCl
\]

(Eq. 91)

Dialkylphosphinoselenoic halides could be prepared in the same
manner as diphenylphosphinoselenoic chloride. However, while
secondary phosphine oxides and sulfides are known; the selenium analogs were not. Therefore, an attempt was made to prepare diphenylphosphine selenide.

A product was isolated from the reaction of selenium and diphenylphosphine in toluene which was believed to be $\text{Se}_2\text{P(Se)H}$; however, it appeared to decompose on standing. It was assumed that these type compounds were unstable and since they would be required for the reaction expressed in Equation 91, this synthetic route was not thought feasible.

Very recently and after the above described work, Maier published (222) the preparation of di-isobutylphosphine selenide as well as that of diphenylphosphine selenide. These were prepared and isolated in the same manner as attempted in this investigation using benzene as the solvent. Maier found that $\text{Se}_2\text{P(Se)H}$ melts at 111-112° and he reports two P-H bands at 2360 cm$^{-1}$ and 2328 cm$^{-1}$ in the infrared. He lists other infrared bands but, unfortunately, these do not extend into the KBr region where $v_{P=Se}$ occurs. These compounds were not especially stable; the phenyl derivative, however, was more stable than the isobutyl one (222). Maier also found that the $P^{31}$ N.M.R. resonance of these gave doublets with relative intensities of 1:1, in agreement with the presence of a P-H bond. The coupling constant, $J_{P-H}$, for $\text{Se}_2\text{P(Se)H}$ is 450 c.p.s.

The studies on diphosphine diselenides were dropped at this point when the above attempts proved unsuccessful.
The sulfur atom(s) may be removed from tetraalkyldiphos- 
phine disulfides by heating with another tertiary phosphine 
(214, 216, 269). This is illustrated by Equations 92 and 93.

\[
\begin{align*}
\text{Me}_2\text{P}(S)\text{P}(S)\text{Me}_2 + 2\text{Bu}_3\text{P} & \rightarrow \\
\text{Me}_2\text{PPMe}_2 + 2\text{Bu}_3\text{PS} & \quad \text{(Eq. 92)} \\
\text{Me}_2\text{P}(S)\text{P}(S)\text{Me}_2 + \text{Bu}_3\text{P} & \rightarrow \\
\text{Me}_2\text{P}(S)\text{PMe}_2 + \text{Bu}_3\text{PS} & \quad \text{(Eq. 93)}
\end{align*}
\]

Maier states that triphenylphosphine will also abstract sulfur 
atoms in this manner (224).

This technique was utilized in an attempt to prepare tetra-
methylidiphosphine monosulfide monoselenide, another type of 
molecule which has not been reported. It was anticipated that 
triphenylphosphine would remove one sulfur atom from tetra-
methylidiphosphine disulfide to form tetramethyldiphosphine 
monosulfide; the reaction of this intermediate with KNCSe would 
then produce the desired product. However, the experimental 
findings indicate that triphenylphosphine does not remove a 
sulfur atom as anticipated.

The donor properties of diphosphine dioxides of type XLII, 
where \( n \) is equal to one or more, have been studied; however, the 
complexing properties of diphosphine dioxides of type XLIII, 
where a phosphorus-phosphorus bond exists, have not.

\[
\begin{align*}
\text{R}_2\text{P}(\text{O})(\text{CH}_2)^n\text{P}(\text{O})\text{R}_2 & \quad \text{XLII} \\
\text{R}_2\text{P}(\text{O})\text{P}(\text{O})\text{R}_2 & \quad \text{XLIII}
\end{align*}
\]

Only aryl diphosphine dioxides of type XLIII are known (173, 174).
An attempt was made to prepare tetraphenyldiphosphine dioxide by an unusual coupling reaction reported in the literature where diphenylchlorophosphine, in the presence of air, a trace of water, and a tertiary amine, forms the diphosphine dioxide. However, the melting point of the compound isolated by this author was never in agreement with that of tetraphenyldiphosphine dioxide. The apparent discrepancy was unexplained until British workers latter reported (241) that the dioxide could not be isolated from the reaction; but that the monoxide, \( \Phi_2P(O)\Phi_2 \), is the material which actually forms in this reaction. They reported the melting point of the monoxide as 155-158\(^\circ\). Thus, the original report of the dioxide preparation is erroneous.

The dioxide also has been reported to result from the reaction of dry air with a toluene solution of tetraphenyldiphosphine (174). Attempts at utilizing this reaction and similar syntheses were unsuccessful.

5. Other intermediates and ligands

In addition to the preparation of tertiary phosphine and arsine chalcogenide ligands, other tertiary phosphine, arsine, and amine ligands as well as bidentate ligands containing these donor atoms were synthesized. The purpose for these will become apparent latter (i.e., sections IIIB, IIIC, and IIIG).
Diphenyl(o-diphenylarsinophenyl)phosphine (XLIV) was prepared by a reaction similar to that used in the synthesis of its parent phosphine (XXXIV), Eq. 29, employing \( \Phi_2 \)PCl in place of \( \Phi_2 \)P(S)Cl.

The preparation of 1,2-bis(diphenylphosphino)ethane was accomplished employing a modification of Chatt and Hart's method (38). The new procedure was devised because of the presence of phenyllithium (a nucleophile) which also results from the cleavage of triphenylphosphine. The phenyllithium produced as a side reaction in the cleavage of triphenylphosphine can be destroyed selectively (4) by addition of t-butyl chloride (Eq. 94).

\[
\Phi Li + (CH_3)_3 CCl \rightarrow C_6 H_6 + LiCl + CH_2 = C(CH_3)_2 \quad (Eq. 94)
\]

After destroying phenyllithium, the resulting solution of lithium diphenylphosphide was mixed with one of 1,2 dichloroethane. The new method does not result in improved yield. This method was also employed to prepare diphenyl(3-dimethylaminopropyl)phosphine as well as diphenyl(2-dimethylaminoethyl)phosphine.

Marxer, who studied (239) the reaction of materials like 3-chloropropylidinethyamine with magnesium to form Grignard species, never obtained a homogeneous Grignard solution in diethyl ether. This investigator found that by use of
tetrahydrofuran, the Grignard could be formed in good yield. Thus, diphenyl(3-dimethylaninopropyl)phosphine was also prepared by the interaction of the Grignard derivative of 3-chloropropyl-dimethylaniline with diphenylchlorophosphine. It was also shown that 2-chloropropyl(dimethylaniline reacts with magnesium in tetrahydrofuran. These reactions are touchy in that they need to be initiated very carefully; but, once started, they proceed smoothly.

This Grignard reaction should prove useful in preparing other mixed phosphorus-nitrogen ligands. These might be very attractive in a study with transition metals because a ligand such as $D[(CH_2)_n DR_2]_3$ (when $D$ is arsenic or phosphorus) produces diamagnetic five-coordinate metal complexes (18), but an analogous all nitrogen system (46) results in spin-free five-coordinate complexes. A mixed phosphorus-nitrogen ligand, which can be prepared by the synthetic methods illustrated in this thesis, might result in nickel complexes where the magnetism would be a function of temperature. The preparation of such a ligand, $P(CH_2CH_2CH_2NMMe_2)_3$, is described in the appendix. The product was isolated by distillation of all volatile materials; it probably would have been better to purify the ligand by high-vacuum distillation.

A derivative of this ligand was prepared by using an excess of methyl iodide and it analyzed for $P(CH_2CH_2CH_2NMMe_2)_3\cdot3MeI$. It is possible that the phosphorus atom was oxidized to a phosphine oxide during handling, although a nitrogen atmosphere was
used. This would account for only three methyliodide groups per ligand; one oxygen atom would not change the percentage composition to any great extent.

Synthesis of mixed phosphorus-nitrogen ligands by a third synthetic route was reported by other workers in March, 1966, at the Pittsburgh Meeting of the American Chemical Society (69). The reaction is illustrated by Equations 95 and 96.

\[
\text{OP}_2\text{PMgBr} + \text{Et}_2\text{NCH}_2\text{CH}_2\text{Br} \rightarrow \\
\text{OP}_2\text{CH}_2\text{CH}_2\text{NEt}_2 + \text{MgBr}_2
\]  
(Eq. 95)

\[
\text{OP(}\text{MgBr}_2\text{)}_2 + 2\text{Et}_2\text{NCH}_2\text{CH}_2\text{Br} \rightarrow \\
\text{OP(}\text{CH}_2\text{CH}_2\text{NEt}_2\text{)}_2 + 2\text{MgBr}_2
\]  
(Eq. 96)

An attempt was made to prepare \(\text{o-BrC}_6\text{H}_4\text{P}_2\) (XXXVI) or a similar intermediate because the literature preparation of this compound is a very difficult reaction yielding the product in small yield (75, 288). If \(\text{o-nitro(diphenylphosphino)}\)benzene could have been prepared, it then could have been reduced to the \(\text{o-amino} \)derivative. This species could be diazotized and reacted with cuprous bromide to produce \(\text{o-bromo(diphenylphosphino)}\)benzene. The tars which resulted when \(\text{o-nitrobromobenzene} \)was treated with \(\text{P}_2\text{O}^-\) may indicate that a reaction occurred with the nitro group instead of nucleophilic displacement of the bromide atom.

Other attempts to prepare \(\text{o-bromo(diphenylphosphino)}\)-benzene were also unsuccessful; for instance, lithium diphenylphosphide does not selectively displace the iodine atom of \(\text{o-bromoiodobenzene}, \) but apparently both halogen atoms are displaced. Very recently, Chiswell and Venanzi have published an
improved new synthesis of o-bromophenyldichlorophosphine, subse­quently of o-bromo(diphenylphosphino)benzene (44); it supposedly can now be prepared in higher yield.

B. Complexes of Monodentate Ligands

1. Tertiary phosphine sulfide and selenide ligands

The donor properties of a few representative tertiary phosphine sulfides and selenides were studied; e.g., trimethylphosphine sulfide, tri(n-butyl)phosphine selenide, triphenylphosphine sulfide, tri(n-butyl)phosphine selenide, triphenylphosphine sulfide, and triphenylphosphine selenide. Although the donor ability of triphenylphosphine sulfide and selenide has been briefly investigated previously, these were reinvestigated as potential ligands in this study since, as pointed out in the introduction, there was some discrepancy concerning their coordinating properties with mercury(II). In addition, the donor properties of tri(p-tolyl)- and tri(m-tolyl)phosphine selenide towards palladium(II) was investigated.

Zinc(II), cadmium(II), and mercury(II)

All the tertiary phosphine sulfide and selenide ligands (aliphatic and aromatic) form mercury(II) complexes. However, the stoichiometry of the complexes vary with the ligand; for example, complexes of form $L\cdot \text{Hg}X_2$ occur with triphenylphosphine sulfide, whereas complexes of composition $L_2\text{Hg}X_2$ are formed with
trimethylphosphine sulfide and tri(n-butyl)phosphine selenide. Bannister and Cotton reported that mercury(II) chloride does not form a complex with triphenylphosphine sulfide and selenide (9). However, Philips and Columbo reported a 1:1 complex of triphenylphosphine sulfide with mercury(II) bromide (275). Recently, Maier has reported the mercury(II) complex, 3HgBr₂·2L, of methylidithethylphosphine sulfide (232). Although disproportionation occurs when trimethylphosphine sulfide is mixed with mercury(II) perchlorate (section II E), Potts and Allred (285) recently reported \([\text{Hg}(\varnothing_3\text{PS})_4]_2(\text{ClO}_4)_2\). They could not prepare the analogous mercury(I) complex of triphenylphosphine sulfide, due to disproportionation.

Both trimethylphosphine sulfide and tri(n-butyl)phosphine selenide form cadmium(II) iodide complexes; i.e., CdL₂I₂. However, no cadmium(II) complexes of triphenylphosphine sulfide or selenide could be isolated. Only trimethylphosphine sulfide forms complexes with zinc(II) iodide and zinc(II) perchlorate; i.e., \(\text{Zn(Me}_3\text{PS})_2\)I₂ and \(\text{Zn(Me}_3\text{PS})_4(\text{ClO}_4)_2\).

Low molar conductance values in acetonitrile for the \(\varnothing_3\text{PS}\cdot\text{HgX}_2\) and \(\text{ML}_2\text{X}_2\) complexes (Table 9) indicate essentially non-electrolyte behavior, albeit values for the \(\varnothing_3\text{PS}\cdot\text{HgX}_2\) complexes are slightly higher. The analogous \(\varnothing_3\text{PSO}\cdot\text{HgX}_2\) complexes are not sufficiently soluble in acetonitrile or acetone for conductivity measurements. In acetonitrile, a uni-univalent electrolyte should give a molar conductance value in the range 140-155; a bi-univalent electrolyte should be about 280-310 (334).
Table 9

Molar Conductance Values (Acetonitrile) of Zn(II), Cd(II), and Hg(II) Complexes with Monodentate Tertiary Phosphine Sulfides and Selenides

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΛM, cm²/ohm-M</th>
</tr>
</thead>
<tbody>
<tr>
<td>(<a href="%5Ctext%7BClO%7D_4">\text{Zn(Me}_3\text{PS})_4</a>_2]</td>
<td>300</td>
</tr>
<tr>
<td>([\text{Zn(Me}_3\text{PS})_2\text{I}_2])</td>
<td>7.8</td>
</tr>
<tr>
<td>([\text{Cd(Me}_3\text{PS})_2\text{I}_2])</td>
<td>12.0</td>
</tr>
<tr>
<td>([\text{Cd((n-Bu)}_3\text{PSe})_2\text{I}_2])</td>
<td>6.8</td>
</tr>
<tr>
<td>([\text{Hg(Me}_3\text{PS})_2\text{Cl}_2])</td>
<td>8.9</td>
</tr>
<tr>
<td>([\text{Hg(Me}_3\text{PS})_2\text{Br}_2])</td>
<td>12.2</td>
</tr>
<tr>
<td>([\text{Hg(Me}_3\text{PS})_2\text{I}_2])</td>
<td>11.1</td>
</tr>
<tr>
<td>([\text{Hg((n-Bu)}_3\text{PSe})_2\text{Br}_2])</td>
<td>6.9</td>
</tr>
<tr>
<td>(\text{PS}^3\text{HgCl}_2)</td>
<td>27.2†</td>
</tr>
<tr>
<td>(\text{PS}^3\text{HgBr}_2)</td>
<td>46.0†</td>
</tr>
<tr>
<td>(\text{PS}^3\text{HgI}_2)</td>
<td>15.7†</td>
</tr>
</tbody>
</table>

† based on dimer

Thus, the complex \([\text{Zn(Me}_3\text{PS})_4](\text{ClO}_4)_2\) is a bi-univalent electrolyte, in agreement with the proposed formula.

The infrared spectrum of \([\text{Zn(Me}_3\text{PS})_4](\text{ClO}_4)_2\) in Nujol mull also shows ionic perchlorate anions as well as the absence of water. The zinc atom of this complex appears to be four coordinate presumably with tetrahedral coordination of the phosphine sulfide groups.
Several structural possibilities exist for cadmium(II) and mercury(II) complexes with tertiary phosphine chalcogenides of empirical formula LMX₂, assuming a dimeric unit with the metal atom being tetrahedrally coordinated. These include structures containing two halogen bridges (3 isomers), two P=X bridges (1 isomer), and one P=X and one halogen bridge (2 isomers). The latter should result in two P=X stretching vibrations. The structure containing two P=X bridging groups would be expected to show P=X stretching vibrations different than in complexes where bridging does not occur. As will be pointed out latter, the infrared data are not consistent with the latter two possibilities; therefore these complexes probably contain halide bridges. The insolubility of complexes prepared in this study precludes molecular weight determinations.

Crystals of \([\text{Cd}((n-\text{Bu})₃\text{PSe})₂\text{I}_₂]\) were sent to Dr. P. J. Wheatley for X-ray analysis. He found absorption to be a severe problem; however, it was ascertained that the crystals were monoclinic and had a face-centered lattice of space group either C2/c or Cc. The lengths of the axes could not be determined, since the crystal was elongated along [110], but the volume was 7448 Å³. The density measured by flotation in a mixture of chloroform and ethylene bromide was 1.634; the calculated density for eight molecules in the unit cell is 1.657. Wheatley states that with \(Z = 8\), and with the intensity distribution, the
true space group is C2/c (no coecular symmetry required).

Copper(I) and silver(I)

An ethanolic solution of trimethylphosphine sulfide reduces copper(II) perchlorate hexahydrate (ligand/metal mole ratio of 4/1) and produces a white, crystalline product for which a total analysis corresponds to the composition Cu(Me3PS)3ClO4. The oxygen analysis is 1.2% low (theory 8.4%) but good agreement with theory is found for the other six elements. The same product is produced when the order of addition is reversed or when the metal salt is dehydrated with dimethoxypropane before reaction. The molar conductivity, based on the above empirical formula, is consistent with a uni-univalent electrolyte (Table 10).

Table 10

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΛM, cm²/ohm-M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(Me₃PS)₃ClO₄</td>
<td>154</td>
</tr>
<tr>
<td>[Cu(Ø₃PS)₄]ClO₄</td>
<td>157</td>
</tr>
<tr>
<td>[Ag(Ø₃PS)₂]ClO₄</td>
<td>141</td>
</tr>
<tr>
<td>[Ag(Ø₃PSc)₂]ClO₄</td>
<td>132</td>
</tr>
</tbody>
</table>

The infrared spectrum (Nujol mull), Figures 1 and 2, of this complex shows no water and gives no evidence of coordinated
Figure 1. Infrared spectrum of \( [\text{Cu(Me}_3\text{PS})_3]_x(\text{ClO}_4)_y \); (Nujol mull).
Figure 2. Infrared spectrum of $\text{[Cu(Me}_3\text{PS)}_3]_x\text{(ClO}_4)_y$; (Nujol mull)
perchlorate. The nature of the bonding in this complex will be
discussed more fully latter.

An ethanolic solution of triphenylphosphine sulfide gave
no evidence of reaction (i.e., no color change) when mixed with
an ethanolic solution of hydrated copper(II) perchlorate
(4:1 mole ratio) and the ligand was recovered unchanged. However,
when $SO_2$ is briskly bubbled through the solution immediately
upon mixing the above reagents, the color of the solution changes
from blue to light green as glissening white crystals form. The
resulting product analyzes for $Cu(\Phi PS)_2ClO_4$ and exhibits uni-
univalent electrolyte properties in acetonitrile (Table 10). The
infrared spectrum (nujol mull) is consistent with this formula
and shows ionic perchlorate groups.

The tertiary phosphine selenide ligands decompose in the
presence of copper(II) salts to produce elemental selenium;
therefore, no copper(I) complexes of phosphine selenides were
obtained. It may be possible to prepare copper(I) complexes of
tertiary phosphine selenides by starting with a copper(I) de-
rivative, however this was not attempted in this study.

The interaction of triphenylphosphine sulfide and tri-
phenylphosphine selenide with anhydrous silver(I) perchlorate
in a 2:1 mole ratio produces colorless complexes of the type
$[AgL_2]ClO_4$. Both the infrared spectra and conductance data
(Table 10) indicate ionic perchlorate groups in these complexes.
Trimethylphosphine sulfide also forms a silver(I) complex, but
it could not be recrystallized. Tri(n-butyl)phosphine selenide does not react with silver(I) perchlorate.

Palladium(II) and platinum(II)

Bannister and Cotton have previously prepared \([\text{Pd}(\phi_3\text{PS})_2\text{Cl}_2]\) and \([\text{Pd}(\phi_3\text{PSe})_2\text{Cl}_2]\) by mixing an acidic, ethanolic solution of palladium(II) chloride with the ligand in dichloromethane (9); however, these complexes were prepared in this study via a different reaction route (Eq. 97).

\[
\text{Na}_2\text{PdCl}_4 + 2\text{L} \rightarrow [\text{PdL}_2\text{Cl}_2] + 2\text{NaCl} \quad (\text{Eq. 97})
\]

In addition, analogous palladium(II) complexes of trimethylphosphine sulfide, tri(p-tolyl)phosphine selenide \([(p-C_6H_5)_3\text{PSe}]]\), and tri(m-tolyl)phosphine selenide \([(m-C_6H_5)_3\text{PSe}]]\) were prepared in a similar manner. A 100% excess of triphenylphosphine sulfide produces only \([\text{Pd}(\phi_3\text{PS})_2\text{Cl}_2]\); also, the isolated complex does not react further with excess ligand in dichloromethane.

The palladium(II) bromide complexes, \([\text{PdL}_2\text{Br}_2]\), of trimethylphosphine sulfide, triphenylphosphine sulfide, and triphenylphosphine selenide were prepared from sodium tetrabromopalladato(II) by a reaction similar to that expressed by Equation 97. However, those three ligands would not displace iodide, thiocyanate, or selenocyanate from the analogous \(\text{PdX}_4^{2-}\) species under similar reaction conditions.

Light tan or flesh colored platinum(II) complexes, \([\text{PtL}_2\text{Cl}_2]\), were analogously prepared with trimethylphosphine sulfide, and triphenylphosphine selenide.
No well defined palladium(II) or platinum(II) complexes of tri(n-butyl)phosphine selenide could be isolated, although ethanolic solutions of this ligand produce dark colored solutions when combined with salts of these metals.

The low molar conductance values of the few complexes of this type, \([ML_2X_2]\), which are sufficiently soluble in acetone or acetonitrile (Table 11) indicate that they are non-electrolytes in solution.

Table 11

Molar Conductance Values of Pd(II) and Pt(II) Complexes with Monodentate Tertiary Phosphine Sulfides and Selenides

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Lambda M), cm(^2)/ohm-M</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Pd}(\text{Me}_3\text{PS})_2\text{Br}_2])</td>
<td>2.4(^\dagger)</td>
</tr>
<tr>
<td>([\text{Pt}(\text{Me}_3\text{PS})_2\text{Cl}_2])</td>
<td>7.4(^\ast)</td>
</tr>
<tr>
<td>([\text{Pd}((\text{m-C}_7\text{H}_7)_3\text{PSe})_2\text{Cl}_2])</td>
<td>3.2(^\dagger)</td>
</tr>
<tr>
<td>([\text{Pd}((\text{p-C}_7\text{H}_7)_3\text{PSe})_2\text{Cl}_2])</td>
<td>2.4(^\dagger)</td>
</tr>
</tbody>
</table>

\(^\dagger\) acetone  
\(^\ast\) acetonitrile

Other metal ions

Trimethylphosphine sulfide, tri(n-butyl)phosphine selenide, and triphenylphosphine selenide react with ethanolic solutions of gold(III) to produce unstable complexes; gold mirrors then form. A yellow gold complex with triphenylphosphine sulfide
of empirical composition $L_3^{\text{Au}}\text{Cl}_7$ was formed; its conductance value, based on this empirical formula, is 143 in acetonitrile. No likely structure is consistent with these data. The formulation $[\text{AuL}_3\text{Cl}]^{2+}$ would require both gold(I) and gold(III) to be present.

Recently, Keen obtained an orange gold(III) complex of triphenylphosphine sulfide, $\text{Au}(\Omega_2\text{PS})\text{Cl}_3$ (165). He was also able to obtain the gold(I) complex, $\text{Au}(\Omega_2\text{PS})\text{Cl}$, by using sodium sulphite as a reducing agent. Potts and Allrod have also reported the latter complex (286).

In addition, Teichmann has recently noted (313) that a variety of tertiary aliphatic and mixed aliphatic-aromatic phosphine sulfides form bis complexes with tin(IV) halides; i.e., $\text{SnX}_4L_2$.

2. Triphenylarsine sulfide

Prior to this investigation, no attempts to ascertain the donor properties of tertiary arsine sulfides or selenides had been reported. Zingaro and Morijanian did mention that the latter caused color changes when mixed with solutions of transition metal ions (343), but he was unable to isolate any solid complexes. Triphenylarsine sulfide was chosen to evaluate the arsine sulfide system as a donor group. The study of the complexing ability of tertiary arsine selenides was not attempted because the arsenic-selenium vibrational frequency, necessary for
characterization, falls below 400 cm$^{-1}$, the lower limit of the infrared instruments readily available.

During the course of this investigation, Merijanian and Zingaro mentioned one cobalt(II) chloride complex of triethylarsine sulfide in a paper (246) concerned with the donor properties of tertiary arsine oxides. However, no infrared or electronic spectral data for the complex was reported. In contrast, this study has shown that triphenylarsine sulfide forms no complexes with divalent first row transition metal ions, at least in oxygenated solvents such as acetone or alcohols.

However, triphenylarsine sulfide reduces ethanolic solutions of copper(II) to colorless copper(I) complexes. This arsine sulfide also forms cadmium(II) iodide and mercury(II) halide complexes of 1:1 stoichiometry. The structure of these is probably similar to that of the triphenylphosphine sulfide and selenide complexes of mercury(II). A 2:1 ligand/metal stoichiometry is found for complexes of silver(I) perchlorate and palladium(II) halides with triphenylarsine sulfide.

Triphenylarsine sulfide reacts with ethanolic solutions of Na$_2$PtCl$_4$ and NaAuCl$_4$ although no products containing simple ligand to metal stoichiometric ratios can be isolated.

The low molar conductance values of the [Pd($\phi_3$AsS)$_2$X$_2$] complexes in acetone and the $\phi_3$AsS·HgX$_2$ complexes in acetonitrile suggest non-electrolytic species (Table 12). Some ionization evidently occurs in the cadmium(II) iodide complex.
Table 12
Molar Conductance Values of Triphenylarsine Sulfide Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΛM, cm²/ohm·M</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃H₅AsS·CdI₂</td>
<td>41.7⁺, *</td>
</tr>
<tr>
<td>C₃H₅AsS·HgCl₂</td>
<td>14.2⁺, *</td>
</tr>
<tr>
<td>C₃H₅AsS·HgBr₂</td>
<td>15.1⁺, *</td>
</tr>
<tr>
<td>C₃H₅AsS·HgI₂</td>
<td>7.7⁺, *</td>
</tr>
<tr>
<td>[Ag(C₃H₅AsS)₂]ClO₄</td>
<td>140⁺</td>
</tr>
<tr>
<td>[Cu(C₃H₅AsS)₄]ClO₄·CH₂Cl₂</td>
<td>157⁺</td>
</tr>
<tr>
<td>[Cu(C₃H₅AsS)Br]ₓ</td>
<td>160⁺, ‡‡</td>
</tr>
<tr>
<td>[Pd(C₃H₅AsS)₂Cl₂]</td>
<td>2**</td>
</tr>
<tr>
<td>[Pd(C₃H₅AsS)₂Br₂]</td>
<td>2**</td>
</tr>
<tr>
<td>[Pd(C₃H₅AsS)₂I₂]</td>
<td>3**</td>
</tr>
</tbody>
</table>

⁺acetonitrile                 *based on dimer
‡‡based on trimer **acetone

The silver(I) and copper(I) complexes of triphenylarsine sulfide are ionic in acetonitrile (Table 12). The value for [Ag(C₃H₅AsS)₂]ClO₄ is in the range for a uni-unielectrolyte. The silver(I) atom in this complex is presumably two coordinate; no solvent or water molecules are visible in its infrared spectrum (Nujol mull). The copper(I) perchlorate complex of triphenylarsine sulfide contained impurities which could only be removed by slow precipitation from a filtered solution of
dichloromethane with n-hexane. The high chlorine content of this complex suggests that one mole of dichloromethane is retained in recrystallization. The species \([\text{Cu}(\mathcal{O}_2\text{AsS})\text{Br}]_x\) exhibits an appreciable conductance; a trimer must be assumed in order for the complex to have a conductivity value in the univalent range (Table 12).

3. Infrared spectra

The P=S and P=Se stretching frequencies of the uncomplexed ligands are recorded in Table 13. A decrease in the position of

<table>
<thead>
<tr>
<th>Ligand</th>
<th>(v_{P=X}) or (v_{\text{As}=X}) found (^\dagger)</th>
<th>Lit. Value cm(^{-1})</th>
<th>(Ref.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Me}_3\text{PS})</td>
<td>565 s. (^{\dagger\dagger})</td>
<td>570</td>
<td>(291)</td>
</tr>
<tr>
<td>(\Phi_3\text{PS})</td>
<td>640 s.</td>
<td>637</td>
<td>(465)</td>
</tr>
<tr>
<td>((\text{n-Bu})_2\text{PSe})</td>
<td>495 m. (^{\dagger\dagger})</td>
<td>511</td>
<td>(291)</td>
</tr>
<tr>
<td>(\Phi_3\text{PSe})</td>
<td>562 s.</td>
<td>560</td>
<td>(291)</td>
</tr>
<tr>
<td>((\text{n-C}_7\text{H}_7)_2\text{PSe})</td>
<td>574 s.</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>((\text{p-C}_7\text{H}_7)_2\text{PSe})</td>
<td>544 s.</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>(\Phi_3\text{AsS})</td>
<td>497 s.</td>
<td>495</td>
<td>(465)</td>
</tr>
</tbody>
</table>

\(^\dagger\) Nujol null

\(^{\dagger\dagger}\) m., medium; s., strong

*not previously reported
this band occurs upon complexation (see Table 14 and Figures 3-12). The P=X vibrations in the complexes are strong, sharp single absorptions (see for example, Figures 7 and 9) except for the complexes of silver(I) perchlorate and the trimethylphosphine sulfide complexes of d^{10} metal halides. In the latter case a shoulder occurs on the high energy side of ν_{P=S}, but this asymmetry results in two distinct peaks only in the case of the [Hg(Me$_3$PS)$_2$Br$_2$] complex (see Figures 3 and 4). Although these d^{10} metal complexes presumably contain tetrahedral coordination of ligands and halides around the metal, flattening of the type as shown in [Hg(Φ$_3$AsO)$_2$Cl$_2$] (192) could result in coupling of the P=S vibration.

Two closely spaced bands are found in the ν_{P=X} region for the silver(I) perchlorate complexes of triphenylphosphine sulfide and selenide (Table 14 and Figure 8). Linear sp-hybridization would be expected for two coordinate silver(I) and therefore only one infrared P=S vibration. Crystal lattice splitting may be responsible for the splitting here and also for asymmetric P=S vibrations in the d^{10} metal complexes of trimethylphosphine sulfide.

The ν_{P=X} vibration in the palladium(II) and platinum(II) complexes is sharp and in no case are two bands discerned in the ν_{P=X} region (e.g., Figures 9 and 11). This suggests the trans square planar structure in the solid state. The cis configuration should give rise to two P=X bands. To confirm
Figure 3. Infrared spectra (a) \([\text{Zn(Me}_3\text{PS)}_4]\text{ClO}_4\) and (b) \([\text{Zn(Me}_3\text{PS)}_2\text{I}_2\text{]}\) in \(\nu_{\text{P-S}}\) region (Nujol mull).
Figure 4. Infrared spectra of (a) [Hg(Me₃PS)₂I₂] and (b) [Hg(Me₃PS)₂Br₂] in $\nu_{\text{P-S}}$ region (Nujol mull).
Figure 5. Infrared spectra of $\phi_3^{PS}$ and its mercury(II) complex, $\cdots$ L·HgCl$_2$; (KBr).
Figure 6. Infrared spectra of \( \text{(n-Bu)_3PSe} \) and its cadmium(II) complex, \( \text{---} \ [\text{CdL}_2\text{I}_2] \); (Nujol mull).
Figure 7. Infrared spectra of \( \phi_3 \text{PSe} \cdot \text{HgI}_2 \), \( \phi_3 \text{PSe} \) (Nujol mull).
Figure 8. Infrared spectra of $\varphi_3^{PSe}$ and $[Ag(\varphi_3^{PSe})_2]ClO_4$ in $\nu_{P-Se}$ region (Nujol mull).
Figure 9. Infrared spectra of \([\text{Pd}(\phi_3\text{PS})_2\text{Cl}_2]\) and \(\phi_3\text{PS}\) (Nujol mull). 

\[
\Delta V = 49 \text{ cm}^{-1}
\]
Figure 10. Infrared spectra of 1,2-bis(diphenylphosphino sulfide) ethane and its palladium(II) complex, $\text{[PdLCl}_2]$ (Nujol mull).
Figure II. Infrared spectra of $-[\text{Pt(Me}_3\text{PS)}_2\text{Cl}_2]$ and $-\text{Me}_3\text{PS. (KBr)}$.
Figure 12. Infrared spectrum of $\nu_{P=S}$ for $[\text{Cu(Me}_3\text{PS)}_3(\text{ClO}_4)]_x$, (Nujol mull).
<table>
<thead>
<tr>
<th>Complex</th>
<th>( v_{p=x} ), cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Zn}(\text{Me}_3\text{PS})_2\text{I}_2])</td>
<td>531 s.</td>
</tr>
<tr>
<td>([\text{Cd}(\text{Me}_3\text{PS})_2\text{I}_2])</td>
<td>541 s.</td>
</tr>
<tr>
<td>([\text{Cd}(n-\text{Bu}_3\text{PSe})_2\text{I}_2])</td>
<td>480 s.</td>
</tr>
<tr>
<td>([\text{Hg}(\text{Me}_3\text{PS})_2\text{Cl}_2])</td>
<td>534 s.</td>
</tr>
<tr>
<td>([\text{Hg}(\text{Me}_3\text{PS})_2\text{Br}_2])</td>
<td>545 s.</td>
</tr>
<tr>
<td>([\text{Hg}(\text{Me}_3\text{PS})_2\text{I}_2])</td>
<td>540 s.</td>
</tr>
<tr>
<td>(\phi_3\text{PS} \cdot \text{HgCl}_2)</td>
<td>593 s.</td>
</tr>
<tr>
<td>(\phi_3\text{PS} \cdot \text{HgBr}_2)</td>
<td>593 s.</td>
</tr>
<tr>
<td>(\phi_3\text{PS} \cdot \text{HgI}_2)</td>
<td>591 s.</td>
</tr>
<tr>
<td>(\phi_3\text{PSe} \cdot \text{HgCl}_2)</td>
<td>545 s.</td>
</tr>
<tr>
<td>(\phi_3\text{PSe} \cdot \text{HgBr}_2)</td>
<td>543 s.</td>
</tr>
<tr>
<td>(\phi_3\text{PSe} \cdot \text{HgI}_2)</td>
<td>542 s.</td>
</tr>
<tr>
<td>([\text{Cu}(\text{Me}_3\text{PS})_2\text{I}_2\text{x} (\text{ClO}_4)_y])</td>
<td>540 s.</td>
</tr>
<tr>
<td>([\text{Cu}(\phi_3\text{PS})_4]\text{ClO}_4)</td>
<td>604 s.</td>
</tr>
<tr>
<td>([\text{Ag}(\phi_3\text{PS})_2]\text{ClO}_4)</td>
<td>605 s.</td>
</tr>
<tr>
<td>([\text{Ag}(\phi_3\text{PSe})_2]\text{ClO}_4)</td>
<td>551 s.†</td>
</tr>
</tbody>
</table>
Table 14 (Contd.)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_{P=S}$, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(Me$_3$PS)$_2$Cl$_2$]</td>
<td>527 s.</td>
</tr>
<tr>
<td>[Pd(Me$_3$PS)$_2$Br$_2$]</td>
<td>523 s.</td>
</tr>
<tr>
<td>[Pt(Me$_3$PS)$_2$Cl$_2$]</td>
<td>526 s.</td>
</tr>
<tr>
<td>[Pd($\phi$$_3$PS)$_2$Cl$_2$]</td>
<td>591 s.</td>
</tr>
<tr>
<td>[Pd($\phi$$_3$PS)$_2$Br$_2$]</td>
<td>587 s.</td>
</tr>
<tr>
<td>[Pt($\phi$$_3$PS)$_2$Cl$_2$]</td>
<td>592 s.</td>
</tr>
<tr>
<td>[Pd($\phi$$_3$PSe)$_2$Cl$_2$]</td>
<td>546 s.</td>
</tr>
<tr>
<td>[Pd($\phi$$_3$PSe)$_2$Br$_2$]</td>
<td>543 s.</td>
</tr>
<tr>
<td>[Pt($\phi$$_3$PSe)$_2$Cl$_2$]</td>
<td>544 s.</td>
</tr>
<tr>
<td>[Pd((n-C$_7$H$_7$)$_3$PSe)$_2$Cl$_2$]</td>
<td>558 s.</td>
</tr>
<tr>
<td>[Pd((p-C$_7$H$_7$)$_3$PSe)$_2$Cl$_2$]</td>
<td>528 s.</td>
</tr>
</tbody>
</table>

\*m. medium; s., strong; sh., shoulder; b., broad

This, a complex of the type [PdLCl$_2$] was prepared with the ligand $\phi$$_2$P(S)CH$_2$CH$_2$P(S)$\phi$$_2$; i.e., which requires the cis-configuration. The P=S vibration of the free ligand occurs at 609 cm$^{-1}$. The presence of two new, closely spaced peaks at lower energy (581 and 572 cm$^{-1}$) in the complex (Fig. 10), assigned to anti-symmetrical and symmetrical P=S vibrations, confirms that the cis-configuration would result in two P=S vibrations. While most palladium(II) complexes of the type PdL$_2$L'$^1$ appear to be the
trans isomer, it is known that \([\text{Pd}(\text{Me}_3\text{P})_2\text{Cl}_2]\) exists in the cis-form, at least in the solid state (49).

Infrared measurements should aid in the structural determination of the \([\text{Cu}(\text{Me}_3\text{PS})_2]_x(\text{ClO}_4)_y\) complex. The complexity of the P=S vibration (Table 14 and Figure 12) suggests the possibility of bridging trimethylphosphine sulfide groups, although no precedent exists for this type of bonding for P=S or P=O ligands. A possible structure is shown in XLV. This would be

\[
\begin{align*}
\text{Me}_3\text{P} & \\
\text{S} & \\
\text{Cu} & \\
\text{Me}_3\text{P} & \\
\end{align*}
\]

XLV

consistent with elemental analysis and conductivity measurements. Otherwise, one must envisage either a three coordinate copper(I) ion, \([\text{Cu}(\text{Me}_3\text{PS})_3]^+\), or a copper-copper bond, \([(\text{Me}_3\text{PS})_3\text{CuCu}(\text{Me}_3\text{PS})_3]^{++}\).

Attempts to grow crystals of this complex suitable for X-ray analysis were unsuccessful. In addition the compound was not sufficiently soluble for NMR resonance studies.

The values of \(\nu_{P=S}\) in the complexes may be compared with other recently published reports. The P=S vibration of triphenylphosphine sulfide in \([\text{Hg}(\phi_3\text{PS})_4](\text{ClO}_4)_2\) is 587 cm\(^{-1}\) (285).
and 590 cm$^{-1}$ in [Au(\(\mathcal{O}_3\)PS)Cl] (286), a decrease of 50-53 cm$^{-1}$ from the free ligand value. This compares with the 47-53 cm$^{-1}$ decrease found in this study for the mercury(II), palladium(II), and platinum(II) halide complexes of triphenylphosphine sulfide. Teichmann reports a decrease of up to 45 cm$^{-1}$ for \(v_{P=S}\) in the tertiary phosphine sulfide complexes of tin(IV) halides (313).

The decrease observed for \(v_{P=S}\) and \(v_{P=Se}\) in their complexes must indicate a net stabilization of canonical form, \(R_3P^+S^-\), over that of \(R_3P=X\); i.e., the bond order of the P=S and P=Se groups is reduced upon coordination. The ranges for the shift of \(v_{P=X}\) are recorded in Table 15.

**Table 15**

Ranges for Shift of \(v_{P=X}\) in Complexes

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Range of (\Delta v_{P=X}), cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mathcal{O}_3PS) (Pd, Pt)</td>
<td>38-42</td>
</tr>
<tr>
<td>(Other)</td>
<td>18-34</td>
</tr>
<tr>
<td>(\mathcal{O}_3PS)</td>
<td>35-53, 47-53†</td>
</tr>
<tr>
<td>(\mathcal{O}_3PSe)</td>
<td>11-20</td>
</tr>
</tbody>
</table>

†excluding the Ag$^+$ and Cu$^+$ complexes

The As=S stretching vibration (Table 13) in triphenylarsine sulfide occurs clearly above the strong phenyl ring vibrations in the 400-475 cm$^{-1}$ region. The As=S vibration in the complexes
is not distinguishable (see Table 16 and Figure 13), presumably

Table 16

Infrared Data for Complexes of Triphenylarsine Sulfide (Nujol Mull)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Peaks in the 400-500 cm⁻¹ region, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>497, v.s., 476 s., 469 s., 460 s.</td>
</tr>
<tr>
<td>L·CdI₂</td>
<td>474 s., 467 s., 450 w.</td>
</tr>
<tr>
<td>L·HgCl₂</td>
<td>477 s., 467 s., 464 sh., 447 m.</td>
</tr>
<tr>
<td>L·HgBr₂</td>
<td>475 s., 463 s., 446 s.</td>
</tr>
<tr>
<td>L·HgI₂</td>
<td>474 s., 464 s., 445 m.</td>
</tr>
<tr>
<td>[PdL₂I₂]</td>
<td>483 m., 468 s., 462 m.</td>
</tr>
<tr>
<td>[CuLBr]ₓ</td>
<td>480 s., 470 s., 461 m.</td>
</tr>
<tr>
<td>[AgL₂]ClO₄</td>
<td>481 sh., 475 s., 468 s., 455 m., 449 sh.</td>
</tr>
</tbody>
</table>

† s., strong; v.s., very strong; m, medium; sh., shoulder
due to its shift to lower energy and coincidental overlap with
the ligand bands. The theoretical amount of sulfur was found
in all of the triphenylarsine sulfide complexes indicating that
the arsine sulfide linkage remained intact.

4. Electronic absorption spectra

The palladium(II) and platinum(II) complexes prepared in
this study were at least sufficiently soluble in dichloromethane
for absorption spectra to be measured. In general, the solution
Figure 13. Infrared spectra of

\[ \varphi_3 \text{AsS} \cdot \text{CdI}_2 \]

\[ \varphi_3 \text{AsS} \]

\[ \equiv \text{As= S} \rightarrow \]

WAVENUMBER, CM$^{-1}$

Figure 13. Infrared spectra of

\[ \varphi_3 \text{AsS} \cdot \text{CdI}_2, \quad \varphi_3 \text{AsS} \text{ (Nujol mull).} \]
spectra of those complexes consists of a well−defined peak with either an inflection point or shoulder on the low energy side (see Table 17 and Figures 14−16).

Several possible transitions may occur in these palladium(II) d⁸ complexes; for example,

(a) d → d (metal)

(b) d_{metal} → d S or Se (vacant)

(c) S or Se nonbonding → d_{metal} (vacant)

(d) S or Se nonbonding → vacant orbitals on S or Se

The transitions are probably due to either type (a) or (c).

Transitions of the type (b) and (d) generally occur in the ultraviolet region. Also an absorption attributable to either (b) or (d) occurs at 2450 Å (extinction coefficient, 11,500) for [Cd(Me₃PS)₂I₂] neither metal nor ligand alone showed absorption in this region.

Good solid state spectra were obtained for several of the complexes (Table 18). Differences are noted when solution spectra of complexes are compared with solid state spectra. The most striking example of this change occurs for the tri(m-tolyl)phosphine selenide complex of palladium(II) (see Figures 15 and 17). This suggests that the structure in solid state is different from that in solution.

The ligands may be placed in a spectrochemical series by comparing the electronic absorption spectra of the palladium(II) complexes (Table 17). One could compare the position of the first band in the visible and use this as a parameter. A basic
Figure 14. Solution electronic spectra of $[\text{PdL}_2\text{Cl}_2]$ complexes ($\text{CH}_2\text{Cl}_2$).
Figure 15. Solution electronic spectra of \([\text{Pd}\, L_2\, \text{Cl}_2]\) complexes (CH₂Cl₂).
Figure 16. Solution electronic spectra of $[\text{PdL}_2\text{Br}_2]$ complexes ($\text{CH}_2\text{Cl}_2$).
Figure 17. Electronic absorption spectra of $[\text{Pd}L_2\text{Cl}_2]$ complexes (Nujol mull).
Table 17

Electronic Spectral Data for [PdL₂X₂] Complexes
(CH₂Cl₂ Solution)

<table>
<thead>
<tr>
<th>L</th>
<th>X</th>
<th>λ max (nm)</th>
<th>ε (cm⁻¹⁻¹)</th>
<th>(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ø PS</td>
<td>Cl</td>
<td>375</td>
<td>26,700</td>
<td>(1150)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>430</td>
<td>23,200</td>
<td>(705)</td>
</tr>
<tr>
<td>Ø PS</td>
<td>Br</td>
<td>425</td>
<td>23,500</td>
<td>(2100)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>20,000</td>
<td>(625)</td>
</tr>
<tr>
<td>(m-C₇H₇)₃PSe</td>
<td>Cl</td>
<td>305</td>
<td>32,800</td>
<td>(16500)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>405</td>
<td>24,700</td>
<td>(950)</td>
</tr>
<tr>
<td>(p-C₇H₇)₃PSe</td>
<td>Cl</td>
<td>358</td>
<td>28,000</td>
<td>(5640)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>460</td>
<td>21,700</td>
<td>(900)</td>
</tr>
<tr>
<td>Ø PSe</td>
<td>Cl</td>
<td>358</td>
<td>28,000</td>
<td>(10000)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>430</td>
<td>23,200</td>
<td>(1350)</td>
</tr>
<tr>
<td>Ø PSe</td>
<td>Br</td>
<td>378</td>
<td>25,400</td>
<td>(2940)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>430</td>
<td>23,200</td>
<td>(1140)</td>
</tr>
<tr>
<td>Me₃PS</td>
<td>Cl</td>
<td>325</td>
<td>30,800</td>
<td>(6150)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>390</td>
<td>25,600</td>
<td>(625)</td>
</tr>
<tr>
<td>Me₃PS</td>
<td>Br</td>
<td>350</td>
<td>28,600</td>
<td>(5200)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>435</td>
<td>23,000</td>
<td>(795)</td>
</tr>
<tr>
<td>Ø AsS</td>
<td>Cl</td>
<td>361</td>
<td>27,700</td>
<td>(9340)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>470</td>
<td>21,300</td>
<td>(1940)</td>
</tr>
<tr>
<td>Ø AsS</td>
<td>Br</td>
<td>378</td>
<td>25,400</td>
<td>(8620)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>460</td>
<td>21,700</td>
<td>(1380)</td>
</tr>
<tr>
<td>Ø AsS</td>
<td>I</td>
<td>355</td>
<td>28,200</td>
<td>(4680)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>445</td>
<td>22,300</td>
<td>(3270)</td>
</tr>
</tbody>
</table>

† inflection point
‡ shoulder

The problem is that, as mentioned earlier, the first band is not well formed and varies from an inflection point to a shoulder on the main band. The position of this band was used as a basis for comparison by the author at the 1966 Pittsburgh Meeting of the American Chemical Society. Perhaps a better band for
Table 18

Electronic Spectral Data for \([\text{PdL}_2X_2]\) Complexes
(Nujol Mull)

<table>
<thead>
<tr>
<th>L</th>
<th>X</th>
<th>Λ_{\text{max}}^{\text{mm}}</th>
<th>λ_{\text{max}}^{\text{cm}^{-1}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\varnothing_2)PS</td>
<td>Cl</td>
<td>335</td>
<td>29,800</td>
</tr>
<tr>
<td>(\varnothing_2)PS</td>
<td>Br</td>
<td>370</td>
<td>27,000</td>
</tr>
<tr>
<td>(m-C(\text{H}_7))_3)PSe</td>
<td>Cl</td>
<td>365</td>
<td>27,400</td>
</tr>
<tr>
<td>(p-C(\text{H}_7))_3)PSe</td>
<td>Cl</td>
<td>365</td>
<td>27,400</td>
</tr>
<tr>
<td>(\varnothing_2)PSe</td>
<td>Cl</td>
<td>365</td>
<td>27,400</td>
</tr>
<tr>
<td>(\varnothing_2)PSe</td>
<td>Br</td>
<td>392</td>
<td>25,500</td>
</tr>
<tr>
<td>Me(\varnothing_2)PS</td>
<td>Br</td>
<td>350</td>
<td>28,600</td>
</tr>
</tbody>
</table>

*\dagger* shoulder

Comparison would be the main band. Roughly the same order is found. Also, one must compare solid and solution spectra individually; however, again basically similar results are obtained.

Comparison of the similar chloride and bromide complexes of the type \([\text{PdL}_2X_2]\) illustrate that, as expected, the bromide analog absorbs at lower energy (see Tables 17 and 18 and Figures 14, 15, and 16). Unexpectedly, the iodide analog of
triphenylarsine sulfide absorbs at higher energy than the chloride or bromide complex. Different structures (cis or trans) in solution may be responsible for this deviation from an expected trend.

The following order of ligand-metal interaction is obtained: \( \text{Me}_3\text{PS} > \phi_3\text{PSe} \geq \phi_3\text{AsS} > \phi_3\text{PS} \). The only discrepancy is the order \( \phi_3\text{PS} > \phi_3\text{PSe} \) as observed when one compares the Nujol mull solid state spectra of \([\text{PdL}_2\text{Cl}_2]\) complexes. The different tertiary aromatic phosphine selenides appear to interact to the same extent with palladium(II) as evidenced by the Nujol mull solid state spectra of their analogous complexes. This is analogous to the decrease of \( \nu_{\text{P-Se}} \) for those complexes which was 16 cm\(^{-1}\) in all cases. A change in order occurs in solution (employing first absorption band); i.e.,

\[(\mu-\text{C}_7\text{H}_7)_3\text{PSe} > \phi_3\text{PSe} > (p-\text{C}_7\text{H}_7)_3\text{PSe}.\]

Dichloromethane solution spectra of the pale flesh-colored platinum(II) complexes show no observable visible transitions except for light orange \([\text{Pt(Me}_3\text{PS})_2\text{Cl}_2]\) which occurs at 370 nm (extinction coefficient, 330).

A solution of \([\text{Pd(\phi}_3\text{P})_2\text{Cl}_2]\) in dichloromethane absorbs at 345 nm with an extinction coefficient of 20,200. The parent phosphine thus creates a stronger field than the analogous phosphine sulfide and selenide for presumably similar complexes.

The analogous arsenic complex, \([\text{Pd(\phi}_3\text{As})_2\text{Cl}_2]\), shows a peak at 358 nm in dichloromethane. The extinction coefficient of this absorption appeared to be concentration dependent,
decreasing with dilution (value found at 1.08 \times 10^{-4} \text{ moles/1, 5200}). The field created by this ligand appears slightly higher than that of \( \phi_2 \text{AsS} \) in an analogous complex.

C. Complexes of Diphenyl(o-diphenylarsinophenyl)-phosphine Sulfide and Diphenyl(o-diphenyl-arsinophenyl)phosphine

It was of interest to prepare and study a bidentate ligand containing a tertiary phosphine sulfide group as one donor. Livingstone states that chelate ligands containing a thioether sulfur together with another different donor often coordinate more strongly than dithioethers(208). Summers and Quagliano have found that while trinethylaniline N-oxide is apparently a poor donor (311), its donor capacity is enhanced by incorporating it into a chelate ligand such as N,N-dimethylethlenediamine N-oxide.

The ligand synthesized for this study was diphenyl(o-diphenylarsinophenyl)phosphine sulfide (XXXIV), abbreviated APS.

\[
\begin{align*}
\text{XXXIV} & : P(S)\phi_2 \quad \text{As}\phi_2 \\
\text{XLVI} & : \text{SMe} \quad \text{AsMe}_2
\end{align*}
\]

It is similar to Livingstone's thioether ligand, dimethyl-\( \phi_2 \text{arsine} \) (XLVI). It was of particular interest to see if APS, a potential chelating ligand, would form complexes with divalent first row metal ions since XLVI forms cobalt(II) and nickel(II) complexes, besides forming complexes with other
metal ions such as Au(I), Pd(II), and Ag(I) (40,41,42,43,198).

The P=S stretching frequency of APS was determined by comparison of its spectrum with that of diphenyl(c-diphenylarsino-phenyl)phosphine (XLIV, abbreviated AP). The P=S vibration is a

\[
\begin{array}{c}
\text{P=O} \\
\text{As=O}
\end{array}
\]

strong band at 638 cm\(^{-1}\) (Nujol mull). This agrees with the analogous vibration in triphenylphosphine sulfide which occurs at 640 cm\(^{-1}\).

It is conceivable that APS could act either as a monodentate or a bidentate ligand. One of the interesting features of this ligand was to ascertain if it would form chelates by coordination of both the diphenylarsino- and diphenylthiophosphoryl-(P=S) groups. Coordination of the thiophosphoryl group may be detected by infrared spectra. In analogy with earlier discussion, if electron density on sulfur were involved in bonding to metal ions, the amount of electron density available for the phosphorus-sulfur bond would decrease and cause reduction in the P=S bond order. Decrease in the frequency of the P=S stretching vibration would, therefore, be expected if the P=S group were coordinated.

No complexes of APS could be isolated with anhydrous halides of cobalt(II) and nickel(II) or perchlorates of
manganese(II), iron(II), cobalt(II), and nickel(II) in several non-aqueous solvents. Slight color changes were observed in solution, but all attempts to isolate a complex resulted in crystallization of free ligand. Thus, APS does not resemble Livingstone ligand (XLV) in chemical behavior because it does not form stable complexes with divalent first row metal ions.

However, copper(II) salts are reduced to copper(I) complexes in the presence of APS. For example, copper(II) perchlorate hexahydrate is reduced to bis[diphenyl(o-diphenylarsinophenyl)-phosphine sulfide] copper(I) perchlorate. Although this complex is very pale green in color, it gives rise to no electronic absorptions in the visible region. The molar conductance value of this complex (Table 19) indicates that it behaves as a univalent electrolyte in acetonitrile.

In addition, the ligand forms palladium(II) and platinum(II) complexes of the type \([\text{M(APS)}X_2]\), where X represents a halogen or pseudohalogen anion. A palladium(II) nitrate complex of composition \([\text{Pd(APS)}_2(\text{NO}_3)_2]\) could also be prepared. The nitrate complex behaves as a 2:1 electrolyte in acetonitrile (Table 19); whereas, the other palladium(II) and platinum(II) complexes are non-electrolytes. The infrared spectrum of \([\text{Pd(APS)}_2(\text{NO}_3)_2]\) shows the non-planar \(\text{NO}_3^-\) deformation at 829 cm\(^{-1}\) (Fig. 18), also indicative of ionic nitrate groups (56).

The disappearance of the strong P=S ligand absorption at 638 cm\(^{-1}\) with the subsequent appearance of a new, strong to
Figure 18. Infrared spectrum of $[\text{Pd(APS)}_2(\text{NO}_3)_2]$ (Nujol mull).
Table 19

Molar Conductance Values of APS Complexes in Acetonitrile

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Lambda M, \text{cm}^2/\text{ohm-M} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Pd(APS)}\text{Cl}_2])</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>([\text{Pd(APS)}\text{Br}_2])</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>([\text{Pd(APS)}\text{I}_2])</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>([\text{Pd(APS)}(\text{SCN})_2])</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>([\text{Pd(APS)}(\text{SeCN})_2])</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">\text{Pd(APS)}_2</a>_2)</td>
<td>281</td>
</tr>
<tr>
<td>([\text{Pt(APS)}\text{Cl}_2])</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>([\text{Pt(APS)}\text{Br}_2])</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>([\text{Au(APS)}\text{Cl}])</td>
<td>12.1</td>
</tr>
<tr>
<td>([\text{Cu(APS)}_2]\text{ClO}_4)</td>
<td>142</td>
</tr>
</tbody>
</table>

Very strong absorption in the range 593-609 cm\(^{-1}\) in the infrared spectra of the complexes (Table 20 and Fig. 19) indicates that APS does indeed act as a chelating ligand (assuming arsenic coordination.

There are two possible configurations for the pseudo-square planar \([\text{Pd(APS)}_2]^{++}\) species. The structure containing \textit{trans} \(P=\text{S}\) groups is suggested because \(\nu_{P=S}\) is a sharp peak at 593 cm\(^{-1}\) (Fig. 18) in the complex. A split band due to symmetric and asymmetric vibrations would be expected if the \(P=\text{S}\) groups were \textit{cis} to each other. The value of \(\nu_{P=S}\) in the nitrate complex is
Table 20

Phosphorus-Sulfur Stretching Frequency\(^a^\dagger\) in the
APS Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v_{P=S}) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{APS})</td>
<td>638 s. (^\dagger)</td>
</tr>
<tr>
<td>([\text{Pd(APS)}\text{Cl}_2])</td>
<td>603 vs. (^\dagger)</td>
</tr>
<tr>
<td>([\text{Pd(APS)}\text{Br}_2])</td>
<td>602 vs.</td>
</tr>
<tr>
<td>([\text{Pd(APS)}\text{I}_2])</td>
<td>603 vs.</td>
</tr>
<tr>
<td>([\text{Pd(APS)}(\text{SCN})_2])</td>
<td>603 vs.</td>
</tr>
<tr>
<td>([\text{Pd(APS)}(\text{SeCN})_2])</td>
<td>603 vs.</td>
</tr>
<tr>
<td>([\text{Pd(APS)}\text{Cl}_2])(\text{NO}_3)_2)</td>
<td>593 vs.</td>
</tr>
<tr>
<td>([\text{Pt(APS)}\text{Cl}_2])</td>
<td>609 vs.</td>
</tr>
<tr>
<td>([\text{Pt(APS)}\text{Br}_2])</td>
<td>602 vs.</td>
</tr>
<tr>
<td>([\text{Au(APS)}\text{Cl}])</td>
<td>637 s.</td>
</tr>
<tr>
<td>([\text{Cu(APS)}_2]\text{ClO}_4)</td>
<td>609 vs.</td>
</tr>
</tbody>
</table>

\(^a^\dagger\)Mujol mulls, s., strong; vs., very strong

The lowest value observed among the APS complexes and may result from a stronger interaction, because in this case the full positive charge of the palladium(II) ion is felt; whereas the charge on palladium is neutralized somewhat by the two negative anions in the \([\text{Pd(APS)}X_2]\) complexes.

It is likely that the platinum(II) derivatives are first obtained in the form of Magnus type salts; i.e., \([\text{PtL}_2][\text{PtX}_4]\),
Figure 19. Infrared spectra of APS and [Pd(APS)Cl₂].
because of their insolubility in solvents such as dichloromethane and also because a more complex infrared spectrum is observed in the 590-600 cm\(^{-1}\) region along with the corresponding loss of the free ligand P=S vibration. Recrystallization by dissolving the complexes in hot dimethylformamide with subsequent reprecipitation with ethanol appears to convert these to monomeric species. After the DMF treatment, they can be subsequently recrystallized from dichloromethane/hexane and then a single phosphorus-sulfur vibration is observed. The presence of several peaks in the \(v_{P=S}\) region is indicative of both cis and trans P=S groups occurring in these Magnus type derivatives, or of a mixture of Magnus type salt and some of the monomeric species.

For complexes of the type \([\text{Pd(APS)X}_2]\), where the P=S group is trans to the X anion, it might be possible that the anion could influence the position of \(v_{P=S}\). This does not happen, as the phosphorus-sulfur stretching vibration remains invariant to changes in the trans X group (Table 20).

The interaction of APS with gold(III) results in reduction of the metal and formation of the gold(I) complex \([\text{Au(APS)Cl}]\), which behaves as a non-electrolyte in acetonitrile (Table 19). The unchanged phosphorus-sulfur vibration in the \([\text{Au(APS)Cl}]\) complex indicates that the ligand acts as a non-dentate ligand, coordinating via arsenic (Fig. 20). Non-coordination of the P=S group in the gold(I) chloride complex most probably is due to the linear character of gold(I) complexes and to the preference for arsenic coordination, since
Figure 20. Infrared spectra of (a) APS and (b) [Au(APS)Cl] in $\nu_{PS}$ region (Nujol mull).
triphenylphosphine sulfide complexes of both Au(I) and Au(III) have been isolated recently (165, 286). The possibility that factors such as coupling might offset the lowering of bond order in the gold(I) chloride complex can be excluded on the basis of the behavior of νₚₛ for the monodentate phosphine sulfide ligands discussed earlier.

The electronic absorption spectra of these palladium(II) APS complexes in solution is recorded in Table 21. These are similar to spectra obtained on the solids in Nujol mulls (Table 22) and indicate that the same species occurs both in the solid and solution. These complexes probably possess a pseudo-square planar coordination around the metal ion since this is the common geometry for four-coordinate d⁸ palladium(II).

The bonding of the thiocyanate and selenocyanate complexes, [Pd(APS)X₂], in terms of whether the anions are coordinated through the nitrogen or chalcogenide atom is of interest. The CN stretching frequencies for the complexes occur in the region expected for chalcogenide bonding (33). The [Pd(APS)(SCN)₂] complex exhibits two sharp peaks at 2119 and 2110 cm⁻¹ (Fig. 21a). This splitting is expected because of the cis configuration of thiocyanate groups. The sharp CN stretching frequency for [Pd(APS)(SeCN)₂] occurs at 2117 cm⁻¹ (Fig. 21b). The cis-selenocyanate configuration failed to split the peak. Some cis-thiocyanate palladium(II) and platinum(II) complexes do not show the expected splitting (33).

Either nitrogen or chalcogenide bonding in thiocyanate and
Table 21
Electronic Absorption Spectra of Palladium(II) APS Complexes (CH₂Cl₂ Solution)

<table>
<thead>
<tr>
<th>Complex</th>
<th>E&lt;sub&gt;max&lt;/sub&gt;, cm⁻¹</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;, μμ</th>
<th>(ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(APS)Cl₂]</td>
<td>26,000</td>
<td>385</td>
<td>(1630)</td>
</tr>
<tr>
<td>[Pd(APS)Br₂]</td>
<td>25,800</td>
<td>388</td>
<td>(2460)</td>
</tr>
<tr>
<td>[Pd(APS)(SCN)₂]</td>
<td>22,700</td>
<td>440</td>
<td>(980)</td>
</tr>
<tr>
<td>[Pd(APS)(SeCN)₂]</td>
<td>21,100</td>
<td>475</td>
<td>(820)</td>
</tr>
<tr>
<td>[Pd(APS)I₂]</td>
<td>20,400</td>
<td>491</td>
<td>(3400)</td>
</tr>
</tbody>
</table>

*shoulder on a stronger absorption band*

Table 22
Electronic Absorption Spectra of Palladium(II) APS Complexes (Nujol Mull)

<table>
<thead>
<tr>
<th>Complex</th>
<th>E&lt;sub&gt;max&lt;/sub&gt;, cm⁻¹</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;, μμ</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(APS)Cl₂]</td>
<td>26,300†</td>
<td>380</td>
</tr>
<tr>
<td>[Pd(APS)Br₂]</td>
<td>25,600†</td>
<td>390</td>
</tr>
<tr>
<td>[Pd(APS)(SCN)₂]</td>
<td>22,000</td>
<td>455</td>
</tr>
<tr>
<td>[Pd(APS)(SeCN)₂]</td>
<td>20,950</td>
<td>478</td>
</tr>
<tr>
<td>[Pd(APS)I₂]</td>
<td>20,000</td>
<td>500</td>
</tr>
</tbody>
</table>

†shoulder
Figure 21. Infrared spectra of (a) [Pd(APS)(SCN)₂] and (b) [Pd(APS)(SeCN)₂] in $\nu_{C=\equiv N}$ region (Nujol mull).
selenocyanate complexes can be assigned more definitively from the CS or CSe stretching frequency. Thus, the CS stretching mode is shifted to higher energy in the spectra of N-bonded thiocyanates and to lower energy in the spectra of S-bonded thiocyanates, relative to the CS stretching frequency of ionic KNCS (36, 316). The following ranges have been stated as being definitive for the type of bonding (316): M-NCS, 780-860 cm\(^{-1}\); M-SCN, 690-720 cm\(^{-1}\). The same effect has been observed for the CSe stretching frequency. Ionic KSeCN absorbs at 538 cm\(^{-1}\) (259), whereas N-bonded and Se-bonded NCS\(^{-}\) groups absorb in the 639-672 and 520-543 cm\(^{-1}\) regions, respectively. These vibrations are weak absorptions; and, unfortunately, intense phenyl vibrations in these regions in the APS complexes make the CS and CSe bonds useless for determining the nature of thiocyanate (selenocyanate) bonding.

Assignment of the type of bonding was supported by electronic spectra and correlation with the spectrochemical series. Although this method has been suggested by Schäffer (297) as a possible means of differentiating between the thiocyanate and isothiocyanate structure, recent workers in this field have not used it. The usual procedure for determining the nature of the bonding has been to prepare a thiocyanate complex and only the analogous chloride complex. The infrared spectra of the two is then compared to determine the location of extra peaks due to NCS\(^{-}\).

The position of the thiocyanate ion in the spectrochemical
series depends on whether it is N- or S-bonded. The same should hold for the selenocyanate ion. A position approximately equal to chloride ion occurs when the thiocyanate ion is S-bonded, whereas when it is N-bonded a stronger field results and its position is between $\text{H}_2\text{O}$ and $\text{NH}_2$ (157,297). The complex $[\text{Cr}(\text{NCX})_6]^{3-}$ exhibits similar field strength when $X$ equal sulfur or selenium and nitrogen bonding occurs (249); i.e., $\Delta E$ equals 17,800 cm$^{-1}$ for the N-bonded thiocyanate and 18,000 cm$^{-1}$ for the N-bonded selenocyanate. This is reasonable since the sulfur or selenium atom is not directly bonded to nitrogen and, therefore, exerts little effect on the electron density of nitrogen. It is also reasonable to assume that a larger differentiation in field strength would occur if chalcogenide bonding occurs in the complexes.

The spectrochemical position would also depend on the system studied. For instance, slight differences in order might be expected depending upon the metal, coordination number, nature of other ligands, or geometry. If the spectra of the $[\text{Pd}(\text{APS})X_2]$ complexes are arranged in order of decreasing energy, the following order of ligand-metal interaction results (Table 21): Cl$^-$ > Br$^-$ > NCS$^-$ > NGSe$^-$ > I$^-$. Thus, the position of thiocyanate and selenocyanate ions falls in between bromide and iodide. If these were N-bonded, the field created by these thiocyanate and selenocyanate anions would have been larger than that created by the chloride anion. Also, the thiocyanate ion creates a field much stronger than the selenocyanate ion (1,600 cm$^{-1}$ difference).
Their field strength would be expected to be very similar if these were both N-bonded. These data augment the infrared data and indicate that the complexes \([\text{Pd}(\text{APS})(\text{SCN})_2]\) and \([\text{Pd}(\text{APS})(\text{SeCN})_2]\) contain S- and Se-bonded NCX groups, respectively.

The ligand diphenyl(o-diphenylarsinophenyl)phosphine (AP) is the parent phosphine of APS. Complexes of this ligand were prepared so as to compare them with the analogous APS complexes. The \([M(\text{AP})X_2], M = \text{Pd}(\text{II}) \text{ and } \text{Pt}(\text{II}), \text{ and } [\text{Pd}(\text{AP})_2](\text{NO}_3)_2\) complexes were all similar to the APS complexes except the thiocyanate complex to be described latter. The nitrate complex contained ionic, non-coordinated nitrate groups as evidenced from its infrared spectrum (\(v_{\text{NO}_3}\) occurs at 829 cm\(^{-1}\)) and conductivity in acetonitrile (Table 23).

Table 23

Molar Conductance Values of AP Complexes in Acetonitrile

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Lambda M, \text{ cm}^2/\text{ohm-M})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Pd}(\text{AP})\text{Cl}_2])</td>
<td>(\dagger)</td>
</tr>
<tr>
<td>([\text{Pd}(\text{AP})\text{Br}_2])</td>
<td>(\dagger)</td>
</tr>
<tr>
<td>([\text{Pd}(\text{AP})\text{I}_2])</td>
<td>3.9</td>
</tr>
<tr>
<td>([\text{Pd}(\text{AP})(\text{SeCN})_2])</td>
<td>3.7</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">\text{Pd}(\text{AP})_2</a>_2)</td>
<td>277</td>
</tr>
<tr>
<td>([\text{Pt}(\text{AP})\text{Cl}_2])</td>
<td>(\dagger)</td>
</tr>
</tbody>
</table>

\(\dagger\) insoluble
The electronic absorption spectra of the palladium(II) AP complexes are given Tables 24 and 25. Again the selenocyanate

### Table 24

**Electronic Absorption Spectra of Palladium(II) AP Complexes (CH$_2$Cl$_2$ Solution)**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{\text{max}}$, cm$^{-1}$</th>
<th>$\lambda_{\text{max}}$, μm</th>
<th>(ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(AP)Cl$_2$]</td>
<td>28,400</td>
<td>353</td>
<td>(5200)</td>
</tr>
<tr>
<td>[Pd(AP)Br$_2$]</td>
<td>26,700†</td>
<td>375</td>
<td>(5500)</td>
</tr>
<tr>
<td>[Pd(AP)(SeCN)$_2$]</td>
<td>23,500</td>
<td>425</td>
<td>(1140)</td>
</tr>
<tr>
<td>[Pd(AP)I$_2$]</td>
<td>20,000†</td>
<td>500</td>
<td>(3040)</td>
</tr>
</tbody>
</table>

†shoulder on a stronger absorption

### Table 25

**Electronic Absorption Spectra of Palladium(II) AP Complexes (Nujol Mull)**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{\text{max}}$, cm$^{-1}$</th>
<th>$\lambda_{\text{max}}$, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(AP)Cl$_2$]</td>
<td>28,600†</td>
<td>350</td>
</tr>
<tr>
<td>[Pd(AP)Br$_2$]</td>
<td>27,000†</td>
<td>370</td>
</tr>
<tr>
<td>[Pd(AP)(SeCN)$_2$]</td>
<td>23,800†</td>
<td>420</td>
</tr>
<tr>
<td>[Pd(AP)I$_2$]</td>
<td>20,800†</td>
<td>480</td>
</tr>
</tbody>
</table>

†shoulder
complex appears to be selenium bonded; i.e., its position is
greater than I⁻ in the spectrochemical series. Its infrared
spectrum exhibits two sharp, closely spaced peaks at 2126 and
2120 cm⁻¹, also indicative of selenium bonding for the seleno-
cyanate ion.

When AP is mixed with an ethanolic solution of [Pd(SCN)₄]²⁻,
an orange product, which is insoluble in a variety of solvents
such as acetonitrile, chloroform, and dichloromethane, precip-
itates immediately. The solubility properties of this compound
differ markedly from the other palladium(II) halide complexes
of this ligand and suggest the possibility of a Magnus type com-
 pound; i.e., [Pd(AP)$_₂$][Pd(SCN)$_₄$]. This formulation is supported
by both its infrared spectrum (Fig. 22a) and electronic spectrum
(Table 26). The reflectance spectrum of this orange compound
is a composite of the spectra of the [Pd(AP)$_₂$]$²^+$ and [Pd(SCN)$_₄$]$²^-$
ions. Its infrared spectrum shows a weak, sharp peak at 2128
cm⁻¹ and an intense absorption in the CN region at 2102 cm⁻¹,
consistent with the [Pd(SCN)$_₄$]$²^-$ ion. The compound turns yellow
in a melting point capillary at approximately 200-220°, and
finally melts at 253.5-254.5° to a red-orange liquid. Dif-
ferential thermal analysis shows that the orange compound under-
goes a strong exothermic reaction at 216 ± 1°.

The orange product dissolves in hot DMF, and addition of
ethanol produces a crystalline, yellow compound of identical
composition; i.e., Pd(AP)(CNS)$_₂$. This yellow isomer is a non-
conductor in acetonitrile ($\Lambda_M = 8.3$ cm$^²$/ohm-moles), a nonomer in
Figure 22. Infrared spectra ($\nu_{\text{CN}}$ region) of (a) orange $[\text{Pd(AP)}_2][\text{Pd(SCN)}_4]$ (b) same, after heating 45 min. at 220°; (Nujol mull).
Table 26

Electronic Absorption Spectra of Orange $\text{[Pd(\text{AP})_2][Pd(SCN)_4]}$ and Similar Species (Nujol Mull)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{max}}$, cm$^{-1}$</th>
<th>$\lambda_{\text{max}}$, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{[Pd(\text{AP})_2][Pd(SCN)_4]}$</td>
<td>20,000</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>25,000</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>28,600$^\dagger$</td>
<td>350</td>
</tr>
<tr>
<td>$\text{<a href="NO_3">Pd(\text{AP})_2</a>_2}$</td>
<td>29,000</td>
<td>345</td>
</tr>
<tr>
<td>$\text{K}_2\text{Pd(SCN)_4}$$^{\dagger\dagger}$</td>
<td>20,000</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>24,400</td>
<td>410</td>
</tr>
</tbody>
</table>

$^\dagger$ shoulder   $^{\dagger\dagger}$ ref. 33

chloroform (Calcd. for $\text{[Pd(\text{AP})(\text{CNS})_2]}$, 713; found 716), and it melts to a red-orange liquid at 253.0°-253.5°. The infrared spectrum of this yellow isomer (Fig. 23) is identical to that of the orange isomer after it had been heated at about 220° for 45 minutes (Fig. 22b).

The infrared spectrum (Nujol mull) of this yellow isomer shows a strong, sharp absorption at 2117 cm$^{-1}$, consistent with $S$-bonded thiocyanate (33) and a strong, broader peak at 2058 cm$^{-1}$, indicative of $N$-bonded thiocyanate (Fig. 23a). This latter absorption is also in the region for ionic $\text{NCS}^-$; however, the complex shows no dissociation in chloroform and is a non-electrolyte in acetonitrile. The splitting is too large to be due to cis SCN$^-$ groups; and, the difference in the nature of the peaks seems to substantiate that two types of thiocyanate groups are
Figure 23. Infrared spectra of yellow [Pd(AP)(NCS)(SCN)] in $\nu_{CN}$ region, (a) Nujol mull (b) CH$_2$Cl$_2$ solution.
present in this compound. The two peaks are not due to a solid state phenomenon since the compound also exhibits two similar peaks at 2122 and 2085 cm\(^{-1}\) in dichloromethane solution (Fig. 23b).

A dichloromethane solution of the yellow isomer exhibits a shoulder at 400 m\(\mu\) (\(E = 25,000\) cm\(^{-1}\), extinction coefficient = 5140), both \(\lambda_{\text{max}}\) and \(\varepsilon_{\text{max}}\) are comparable to that of \([\text{Pd}(\text{AP})\text{Br}_2]\) (Table 24). These values differ from the spectral data found for the \([\text{Pd}(\text{APS})X_2]\) complexes, where two S-bonded thiocyanates occur. If both thiocyanate groups were N-bonded in this yellow complex, the energy of the electronic transition in \([\text{Pd}(\text{AP})(\text{CNS})_2]\) should be greater than that for the analogous chloride complex. Also, the extinction coefficients of the \([\text{Pd}(\text{AP})X_2]\) and \([\text{Pd}(\text{APS})X_2]\) complexes are much lower than for the analogous halide complexes when chalcogenide bonding of NCS\(^-\) or NCS\(e^-\) occurs.

Thus, an unusual type of isomerization occurs in this yellow complex; it is postulated to be \([\text{Pd}(\text{AP})(\text{NCS})(\text{SCN})]\) where two different types of coordinated thiocyanate groups appear in the same molecular complex. The nature of the bonding in this complex is an interesting problem and is discussed in a latter section (IIIG).

A comparison of the electronic absorption spectra of palladium(II) complexes of the phosphine sulfide (APS) and the phosphine (AP) (Tables 21 and 24) show that the ligand field strength of AP is greater than that of APS. This is also illustrated in Figure 24. The extinction coefficients for the APS complexes are appreciably lower than those for the analogous
Figure 24. Electronic absorption spectra of [Pd(AP)Cl₂] and [Pd(APS)Cl₂] in CH₂Cl₂ solution.
AP complexes. This will be discussed later (section IIIF).

D. Complexes of Tetraalkyldiphosphine Disulfides

The P=S groups of tetraalkyldiphosphine disulfides are in the trans configuration in the uncomplexed state (section IA). As a consequence, these ligands could coordinate to metal ions in several ways. Conceivably they could retain their trans configuration and either one or both P=S groups could function as donors toward metals. If both P=S groups coordinate, the trans configuration of the ligand would necessitate two metal ions. Another possibility is that both P=S groups would coordinate to the same metal ion forming a five-membered chelate ring containing no carbon atoms; i.e., XLVII.

\[
\left[ \begin{array}{c}
S=PR_2 \\
\text{N} \\
S=PR_2
\end{array} \right]^{n+}
\]

ANALOGOUS TO THE OTHER PHOSPHINE SULFIDE LIGANDS, tetralkyldiphosphine disulfides do not complex with divalent or trivalent first row metals. However, they behave similar to these in that they reduce copper(II) salts in ethanolic solution to copper(I) complexes. They also form well-defined complexes with silver(I) perchlorate as well as with cadmium(II) and mercury(II) iodide.

The conductance data for the copper(I) and silver(I)
perchlorate complexes of tetraalkyldiphosphine disulfides (Table 27) indicate that these complexes should be formulated as \([ML_2]ClO_4\). Also, their infrared spectra (Nujol mull) show ionic perchlorate groups. The conductance data (Table 27) on complexes of empirical formula \([CuLX]\) are also typical of univalent electrolytes in acetonitrile, if \(y\) is two. Their infrared spectra resemble those of the \([CuL_2]ClO_4\) species except for the absence of perchlorate bands (for example, see Fig. 25). Therefore, these complexes should be formulated as \([CuL_2][CuX_2]\).

Mixing "CuBrCl" with tetramethyldiphosphine disulfide produces a complex whose conductance value in acetonitrile (Table 27) and elemental analysis agrees with the formulation \([CuL_2][CuBrCl]\). Anionic cuprous species of the type \(CuX^-\) are known (102,197). Conductance data, where obtainable, for the \(CdLI_2\) and \(HgLI_2\) complexes indicate a non-electrolyte character (Table 27).

Although copper(II) is reduced when treated with tetraalkyldiphosphine disulfides, the yields of complexes (based on equations given in the experimental section -IIIE3) indicate that the ligand is not oxidized. The solvent is probably the species oxidized. Cuprous(I) iodide reacts with tetramethyldiphosphine disulfide to form a "CuLX" complex. This composition is the same as that which results from the reduction of copper(II) bromide in the presence of tetramethyldiphosphine disulfide.

The trace amount of a white complex isolated from the reaction product of tetramethyldiphosphine disulfide with silver(I) nitrate analyzes for the composition \(C_2H_6AsPS_2\) and
Table 27
Molar Conductance Values for Tetraalkyldiphosphine Disulfide Complexes (Acetonitrile)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Complex</th>
<th>$\Lambda_M^\circ$, cm$^2$/ohm-m</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$</td>
<td>$[\text{CuL}_2]\text{ClO}_4$</td>
<td>149.7†</td>
</tr>
<tr>
<td></td>
<td>$[\text{CuLBr}]_x$</td>
<td>92.7†</td>
</tr>
<tr>
<td></td>
<td>$[\text{CuL}_2][\text{CuBrCl}]$</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>$[\text{CuL}]_x$</td>
<td>151††</td>
</tr>
<tr>
<td></td>
<td>$[\text{AgL}]_2\text{ClO}_4$</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>$\text{CdLI}_2$</td>
<td>14.8</td>
</tr>
<tr>
<td></td>
<td>$\text{HgLI}_2$</td>
<td>†††</td>
</tr>
<tr>
<td>$\text{Et}_2\text{P}(\text{S})\text{P}(\text{S})\text{Et}_2$</td>
<td>$[\text{CuL}_2]\text{ClO}_4$</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td>$[\text{CuCl}]_x$</td>
<td>131††</td>
</tr>
<tr>
<td></td>
<td>$[\text{CuLBr}]_x$</td>
<td>135††</td>
</tr>
<tr>
<td></td>
<td>$[\text{AgL}_2]\text{ClO}_4$</td>
<td>139</td>
</tr>
<tr>
<td>(n-Pr)$_2\text{P}(\text{S})\text{P}(\text{S})(\text{n-Pr})_2$</td>
<td>$[\text{CuL}_2]\text{ClO}_4$</td>
<td>143</td>
</tr>
</tbody>
</table>

† nitromethane †† based on dimer ††† insoluble

its infrared spectrum (Fig. 26) corresponds to that of the metal complexes of dimethyldithiophosphinato, $\text{Mo}_2\text{PS}_2^-$ (48). The value of $\nu_{\text{P=S}}$ is 592 cm$^{-1}$ whereas that of $\nu_{\text{P=S}}$ occurs at 492 cm$^{-1}$ for this silver complex. It apparently results from cleavage of the tetramethyldiphosphine disulfide ligand. The black products formed via the interaction of silver(I) perchlorate with tetraalkyldiphosphine disulfides (one to one mole ratio) (see section IIIE3) are probably organic cleavage products mixed...
Figure 25. Infrared spectra of typical Me₄P₂S₂ complexes of copper(I).
Figure 26. Infrared spectrum of $[\text{Ag}(\text{S}_2\text{PMe}_2)]^+$(KBr).
with elemental silver. Mercury(I) is known to cleave tetraalkyl-
diphosphine disulfides but complexed metal products are not
formed; e.g., Eq. 98 (213).

\[ R_2P(S)P(S)R_2 + Hg_2Cl_2 \rightarrow 2R_2P(S)Cl + 2Hg \]  
(Eq. 98)

However, the similarity between the infrared spectra of
a given \( R_2P(S)P(S)R_2 \) ligand and its complexes of copper(I),
cadmium(II), and mercury(II) metal ions as well as those of
silver(I) perchlorate (two to one mole ratio of ligand to metal)
suggests that in these the ligands coordinate intact (e.g., see
Figure 27). In fact, tetraethylidiphosphine disulfide could be
recovered from its \([CuL_2]ClO_4 \) complex.

Tetrahedral coordination is common for copper(I),
cadmium(II), and mercury(II) in their complexes. Since Nujol
mulls of the complexes show only the tetraalkyldiphosphine di-
sulfide ligands in a species such as \([CuL_2]^+ \), all four P=S
groups must be coordinated to copper(I) in order to achieve
four-coordinate, tetrahedral coordination. This would require
either the cis or a skew configuration of the ligand. The
copper(I) cations could then be represented as XLVIII in which
the copper(I) ion is probably surrounded by a tetrahedron of
four sulfur atoms.

\[
\begin{array}{c}
\text{XLVIII}
\end{array}
\]
Figure 27: Infrared spectra of (a) $\text{Me}_4\text{P}_2\text{S}_2$ and (b) its cadmium(II) iodide complex.
Two possibilities exist for the structure of the CdLI$_2$ and HgLI$_2$ complexes, both involving tetrahedral coordination around the metal. One is with both P=S groups and two iodide anions coordinated to a single mercury atom and the second a dimer formulation containing bridging iodide anions where only one P=S group of each ligand would be coordinated. The similarity of the infrared spectra of these complexes with the [CuL$_2$]$^+$ unit suggests that the former structure is the most likely (see Figure 27b and compare with Figure 25), assuming XLVIII is the correct structure of the [CuL$_2$]$^+$ unit. The low solubility of these complexes prevents determination of molecular weight or N.M.R. spectra. The structure of the [AgL$_2$]ClO$_4$ complexes are discussed later.

When the infrared and Raman bands for the free ligands are compared with those in the complexes, the center of symmetry is seen to no longer exist in the latter; i.e., the ligands do not possess the trans configuration in these complexes.

The infrared and Raman data for tetramethyldiphosphine disulfide are recorded in Table 28. The values and assignments are taken from a preprint of a paper supplied by Dr. A. H. Cowley (60).

The infrared spectrum of tetramethyldiphosphine disulfide (Figure 27a) is relatively simple; the only peak in the 400-700 cm$^{-1}$ region occurs at 568 cm$^{-1}$ and is assigned to the P=S asymmetric stretch. The strong Raman band at 620 cm$^{-1}$ is assigned to the P=S symmetric stretching mode. Van der Linde
Table 28

Infrared and Raman Data for Me₂P(S)P(S)Me₂ (cm⁻¹)

<table>
<thead>
<tr>
<th>I.R.</th>
<th>Raman</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>445 s.†</td>
<td></td>
<td>P-P stretch</td>
</tr>
<tr>
<td>568 v.s.†</td>
<td></td>
<td>P=S asymmetric stretch</td>
</tr>
<tr>
<td>620 m.†</td>
<td></td>
<td>P=S symmetric stretch</td>
</tr>
<tr>
<td>733 v.s.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>746 v.s.</td>
<td></td>
<td>P-C asymmetric stretches</td>
</tr>
</tbody>
</table>

† s., strong; v.s., very strong; m., medium

and Hooge report 610 cm⁻¹ for this vibration (45). The bands at 733 and 746 cm⁻¹ are assigned to P-C antisymmetric stretching modes, in agreement with similar assignments for other alkyl substituted phosphorus compounds (115). The Raman band at 445 cm⁻¹ is assigned to the P-P stretching mode, consistent with values in other tetraalkyldiphosphines (14,308).

The trans C₂ᵥ symmetry of the C₂P(S)P(S)C₂ skeleton is supported by the presence of only one P=S vibration in the infrared and by the fact that none of the Raman bands has a coincident infrared band; i.e., the molecule contains a center of symmetry. As mentioned in the introduction, X-ray data confirms the trans configuration of Et₂P(S)P(S)Et₂.

On coordination of tetramethyldiphosphine disulfide to Cu(I), [Cu(Me₄P₂S₂)₂]ClO₄, four strong bands appear in the
400-700 cm⁻¹ region of the infrared spectrum (Table 29). The

Table 29
Infrared and Raman Data for \([\text{Cu(Me}_4\text{P}_2\text{S}_2)]\text{ClO}_4(cm⁻¹)\)

<table>
<thead>
<tr>
<th>I.R.</th>
<th>Raman †</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>430 m.</td>
<td>428 v.s. ††</td>
<td>P-P stretch</td>
</tr>
<tr>
<td></td>
<td>500 s. ††</td>
<td>?</td>
</tr>
<tr>
<td>563 s.</td>
<td></td>
<td>P=S asymmetric stretch</td>
</tr>
<tr>
<td>598 s.</td>
<td>600 s.</td>
<td>P=S symmetric stretch</td>
</tr>
<tr>
<td>625 v.s.</td>
<td></td>
<td>ClO₄⁻, v₄</td>
</tr>
<tr>
<td>733 s.</td>
<td>732 m. ††</td>
<td></td>
</tr>
<tr>
<td>760 s.</td>
<td>759 m.</td>
<td>P-C asymmetric stretch</td>
</tr>
</tbody>
</table>

† crystalline sample
†† s., strong; v.s., very strong; m., medium

very strong absorption at 625 cm⁻¹ is due to uncoordinated perchlorate ion. Two peaks at 598 and 563 cm⁻¹ are present in the P=S stretching region, in place of the 568 cm⁻¹ band of the free ligand. In addition, there is a strong peak at 430 cm⁻¹ in the infrared. The P-C asymmetric stretching vibrations at 733 are 760 cm⁻¹ are separated to a greater extent than in the free ligand. The methyl C-H vibrations of tetramethyldiphosphine disulfide are split into two sharp peaks in this complex as well as in the other complexes of this ligand (this is exemplified by Figure 28 for the \([\text{AgL}_2]\text{ClO}_4\) complex of tetramethyldiphosphine disulfide).
Figure 28. Infrared spectrum of [Ag(Me$_4$P$_2$S$_2$)$_2$]ClO$_4$; (KBr).
The Raman data for the \([\text{Cu(Me}_4\text{P}_2\text{S}_2)_2]\text{ClO}_4\) complex are also given in Table 29. Five bands are present in the 400-800 cm\(^{-1}\) region. Four of these coincide with infrared absorptions. Only one of the two groups who obtained Raman spectra found a band at 500 cm\(^{-1}\); it has no counterpart in the infrared spectrum. The origin of this peak is open to question.

To reiterate, the presence of bands which are both Raman and infrared active indicates that the tetramethyldiphosphine ligand has lost its center of symmetry in the complex (53).

The two infrared bands in the P=S region indicates a cis arrangement of P=S groups.

If tetramethyldiphosphine disulfide remains in the trans configuration, with each P=S group coordinated to a different metal, the ligand should still contain a center of symmetry. The diphosphine disulfide ligand could also retain trans P=S groups if only one of them were coordinated; the presence of the metal would then destroy the center of symmetry. Two coordinate copper(I) is not unknown and the \([\text{CuL}_2]^+\) unit could be of the form \([\text{Me}_2(S)\text{P(Me}_2)_2]^-\cdot\text{Cu} \cdot \text{SP(Me}_2)_2\cdot\text{P(S)Me}_2\cdot\text{Cu} \cdot \text{SP(Me}_2)_2\cdot\text{P(S)Me}_2\cdot\text{Cu}\). However, one would then expect three bands in the P=S stretching region; the symmetric and asymmetric stretches as well as one of these being split as for \(\nu_{\text{P=S}}\) for the monodentate \([\text{AgL}_2]^+\) complexes. The total data, however, can best be interpreted in terms of chelating ligands coordinated around four-coordinate copper(I).

One must concentrate on the symmetry of the ligand in the complex and not on the symmetry of the total compound. This is
a simplification since the vibrational modes will depend not only on the intrinsic symmetry of the molecule itself but on the symmetry of the environment. However, to a first approximation, the vibrational modes are localized on certain groups of the total unit.

Thus, ideally, the symmetry of the ligand would be $C_{2v}$, if it complexed with cis P=S groups; and one vertical plane would contain the two phosphorus and two sulfur atoms. In a complex such as $[CuL_2]^+$, the tetrahedral coordination of sulfur atoms about the copper atom could be achieved by arranging the two ligands with P-P bonds perpendicular to each other. However, a $C_2$ (skew) configuration of the ligand, where the four phosphorus and sulfur atoms are not all in the same plane, would also produce tetrahedral coordination about the copper atom.

Using the technique described by Drago (72), a total representation for the $C_{2v}$ structure of $Me_2P(S)P(S)Me_2$ is given in Table 30.

<table>
<thead>
<tr>
<th>$\text{E}$</th>
<th>$C_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma_v''(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total representation</td>
<td>24</td>
<td>0</td>
<td>4</td>
</tr>
</tbody>
</table>

This symmetry would require six $A_1$, four $A_2$, five $B_1$, and three
fundamental vibrations. Of these, only $\Lambda_2$ is Raman active alone; the others are both infrared and Raman active. In the skew ($C_2$) configuration, both $\Lambda$ and $B$ modes are infrared and Raman active. This is then to be compared with the spectra of the $[\text{Cu(Me}_4\text{P}_2\text{S}_2)]^+$ complex, where one Raman, one infrared, and four Raman and infrared active vibrations are found. This is consistent with $C_{2\nu}$ symmetry if the P=S asymmetric stretch (I.R. active only) also occurred in the Raman. It is possible, that for some reason, the intensity of this band in the Raman is zero.

The infrared data for the other complexes of tetramethylidiphosphine disulfide (excluding the $Ag^+$ complex) are recorded in Table 32. The decreases for $\nu_{P=S}$ in the complexes are listed in Table 31:

### Table 31

<table>
<thead>
<tr>
<th>$P=S$ sym.</th>
<th>$P=S$ asym.</th>
</tr>
</thead>
<tbody>
<tr>
<td>22-32 cm$^{-1}$</td>
<td>5-14 cm$^{-1}$</td>
</tr>
</tbody>
</table>

The infrared data for tetraethylidiphosphine disulfide (60) and its complexes (excluding that of $Ag^+$) are recorded in Table 33. Figure 29 shows the infrared spectrum of a typical $Et_4P_2S_2$ complex. The complexes of tetraethylidiphosphine disulfide show four sharp, distinct peaks in the C-H region.
Table 32
Infrared Data\(^\dagger\) for Other Me\(_2\)P(S)P(S)Me\(_2\) Complexes

<table>
<thead>
<tr>
<th></th>
<th>[CuLBr(_x)]</th>
<th>[CuLI(_x)]</th>
<th>CdLI(_2)</th>
<th>HgLI(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>426 m.(^\dagger\dagger)</td>
<td>426 m.</td>
<td>424 m.</td>
<td>423 m.</td>
<td></td>
</tr>
<tr>
<td>551 s.(^\dagger\dagger)</td>
<td>554 s.</td>
<td>551 s.</td>
<td>550 s.</td>
<td></td>
</tr>
<tr>
<td>590 v.s.</td>
<td>590 v.s.</td>
<td>588 s.</td>
<td>588 s.</td>
<td></td>
</tr>
<tr>
<td>723 s.</td>
<td>731 v.s.</td>
<td>724 s.</td>
<td>723 s.</td>
<td></td>
</tr>
<tr>
<td>735 v.s.</td>
<td>759 s.</td>
<td>729 s.</td>
<td>726 s.</td>
<td></td>
</tr>
<tr>
<td>762 s.</td>
<td>758 m.</td>
<td>755 m.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{\dagger}\) Nujol mulls

\(^{\dagger\dagger}\) s., strong; v.s., very strong; m., medium

(infrared) (see Figure 30). The P=S vibration for uncomplexed tetraethylidiphosphine disulfide occurs at 549 cm\(^{-1}\).

The Raman active P=S symmetric stretch for tetraethylidiphosphine disulfide occurs as a strong absorption at 625 cm\(^{-1}\) (60); Van der Linde and Hooge report 604 cm\(^{-1}\) (45). The Raman data reported by Cowley (60) for this ligand show no band assignable to the P-P stretching mode and he concludes that it must be obscured by stray radiation. Raman data for two complexes of tetraethylidiphosphine disulfide were obtained (Table 34).

The band for the complexes of tetraethylidiphosphine in the region 590-598 cm\(^{-1}\) which is both Raman and infrared active is assigned to the P=S symmetric stretch, a decrease of 27-35 cm\(^{-1}\) from the free ligand value (Tables 33 and 34). The band which
Figure 29. Infrared spectrum of \([\text{Cu(Et}_4\text{P}_2\text{S}_2)_2]\text{[CuBr}_2]\) (Nujol mull).
Figure 30. Infrared spectrum of \([\text{Cu(}\text{Et}_4\text{P}_2\text{S}_2)\text{]}\text{ClO}_4\]; (KBr).
Table 3.3

Infrared Data $^\dagger$ for $\text{Et}_2\text{P(S)P(S)Et}_2$ and its Complexes

<table>
<thead>
<tr>
<th>L</th>
<th>$[\text{CuL}_2]\text{ClO}_4$</th>
<th>$[\text{CuLCl}]_x$</th>
<th>$[\text{CuLBr}]_x$</th>
<th>CdL$\text{I}_2$</th>
<th>HgL$\text{I}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>437 s.$^{\dagger\dagger}$</td>
<td>417 m.$^{\dagger\dagger}$</td>
<td>410 m.</td>
<td>411 n.</td>
<td>412 n.</td>
</tr>
<tr>
<td></td>
<td>549 v.s.$^{\dagger\dagger}$</td>
<td>470 w.$^{\dagger\dagger}$</td>
<td>426 s.</td>
<td>425 s.</td>
<td>466 m.</td>
</tr>
<tr>
<td></td>
<td>684 v.s.</td>
<td>500 m.</td>
<td>518 s.</td>
<td>517 s.</td>
<td>502 m.</td>
</tr>
<tr>
<td></td>
<td>738 v.s.</td>
<td>543 s.</td>
<td>539 v.s.</td>
<td>538 v.s.</td>
<td>531 s.</td>
</tr>
<tr>
<td></td>
<td>772 v.s.</td>
<td>590 s.</td>
<td>598 m.</td>
<td>597 m.</td>
<td>583 s.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>625 v.s.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>679 v.s.</td>
<td>687 s.</td>
<td>680 b.,s.</td>
<td>675 s.</td>
<td>676 s.</td>
</tr>
<tr>
<td></td>
<td>703 s.</td>
<td>681 s.</td>
<td>699 s.</td>
<td>707 s.</td>
<td>705 s.</td>
</tr>
<tr>
<td></td>
<td>710 s.</td>
<td>700 s.</td>
<td>740 s.</td>
<td>731 s.</td>
<td>737 s.</td>
</tr>
<tr>
<td></td>
<td>743 s.</td>
<td>741 s.</td>
<td>772 v.s.</td>
<td>766 v.s.</td>
<td>766 v.s.</td>
</tr>
<tr>
<td></td>
<td>766 v.s.</td>
<td>775 v.s.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{\dagger}$Wujol nulls
$^{\dagger\dagger}$s., strong; v.s., very strong; m., medium; w., weak; b., broad

Table 3.4

Raman Data for Complexes of $\text{Et}_2\text{P(S)P(S)Et}_2$$^{a,b}$$^\dagger$

<table>
<thead>
<tr>
<th>$[\text{CuL}_2]\text{ClO}_4$</th>
<th>CdL$\text{I}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>590 s.$^{\dagger\dagger}$</td>
<td>590 s.</td>
</tr>
<tr>
<td>500 v.s.$^{\dagger\dagger}$</td>
<td>500 v.s.</td>
</tr>
</tbody>
</table>

$^{\dagger}$a, 400-800 cm$^{-1}$ region b, crystalline sample
$^{\dagger\dagger}$s., strong; v.s., very strong
appears in the infrared spectrum of the complexes in the 531-543 cm\(^{-1}\) region is assigned to the P=S asymmetric stretch, a decrease of 6-18 cm\(^{-1}\) from the free ligand value. By analogy with the assignment in the complexes of tetramethyldiphosphine disulfide, the band in the tetraethyldiphosphine disulfide complexes which is both infrared and Raman active at 500-517 cm\(^{-1}\) is assigned to the P-P stretching vibration of the ligand. There is no free ligand value for comparison.

No Raman data were obtained for the one copper(I) perchlorate complex of tetra(n-propyl)diphosphine disulfide but the infrared data for the ligand (60) and the complex are given in Table 35 (see Figure 31). The assignments for this complex are

Table 35

<table>
<thead>
<tr>
<th>L</th>
<th>[CuL(_2)]ClO(_4)(^{\dagger})</th>
</tr>
</thead>
<tbody>
<tr>
<td>411 s.(^{\dagger\dagger})</td>
<td>426 n.(^{\dagger\dagger})</td>
</tr>
<tr>
<td>524 v.w. (^{\dagger\dagger})</td>
<td>447 w.(^{\dagger\dagger})</td>
</tr>
<tr>
<td>583 v.s.(^{\dagger\dagger})</td>
<td>475 w.</td>
</tr>
<tr>
<td>617 v.w.</td>
<td>493 w.</td>
</tr>
<tr>
<td></td>
<td>518 n.</td>
</tr>
<tr>
<td></td>
<td>539 w.</td>
</tr>
<tr>
<td></td>
<td>570 s.</td>
</tr>
<tr>
<td></td>
<td>596 s.,b.(^{\dagger\dagger})</td>
</tr>
<tr>
<td></td>
<td>624 s.</td>
</tr>
</tbody>
</table>

\(^{\dagger}\) Nujol null

\(^{\dagger\dagger}\) s., strong; v.s., very strong; n., medium w., weak; v.w., very weak; b., broad
Figure 31. Infrared spectrum of \([\text{Cu}(n-\text{Pr}_4\text{P}_2\text{S}_2)\text{ClO}_4]\) (Nujol mull).
recorded in Table 36. Cowley (60) describes no Raman data for

describe no Raman data for

**Table 36**

Assignment of P=S Vibrations for the \([\text{CuL}_2]\text{ClO}_4\)
Complex of \((\text{n-Pr})_2\text{P(S)P(S)(n-Pr)}_2\)

<table>
<thead>
<tr>
<th>I.R. band, cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>596</td>
<td>P=S symmetric stretch</td>
</tr>
<tr>
<td>570</td>
<td>P=S asymmetric stretch</td>
</tr>
</tbody>
</table>

\(\dagger\)Nujol null

tetra(n-propyl)diphosphine disulfide; therefore, no value for
the P-P stretch or P=S symmetric stretching vibration are known
for this ligand. The asymmetric P=S stretching vibration is
decreased 13 cm\(^{-1}\) upon complexation (free ligand value 583 cm\(^{-1}\)).

The stoichiometry of the tetraalkyldiphosphine disulfide
silver(I) perchlorate complexes corresponds to \([AgL_2]\text{ClO}_4\) . It
is possible that these might contain two-coordinate silver(I)
ions if only one P=S group of each ligand were coordinated. How­
ever, the similarity between the infrared spectra of the
\([AgL_2]\text{ClO}_4\) and \([\text{CuL}_2]\text{ClO}_4\) complexes (compare values in Table 37
with Table 29 and 32 and see also Figure 32) indicates the same
type of coordination in both. This would require all four sul­
fur atoms to be coordinated to silver in a tetrahedral fashion.
This appears reasonable since the coordination number of
Figure 32. Infrared spectra of $\text{[Ag(Me}_4\text{P}_2\text{S}_2\text{)ClO}_4$ and $\text{[Cu(Me}_4\text{P}_2\text{S}_2\text{)ClO}_4$ (KBr).
Table 37

Infrared Data for [AgL₂]ClO₄ Complexes of R₂P(S)P(S)R₂

<table>
<thead>
<tr>
<th>L</th>
<th>Absorptions in 400-600 cm⁻¹ region †</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂P(S)P(S)Me₂</td>
<td>420 m., b. ††</td>
</tr>
<tr>
<td></td>
<td>559 s. ††</td>
</tr>
<tr>
<td></td>
<td>595 s.</td>
</tr>
<tr>
<td>Et₂P(S)P(S)Et₂</td>
<td>418 m.</td>
</tr>
<tr>
<td></td>
<td>469 w. †</td>
</tr>
<tr>
<td></td>
<td>500 w.</td>
</tr>
<tr>
<td></td>
<td>547 s.</td>
</tr>
<tr>
<td></td>
<td>594 s.</td>
</tr>
</tbody>
</table>

†Nujol mulls
††s., strong; m., medium; w., weak; b., broad

Silver(I) can vary and sp³ hybridization of Ag⁺ is known, especially with S, Se, P, and As ligands (57).

The occurrence of only the trans configuration for R₂P(S)P(S)R₂ in the uncomplexed state probably results from repulsive forces of the unbonded electrons on sulfur. The cis form can be stabilized by complexation. Tetraethylidiphosphine disulfide reverts to the trans form when displaced from the metal, as evidenced from its infrared spectrum.

Definite proof of the symmetry of the ligands in these complexes could be obtained by X-ray analysis. However, no suitable crystals of [Cu(Me₄P₂S₂)₂]ClO₄ have been obtained, but
Dr. Wheatley examined some crystals of $[\text{Cu(Et}_4\text{P}_2\text{S}_2)_2]\text{ClO}_4$. Unfortunately, these were twinned; nevertheless, he obtained the following crystallographic constants. The crystals were monoclinic, $a = 13.47$, $b = 16.21$, $c = 13.70$, $\beta = 91.4^\circ$, $V = 2990 \, \text{Å}^3$, $D_x = 1.438$, $D_m = 1.426$ (by flotation in a mixture of 1,3-dichloro-2-propanol and trichloroethylene). $Z = 4$. Space group $P2_1/c$; no crystallographic symmetry required.

During the course of this investigation other reports of tetraalkyldiphosphine disulfide complexes have appeared. Thus, Baker and Fowles have prepared titanium(IV) chloride and bromide complexes of the type TiX$_4$L with tetraethyldiphosphine disulfide (6). They present no evidence that both P=S groups are coordinated in a cis fashion but assume that tetraethyldiphosphine disulfide is a bidentate ligand. They incorrectly assign a band at 776 cm$^{-1}$ in the infrared spectra of the complexes as the P=S vibration and do not record bands in the KBr region. Teichmann (313) has also recently reported that tetraalkyldiphosphine disulfides form tin(IV) halide complexes; i.e., SnX$_4[R_2P(S)P(S)R_2]$. No infrared assignments were reported for these complexes. Finally, Dr. L. Maier has informed Dr. Meek that both the meso and $d,l$ forms of 1,2-dimethyl 1,2-diphenyldiphosphine disulfide complex with mercury(II) halides (220).
E. Donor Properties of Tertiary Phosphine Sulfides, Phosphine Selenides, and Arsine Sulfides

1. Compared with analogous phosphine and arsine oxides

As pointed out in the introduction, tertiary phosphine and arsine oxides characteristically form complexes with first row transition metal ions of +2 and +3 charge; i.e., class (a) metals. It was found in this study that the sulfide and selenide ligands do not complex with first row metals; but instead, form stable coordination complexes of class (b) metals such as copper(I), silver(I), cadmium(II), mercury(II), palladium(II), and platinum(II). This intrinsic difference in the donor properties of the group five oxide ligands, compared with the other chalcogenide ligands, precludes any direct comparison with the same metal.

2. Compared with each other

These tertiary phosphine sulfides, phosphine selenides, and arsine sulfides may be compared in the following categories:

1) Stoichiometry of complexes;

2) Differentiation of coordinating ability even among class "b" metal ions;
3) Different degrees of stabilization of low oxidation state;

4) Decrease in $\nu_{P-X}$ for complexes; and

5) Apparent position in spectrochemical series.

These points will be discussed section IIIF.

3. Compared with other ligands

The position of these ligands in the spectrochemical series, as compared with their parent phosphinos and arsines, is:

\[ \phi_2^{3} \text{As} > \phi_2^{3} \text{AsS} \]
\[ \phi_2^{3} \text{P} > \phi_2^{3} \text{PS}, \phi_2^{3} \text{PSe} \]
\[ \Delta P > \Delta \text{PS} \]

In each case, addition of a sulfur or selenium atom to the group V donor decreases the apparent ligand field strength of the molecule.

That arsenic is a stronger donor toward gold(I) than the tertiary aromatic P=S group is shown by the fact that the APS ligand coordinates only through the arsenic atom.

Furthermore, the following order of relative donor strength can be assessed from displacement data on palladium:

\[ \text{I}^-, \text{SCN}^-, \text{SeCN}^- > \text{Me}_2\text{PS}, \phi_2^{3} \text{PS}, \phi_2^{3} \text{PSe} > \text{Cl}^-, \text{Br}^- \text{ and} \]
\[ \phi_2^{3} \text{AsS} > \text{Cl}^-, \text{Br}^-, \text{I}^- \]

The donor properties of $R_2^{3} \text{PS}, R_2^{3} \text{PSe}$, and $R_2^{2} \text{P(S)P(S)R}_2$ groups cannot be compared directly with $R_2^{2} \text{P(S)S}^-, R_2^{2} \text{P(Se)Se}^-$, $(\text{RO})_2^{2} \text{P(S)S}^-$, or $(\text{RO})_2^{2} \text{P(Se)Se}^-$ ligands because the latter form inner complexes with class (a) metal ions.
These ligands containing the P=S and As=S groups show donor properties similar to the C=S donor group of thiourea. Thus, thiourea also forms strong complexes with class (b) metal ions such as Cu(I), Ag(I), Au(I), and Hg(II) (205). Thiourea also reduces Cu(II) to Cu(I) as well as Au(III) to Au(I) (205). In addition, the P=Se donor group resembles selenoureia (206).

Similarly, the sulfur and selenium ligands investigated in this study behave analogously to thioethers and selenoethers ($R_2X$) in that they form complexes of similar stoichiometry with similar metal ions. For example, the tertiary phosphine sulfide complexes of mercury(II) halides discussed in section IIIB1 are analogous to those of thioethers (83,307); i.e., the latter form Hg(II) complexes of stoichiometry ($R_2S)_2HgX_2$, halogen-bridged dimeric species [(R$_2$S)HgX$_2$]$_2$ as well as those of uncertain structure $R_2S \cdot 2HgX_2$.

**F. Nature of Bonding in Complexes of Tertiary Phosphine and Arsine Chalcogenides**

As discussed in section IB5, at present there are two theories which may be used to rationalize differences in donor properties between oxygen and sulfur ligands. These are based on what is considered the major stabilization factor in the complex. For ligands such as sulfur these are

- **a** polarizability or
- **b** delocalization of metal's d-electron density onto empty ligand orbitals. While one might rationalize the TiX$_4$[$Et_2P(S)P(S)Et_2$] complexes of Baker and Fowles (6) by only employing the concept of polarizability of the ligand, polarizability as well as
backbonding of filled metal d-orbital electrons onto empty d-orbitals of sulfur or selenium may be used to explain the results of this investigation.

For instance, sulfur and selenium are capable of having their outer electrons distorted; i.e., they are easily polarized. The polarizabilities of sulfur ligands decrease in the order $S^{2-} > RS^- > R_2S$; the number of lone pairs decreases in the same order (200). Williams has suggested (329) that the principal difference between thioethers and thiols as ligands is that the former, while not as polarizable, are more effective $d_\pi$-electron acceptors than the latter. The ligands used in this study are electron rich donors (i.e., good $\sigma$-donors) due to canonical form $R_3P^+ - S^-$. On the other hand, the $R_3P=S$ ligands also could be effective $d_\pi$-electron acceptors via the canonical form $R_3P=S$.

The cations which formed stable complexes are those capable of extensive orbital overlap because of the large orbitals; i.e., $Ag^+$, $Cu^+$, and $Hg^{2+}$. The permanent dipole moment of the ligands probably is relatively unimportant when compared with the induced dipole moment due to the delocalized $P=S$, $P=Se$, or $As=S$ groups.

The ability of trinethylphosphine sulfide, triphenylarsine sulfide, and the tetramethyldiphosphine disulfide ligands to stabilize copper(I) also indicates more effective overlap by the larger $Cu(I)$ orbitals, in comparison with $Cu(II)$, with the empty $d$-orbitals on sulfur.
Trimethylphosphine sulfide, tri(n-butyl)phosphine selenide, and triphenylphosphine selenide reduce gold(III) to elemental gold, whereas triphenylphosphine sulfide bonds with gold(III) without reduction.

The differentiation shown in $\Delta v_{P=X}$ can be interpreted by assuming varying degrees of $\pi$-backbonding to empty $d$-orbitals on sulfur or selenium. Backbonding could lead, by increasing electron density on the chalcogenide atom, to an increased phosphorus-chalcogenide bond order. Strong $\sigma$-bonding of the sulfur or selenium atoms would affect the phosphorus-chalcogenide bond in the opposite manner.

The small decrease for $v_{P=Se}$ observed in the complexes of tertiary phosphine selenides could indicate a high degree of $\pi$-bonding from filled metal $d$-orbitals to empty $d$-orbitals on selenium.

Triphenylphosphine sulfide appears to have limited $\pi$-backbonding capacity. This ligand, by itself, will not reduce Cu(II); and, although a Au(I) complex is known, the Au(III) complex of this ligand can be prepared without reduction of the metal to Au(I) (165). The occurrence of $v_{P=S}$ in all the triphenylphosphino sulfide complexes is approximately constant. Also, the decrease of this vibration upon complexation is the largest found. The value of $v_{P=S}$ in $[Cu(\phi_2PS)_4]ClO_4$ and $[Ag(\phi_2PS)_2ClO_4$ is not as low as for the other complexes and indicates some $\pi$-bonding in these; however, the charge on these metals is only +1, whereas the other metals are divalent and greater $\sigma$-bonding may occur with the latter.
Another possible explanation for the large decrease of ν_p=S in the triphenylphosphine sulfide complexes could be mesomeric stabilization factors such as shown in XLIX.

![Diagram XLIX](image)

XLIX

However, one would have expected the same to occur in the aryl phosphine selenide complexes (L).

![Diagram L](image)

L

Another possibility for the small decreases for ν_p=Se in the tertiary phosphine selenide complexes is that this may result because of the small electronegativity difference between phosphorus and selenium. In the free ligand only a small charge separation would be present; therefore, those ligands may act as poor σ-donors.

The differentiation shown in the complexing ability of the ligands toward d^10 metal ions and the stoichiometry of the mercury(II) and cadmium(II) complexes may be due to the degree to which the phosphorus(arsenic)-chalcogenide bond is polarized by the metal; i.e., the relative σ-strength of the donor atom. The more basic ligands would be more effective in breaking up the polymeric d^10 metal halide structures.
Triphenylarsine sulfide forms cadmium(II) and mercury(II) complexes of the type $\text{LMX}_2$ whereas triphenylphosphine sulfide forms only the analogous mercury(II) halide complexes. This difference in donor behavior must be due to the difference in donor properties of the $\text{P=S}$ group compared with that of the $\text{A=S}$ group. Since the electronegativity of arsenic is lower, the order of donor strength would be $\mathcal{O}_{3\text{AsS}} > \mathcal{O}_{3\text{PS}}$, in agreement with the observed trends.

Triphenylphosphine sulfide and selenide form mercury(II) halide complexes of only type $\text{LHgX}_2$. On the basis of electronegativity differences between phosphorus and the chalcogenide atom, one would expect triphenylphosphine sulfide to be a stronger $\sigma$-donor. The electronegativity differences may be too slight to produce this differentiation.

Different organic substitution of the $\text{P=S}$ and $\text{P=Se}$ groups also leads to apparent differences in donor strength. Thus, both trimethylphosphine sulfide and tri(n-butyl)phosphine selenide form mercury(II) halide complexes of the type $\text{L}_2\text{HgX}_2$; i.e., greater $\text{L:HgX}_2$ ratio. In addition, these aliphatic phosphine sulfide and selenide ligands also form $\text{L}_2\text{CdX}_2$ complexes, whereas triphenylphosphine sulfide and triphenylphosphine selenide form no stable complexes with cadmium(II). Also, trimethylphosphine sulfide forms $\text{L}_2\text{ZnI}_2$ and $[\text{ZnL}_4](\text{ClO}_4)_2$ complexes, whereas tri(n-butyl)phosphine selenide forms no
Zn(II) complexes. These results indicate the following order of donor strength:

\[
\text{Me}_3\text{PS} > (\text{n-Bu})_3\text{PSe} \\
\text{Me}_3\text{PS} > \Phi_3\text{PS} \\
(\text{n-Bu})_3\text{PSe} > \Phi_3\text{PSe}
\]

Considering the electron density around sulfur or selenium, the positive inductive effect of the alkyl groups should increase the \(\sigma\)-donor ability of the sulfur or selenium atoms; i.e., raise the basicity (183). The negative inductive effect of the phenyl group, employing the same premise, should result in lower basicity of the sulfur and selenium atoms. For example, the coordinating ability of bis(chloroethyl)sulfide, \((\text{ClCH}_2\text{CH}_2)_2\text{S}\), is weaker than that of diethyl sulfide (203).

\(\pi\)-bonding ability of the Group VI chalcogenide atom may also be important in determining the stoichiometry of these \(d^{10}\) complexos; e.g., infrared data show that trimethylphosphine sulfide is probably also a better \(\pi\)-bonder than triphenylphosphine sulfide.

The two alkyl-substituted ligands containing sulfur and selenium, \(\text{Me}_3\text{PS}\) and tri(\(\text{n-Bu}\))\(_3\)\(\text{PSe}\), cannot really be compared because of the difference in alkyl groups. It is possible that steric requirements may be involved in determining the donor ability of these ligands.

The remote possibility exists that steric requirements of the phenyl ring might explain the stoichiometry of the \(\text{L} \cdot \text{HgX}_2\) complexes and also be responsible for the lack of donor
ability of triphenylphosphine sulfide and selenide toward cadmium(II) and zinc(II); however, triphenylarsine sulfide does complex with cadmium(II). Also, since the phenyl rings are two atoms removed from the metal in these, this effect may be discounted.

The spectrochemical order of ligands

\[ \text{Me}_2\text{PS} > \text{Ph}_2\text{PSe} \geq \text{Ph}_2\text{AsS} > \text{Ph}_2\text{PS} \]

may be rationalized by considering the amount of polarization for the P=S, As=S, and P=Se moieties; the greater this is, the larger the ligand-metal interaction. In addition, the possibility exists that the order found is determined or influenced by the degree of π-backbonding ability of the sulfur or selenium atom. This also would increase metal-ligand interaction. The low position of triphenylphosphine sulfide would fit this argument. The rationalization for the remaining order must remain ipso facto, however.

The lower extinction coefficients for the absorptions of the \([\text{Pd(CAPS)}X_2]\) complexes compared with those of the analogous AP complexes may indicate either less extensive delocalization of metal's d-electrons onto sulfur than for phosphorus or stronger σ-bonding of phosphorus.

The similarity in the energy of electronic transitions in palladium complexes of tri(p-tolyl)phosphine selenide, tri(α-tolyl)phosphine selenide, and triphenylphosphine selenide indicates that availability of electron density on selenium is
relatively unimportant. The selenium's electron density must increase as the phosphorus-selenium double bond character decreases and the following order of decreasing phosphorus-selenium double bond character is found (as observed from $\nu_{P=S}$):

$\text{(n-C}_7\text{H}_7)_3\text{PSe (574 cm}^{-1}) > \phi_3\text{PSe (560 cm}^{-1}) > (\text{p-C}_7\text{H}_7)_3\text{PSe (544 cm}^{-1})$. Yet, no differentiation is shown in the spectrochemical order (solid state). The solution results are suspect because of the possibility of structural change upon dissolution in dichloromethane since some of the spectra change.

While class (a) metal complexes of these ligands are unknown, materials such as ZnS and CdS can be doped with small amounts of other metal ions and the solid spectra of chromophores such as $\text{M(II)S}_4$ ($\text{M} = \text{Fe, Co, Ni, Cu}$) can be obtained (266,325,326). These results indicate that $\delta$ is larger than for $\text{M(II)Cl}_4$ and that the nephelauxetic effect is greater. Mixed sulfide or selenide analogs of the spinels have also been studied (114); i.e., $\text{CuCrS}_2$ contains the Cr(III)$\text{S}_6$ and Cu(I)$\text{S}_4$ chromophores. The latter is analogous to the Cu(I)$\text{P}_4\text{P}_2\text{S}_2$ and Cu(I)$\phi_3\text{PS}$ complexes prepared in this study; however, the copper(I) is surrounded by four $\text{P=S}$ groups in these complexes instead of four sulfide ions.

Just as a combination of the polarization theory coupled with $\pi$-bonding theory (electron delocalization) may be offered to explain the observations concerning the donor ability of the various tertiary phosphine or arsine chalcogenides, either one or both may be employed to explain the difference in donor
properties between tertiary phosphine and arsine oxides compared with their sulfide and selenide analogs.

The tertiary Group V oxides show class (a) or hard base character because they combine with metal ions showing hard acid character. On the other hand, tertiary phosphine sulfide and selenide donors show class (b) or soft base character because they preferentially coordinate with soft acid metal ions.

Thus, the differentiation shown by these oxide, sulfide, and selenide systems is similar to other ligands containing these donor groups; oxygen is a hard base, sulfur and selenium are soft bases. For example, low spin \(d^8\) ions Pd(II), Pt(II), and Au(III) as well as the \(d^{10}\) ions Cu(I), Ag(I), and Hg(II) have the highest formation constants with the heavy halides and with sulfur ligands (201). Analogously (202), thioethers do not coordinate very strongly to metals apart from Pt(II), Pd(II), Ir(III), Rh(III), and Hg(II). Complexes of selenoethers closely resemble the thioether complexes; however, corresponding complexes of telluroethers are much less stable (202).

The differentiation is not surprising since oxide ligands possess all the characteristics of "hardness" while sulfide and selenide ligands, including those studied in this work, are characterized by large size, high polarizability, low electronegativity, are easily oxidized, and are associated with empty, low lying orbitals; i.e., are soft donors.

For the ligands studied here, the larger size of the sulfur and selenium atoms as compared with the oxygen atom should have
led to weaker interactions with small, hard metals; however, the large diffuse character of the sulfur and selenium orbitals in the P=S, As=S, and P=Se groups could lead to effective orbital overlap with large, polarizing metals such as Pd$^{2+}$ and Pt$^{2+}$. The balance of these two factors determines the relative coordinating ability of these two systems. Also, the further possibility of π-bonding between d-orbitals of the acceptor atom and unfilled d-orbitals on sulfur and selenium may be an important stability factor; this is non-existent for the oxide analogs. However, the same conclusions will follow if one argues that polarization is the major factor in formation of the complexes.

G. The Nature of Thiocyanate Bonding in Palladium(II) Complexes Containing Bidentate Ligands

The remainder of the dissertation is concerned with the elucidation of the mode of thiocyanate coordination in palladium(II) complexes containing a variety of bidentate ligands.

The thiocyanate anion contains two basic sites; either one of which is capable of bonding to metal ions. The nature of the bonding shown by this anion (thiocyanato - M-SCN, isothiocyanato - M-NCS) is related to the order of halide stability exhibited by the metal ion (196,250). The differentiation in bonding toward different metal ions can also be explained by the "hard" and "soft" acid-base concept of Pearson (272); the nitrogen end of the thiocyanate anion being a hard donor while the sulfur end is a soft donor.
When the thiocyanate anion is coordinated along with other ligands in a given metal complex, the nature of the other ligands seems to influence whether N- or S-bonding of NCS\(^-\) will occur. This is particularly true with palladium(II) and platinum(II) complexes (33,316). In such systems, ligands capable of \(\pi\)-bonding (M-L), such as PEt\(_3\), yield complexes containing N-bonded thiocyanate; whereas similar complexes containing non-\(\pi\)-bonding ligands, such as NH\(_2\), form S-bonded complexes.

Wojcicki and Farina found (331) that manganese(I) carbonyl, Mn(CO)\(_5\)SCN, is sulfur bonded and they suggest (84) that the extent of M=CO \(\pi\)-backbonding in complexes of this nature might be important in determining the mode of thiocyanate coordination. Thus, in Mn(CO)\(_5\)SCN, where \(\pi\)-bonding is relatively weak, the more polarizable sulfur end is preferred by the metal. This would enhance the negative charge on the metal and result in greater M=C=O bonding.

A low oxidation state of the metal results in greater M=C=O bonding and, therefore, there is no preference or drawing force for sulfur coordination. Thus, the ion Cr(CO)\(_5\)NCS\(^-\) is nitrogen bonded (332). Stronger metal-carbon monoxide interaction would also be promoted when carbon monoxide is replaced by ligands of smaller \(\pi\)-bonding capacity. This argument is used (84) to explain the type of bonding in substituted complexes like Mn(CO)\(_4\)L(CNS) and cis- or trans-Mn(CO)\(_4\)L\(_2\)(CNS). The formula CNS is employed when either N- or S-bonding may occur and neither is pointed out specifically.
The argument used by Turco and Pecile (316) to rationalize the M-CNS bonding in square planar palladium(II) and platinum(II) complexes containing ligands of variant π-bonding ability is similar. If filled metal d-electron density is available, additional stability of the M-S bond over the M-N bond may result because the sulfur atom contains antibonding π-orbitals localized on the sulfur atom which, together with the sulfur atom's vacant d-orbitals, can accept electron density from filled non-bonding d-orbitals of the metal. Having other strong π-electron acceptors coordinated to the metal can decrease the availability of the metal's d-orbital electrons, thus eliminating this source of additional stability which would promote M-S bonding.

Burneister and Basolo state (33) that the presence of ligands capable of π-bonding in these systems tends to change class (b), or soft metals, to class (a), or hard metals, by reduction of electron density on the metal.

The importance of steric factors in these complexes has also been noted (12,84). This results because the steric requirements of M-SCN bonding is greater than M-NCS due to the angular M-SCN linkage, whereas the NCS group is usually linear in M-NCS complexes (187). This is used to explain why

\[
\text{Pd}[\text{HN(\(\text{CH}_2\text{CH}_2\text{NH}_2\))}_2](\text{SCN})^+ \text{ contains S-bonded thiocyanate, whereas Pd}[\text{HN(\(\text{CH}_2\text{CH}_2\text{NEt}_2\))}_2](\text{NCS})^+ \text{ contains N-bonded thiocyanate (12).}
\]

Recently, the less stable S-bonded isomer of the latter complex has been prepared (13). It is believed that the change from the S- to N-bonded species is due to the steric interaction of the
four ethyl groups (12). Electronic effects are minimized since neither amine ligand has empty d-orbitals for π-bonding.

Steric arguments may be used both ways as shown by the rationalization of Farona and Wojcicki (84), on steric grounds, as to why cis-Mn(CO)₃(η₃-As)₂SCN and cis-Mn(CO)₃(η₃-Sb)₂SCN were S-bonded whereas other complexes of this type were N-bonded. They state that models show that steric strain occurs when two triphenylarsine or -stibine groups are located in cis positions in these complexes. However, it was also suggested that linear M-NCS groups result in considerable interaction of the carbon and sulfur atoms with the phenyl groups; but that the angular M-S-CN linkages place the -CN moiety away from the phenyl rings.

Also, it has been postulated (33) that the difference in thiocyanate coordination caused by triphenylphosphine and -stibine in palladium(II) and platinum(II) complexes, the latter resulting in M-SCN and the former in M-NCS linkages, may be due to either electronic or steric effects, or possibly both. Thus, it is argued that triphenylphosphine is a better π-bonding ligand and, because of the smaller size of the phosphorus atom, the phenyl groups are closer to the metal, thereby producing a greater steric hindrance. Both effects would promote M-NCS bonding. The antimony atom, being much larger, places the bulky phenyl groups away from the metal, thereby resulting in less steric hindrance. Therefore, both steric and electronic factors favor M-SCN bonding when triphenylantimony is present.

The mode of thiocyanate coordination found in this study
for palladium(II) APS and AP complexes is unusual when compared with earlier investigations. Previous work has shown (33) that the thermodynamically stable isomer of \([\text{Pd} (\Phi_3 \text{As})_2 (\text{CNS})_2]\) is the N-bonded species. The S-bonded species is the kinetic product isolated at low temperature and it isomerizes to the N-bonded species upon heating or dissolution in solvents. This was explained on the basis that triphenylarsine exhibits \(\pi\)-bonding properties of borderline character or only slightly favoring N-bonding. Yet, in the APS complex, \([\text{Pd} (\text{APS}) (\text{SCN})_2]\), where the ligand contains one arsenic atom, no N-bonded isomer is observed; the S-bonded species apparently being stable under the experimental reaction conditions. Also, the phosphine sulfide group would be expected to be capable of \(\pi\)-bonding with palladium. On the basis of the \(\pi\)-bonding argument, this also should have favored N-bonding for NCS.

One major difference exists between \([\text{Pd} (\text{APS}) (\text{SCN})_2]\) and the \([\text{Pd} (\Phi_3 \text{As})_2 (\text{NCS})_2]\) complex. The former contains cis-thiocyanate groups whereas the latter contains trans-thiocyanate groups. Since the thiocyanate groups must, of necessity, compete directly with the trans P=S and As donor groups in the \([\text{Pd} (\text{APS}) (\text{SCN})_2]\) complex, these groups must be weaker \(\pi\)-bonding moities than the sulfur end of SCN\(^-\). This might explain the kinetic product, \([\text{Pd} (\Phi_3 \text{As})_2 (\text{SCN})_2]\), and the thermodynamic product, \([\text{Pd} (\Phi_3 \text{As})_2 (\text{NCS})_2]\), as well as the difference between this system and the APS complex.
This argument can also be used to explain the bonding in \([\text{Pd(AP)(NCS)(SCN)}]\). The monomeric yellow AP complex must be one of two isomers (LI, LII). The phosphorus and arsenic atoms are in direct competition with trans CNS\(^-\) groups for palladium's electron density. If the phosphorus atom is a better competitor than arsenic, then isomer LI is the likely configuration based on \(\pi\)-bonding arguments.

Unfortunately, there is no precedent to confirm or disallow this hypothesis. While Burmeister and Basolo have studied a variety of monodentate ligands which give trans complexes (33), they have not examined the behavior of many bidentate ligands. The only bidentate ligands investigated with palladium(II) were 1,10-phenanthroline and 2,2\(^\text{'}\)-bipyridine. They found that the latter forms both N- and S- linkage isomers; the N-bonded form is the thermodynamically controlled product. The 1,10-phenanthroline ligand forms only the S-bonded isomer. This work has been repeated by Bertini and Sabatini (22) and extended to other ligands by placing substituents on the phenanthroline rings. They conclude that bipyridine tends to draw the electrons from the palladium more strongly than 1,10-phenanthroline. These workers also suggest that electronegativity of the donor atoms
may be important in assessing relative ability of the donor to participate in π-backbonding.

Possibly the relative greater electronegativity of the phosphorus atom compared with arsenic in conjugation with direct competition with trans CNS^- groups might account for the bonding in [Pd(AP)(NCS)SCN)]. It is hard to predict electronegativity values of atoms in organic compounds but apparently the P=S group of APS has about the same value as the arsenic atom in that ligand; at least this would be a rationalization for the experimental data.

However, the possibility exists that the bulky phenyl groups around phosphorus might result in steric hindrance which would favor isomer LII. Because of the size of the donor, the phenyl groups would be further removed on arsenic and in [Pd(APS)(SCN)_2]. Thus, steric factors might offer a logical explanation. However, this is not thought necessary since only two phenyl groups would be in a position for steric hindrance instead of three as in triphenylphosphine. Farona and Wojcicki use this argument in regard to Mn(CO)_3(\(\Phi_2\)PCH\_2CH\_2P\(\Phi_2\))NCS(84).

The experimental data obtained with the AP ligand (section IIIC) suggests that although both arsenic and phosphorus are capable of π-bonding with palladium, the phosphorus atom apparently is able to do this to a greater extent than the arsenic atom. The magnitude of difference in character between phosphorus and arsenic is somewhat surprising; but a recent paper at an ACS meeting (255) describes a similar differentiation,
that is, while triphenylphosphine displaces a carbonyl group from $[\text{Fe(NO)}_2(\text{CO})_2]$ in toluene to form $[\text{Fe(O}_2\text{P})(\text{NO})_2\text{CO}]$, triphenylarsine does not.

The same type of thiocyanate coordination shown in $[\text{Pd(AP)}_2(\text{NCS})(\text{SCN})]$ would be expected if a bidentate ligand, which contained one donor atom capable of strong $\pi$-bonding and a second devoid of this ability, were used. Diphenyl(2-dimethylaminoethyl)phosphine, PN, would be an example of such a ligand.

To test this theory, the complex $[\text{Pd(PN)}(\text{CNS})_2]$ was prepared. It is a non-electrolyte in acetone ($\Lambda^\infty = 1.2 \text{ cm}^2/\text{ohm-M}$) and a monomer in DMF (theoretical value, 480; found, 445). The infrared spectrum of this complex exhibits two peaks of different character in the CN region; a strong, sharp peak at 2126 cm$^{-1}$ together with a strong, relatively broader peak at 2108 cm$^{-1}$ (Fig. 33a). Two distinct peaks remain in this region upon dissolution in dichloromethane (Fig. 33b); in fact, the splitting is accentuated, being 2127 and 2087 cm$^{-1}$, respectively. The different shapes of the two peaks suggest two types of coordinated thiocyanate linkages in the complex, similar to the AP analog. The separation between these peaks is much larger than the small splittings of cis-bonded thiocyanate complexes (less than 10 cm$^{-1}$); if this did occur, the nature of the peaks should be similar. No examples of splitting due to the cis-configuration have been reported in the cis-isothiocyanato complexes. Therefore, one might have expected just the broad peak if cis-nitrogen coordination occurred.
Figure 33. Infrared spectra of $[\text{Pd(PN)(NCS)}(\text{SCN})]$ in $\nu_{CN}$ region (a) Nujol mull (b) CH$_2$Cl$_2$ solution.
A comparison of the infrared spectrum of [Pd(PN)Br\textsubscript{2}] with the CNS\textsuperscript{−} analog in the CS stretching region (Fig. 3) shows a weak peak in the latter at 816 cm\textsuperscript{−1}. This indicates that at least one of the thiocyanate groups is N-bonded and definitely rules out the possibility that the two peaks in the CN region of the infrared are due to splitting of two S-bonded thiocyanates.

The electronic spectral data for a series of PN complexes with palladium(II) are given in Tables 38 and 39. The order of

<table>
<thead>
<tr>
<th>X</th>
<th>Abs\textsubscript{max}</th>
<th>(\epsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m\textsubscript{μ}</td>
<td>cm\textsuperscript{−1}</td>
</tr>
<tr>
<td>Cl</td>
<td>330</td>
<td>30,200</td>
</tr>
<tr>
<td>(NCS)(SCN)</td>
<td>338</td>
<td>29,600</td>
</tr>
<tr>
<td>Br</td>
<td>360</td>
<td>27,800</td>
</tr>
<tr>
<td>I</td>
<td>453</td>
<td>22,000</td>
</tr>
</tbody>
</table>

\textdagger inflection point

the spectrochemical series (solution spectra) Cl\textsuperscript{−} > CNS\textsuperscript{−} > Br\textsuperscript{−}. This is reasonable to expect if both N- and S-bonded species are present. The order Br\textsuperscript{−} > CNS\textsuperscript{−} > I\textsuperscript{−} is observed when both thiocyanate groups are S-bonded. If both groups had been N-bonded, the order of the spectrochemical series should have been CNS\textsuperscript{−} > Cl\textsuperscript{−} > Br\textsuperscript{−}. The extinction coefficient of the band
Figure 34. Infrared spectra in $\nu_{CS}$ region (Nujol mull) for (a) $[\text{Pd(PN)Br}_2]$ and (b) $[\text{Pd(PN)(NCS)(SCN)}]$
Table 39

Electronic Spectral Data for [Pd(PN)X₂] Complexes
(Nujol Mull)

<table>
<thead>
<tr>
<th>X</th>
<th>Abs max cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl (NCS)(SCN)</td>
<td>480, 20,800 sh.†</td>
</tr>
<tr>
<td>Br</td>
<td>425, 23,600 sh.</td>
</tr>
<tr>
<td>I</td>
<td>465, 21,500</td>
</tr>
</tbody>
</table>

†sh., shoulder

in [Pd(PN)(NCS)(SCN)] is higher than the extinction coefficients for the halide complexes by a factor of two.

The probable structure of [Pd(PN)(NCS)(SCN)], based on π-bonding arguments, would have the thiocyanate group trans to the nitrogen and the isothiocyanate group trans to the phosphorus atom. To be certain that the CNS⁻ opposite the -NMe₂ group is S-bonded, the analogous palladium(II) complex of tetramethylethylenediamine (TMEN) was made. It was anticipated that the [Pd(TMEN)(CNS)₂] complex would have both anions S-bonded in agreement with the π-bonding argument. Non-electrolyte behavior is found for this complex in acetone (\(\Lambda_M = 0.75 \text{ cm}^2/\text{ohm-M}\)). A strong, broad peak (Nujol mull) at 2112 cm⁻¹ occurs in the infrared spectrum of [Pd(TMEN)(CNS)₂]. This is the region for S-bonded species, but the absorption
is quite broad, (Fig. 35) in contrast to the sharp peaks observed in all other S-bonded species. Furthermore, a peak of medium intensity is found at 837 cm$^{-1}$ for this complex (by comparison with the spectrum of [Pd(TMEN)I$_2$] (Fig. 36). This clearly discernible CS vibration is indicative of N-bonding. This peak does not appear to be an overtone of a fundamental peak in the 400-420 cm$^{-1}$ region. No absorption due to $\nu_{CS}$ of a S-bonded thiocyanate group is discernable.

The electronic absorption spectra for a series of palladium(II) TMEN complexes are listed in Tables 40 and 41. These data indicate the following spectrochemical series: CNS$^{-} > Cl^{-} > Br^{-} > I^{-}$. The CNS$^{-}$ complex exerts an appreciably stronger field than the chloride complex and the extinction coefficient for the absorption spectra of [Pd(TMEN)(CNS)$_2$] is much higher than the analogous halide complexes. The infrared data, together with electronic absorption data, clearly indicate that both thiocyanate groups are N-bonded; e.g., [Pd(TMEN)(NCS)$_2$].

This result contradicts the qualitative predictions based on $\pi$-bonding arguments. To rationalize this observation, one could postulate that the dimethylamino- groups are sufficiently bulky to interact with the angular M-SCN linkage, thereby making the linear M-NCS linkage the preferred mode of coordination. This idea can be tested adequately with the ligands Mo$_2$NCH$_2$CH$_2$NH$_2$ and Me(H)NCH$_2$CH$_2$N(H)Me. If this postulate is correct, both $\pi$-bonding and steric interactions would favor the
Figure 35. Infrared spectrum of \([\text{Pd(TMEN)}(\text{NCS})_2]\) in \(\nu_{\text{CN}}\) region (Nujol mull).
Figure 36. Infrared spectra in $\nu_{C-S}$ region (Nujol mull) for (a) $[\text{Pd(TMEN)}I_2]$ and (b) $[\text{Pd(TMEN)}(\text{NCS})_2]$.
Table 40
Electronic Spectral Data for \([\text{Pd(TMEN)}X_2]\) Complexes
\((\text{CH}_2\text{Cl}_2\,\text{Solution})\)

<table>
<thead>
<tr>
<th>(X)</th>
<th>(\text{Abs}_{\text{max}}) (\mu) (\text{cm}^{-1})</th>
<th>(\varepsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCS</td>
<td>355</td>
<td>28,200</td>
</tr>
<tr>
<td>Cl</td>
<td>395</td>
<td>25,300</td>
</tr>
<tr>
<td>Br</td>
<td>358</td>
<td>27,900</td>
</tr>
<tr>
<td></td>
<td>440</td>
<td>22,700 sh.†</td>
</tr>
<tr>
<td>I</td>
<td>435</td>
<td>23,000 sh.</td>
</tr>
<tr>
<td></td>
<td>490</td>
<td>20,400</td>
</tr>
</tbody>
</table>

†sh., shoulder

Table 41
Electronic Spectral Data for \([\text{Pd(TMEN)}X_2]\) Complexes
\((\text{Nujol Mull})\)

| \(X\) | \(\text{Abs}_{\text{max}}\) \(\mu\) \(\text{cm}^{-1}\) |
|-------|-----------------|-----------------|
| NCS   | 340             | 29,400          |
| Cl    | 385             | 26,000          |
|       | 475             | 21,000 sh.†     |
| Br    | 360             | 27,800 sh.      |
|       | 405             | 24,700          |
| I     | 425             | 23,600 sh.      |
|       | 487             | 20,900          |

†sh., shoulder
isothiocyanate group being trans to phosphorus and cis to nitrogen in [Pd(PN)(NCS)(SCN)].

The extinction coefficients for the CNS⁻ complexes studied thus far show that small values occur with S-bonding and high values with N-bonding, whereas values comparable with halide anions are obtained when the (NCS)(SCN) grouping is present. Extinction coefficients may be another diagnostic test to determine the nature of thiocyanate bonding.

Consistent with the results for the AP ligand, when the diphenylarsino- group is in direct competition with the thiocyanate group, as in 1,2-bis(diphenylarsino)ethane (AA), the S-bonded species, [Pd(AA)(SCN)]₂, is formed. The selenocyanate group in the analogous complex is also bonded through the chalcogenide atom. Both complexes are non-electrolytes in acetone; ƛ_M = 1.6 cm²/ohm-M for the thiocyanate and ƛ_M = 0.8 cm²/ohm-M for the selenocyanate complex. The molecular weight found for [Pd(AA)(SCN)]₂ in chloroform shows that it is essentially monomeric (found, 810; theory, 709).

The energy of the first electronic transition (Tables 42 and 43) in the [Pd(AA)X₂] complexes produces the following spectrochemical series: Cl⁻ > Br⁻ > SCN⁻ > SeCN⁻ > I⁻. Again, the extinction coefficients for the thiocyanate and selenocyanate complexes are much lower than in the analogous halide complexes.

Both the thiocyanate and selenocyanate complexes show absorptions in the v_CN region (Nujol mull) indicative of S- and Se-bonding, respectively. Each of the CN absorptions is split into two closely spaced peaks: [Pd(AA)(SCN)]₂, 2116 and 2112 cm⁻¹.
Table 42
Electronic Spectral Data for \([\text{Pd}(\text{AA})X_2]\) Complexes
(CH\(_2\text{Cl}_2\) Solutions)

<table>
<thead>
<tr>
<th>X</th>
<th>(\text{Abs}_{\text{max}})</th>
<th>(\text{cm}^{-1})</th>
<th>((e))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>367</td>
<td>27,200</td>
<td>(4450)</td>
</tr>
<tr>
<td>Br</td>
<td>350</td>
<td>28,600 sh. (\dagger)</td>
<td>(2040)</td>
</tr>
<tr>
<td></td>
<td>388</td>
<td>25,800</td>
<td>(4920)</td>
</tr>
<tr>
<td>SCN</td>
<td>400</td>
<td>25,000</td>
<td>(1870)</td>
</tr>
<tr>
<td>SeCN</td>
<td>433</td>
<td>23,100</td>
<td>(1180)</td>
</tr>
<tr>
<td>I</td>
<td>440</td>
<td>22,700</td>
<td>(5850)</td>
</tr>
</tbody>
</table>

\(\dagger\) sh., shoulder

Table 43
Electronic Spectral Data for \([\text{Pd}(\text{AA})X_2]\) Complexes
(Nujol Mull)

<table>
<thead>
<tr>
<th>X</th>
<th>(\text{Abs}_{\text{max}})</th>
<th>(\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>370</td>
<td>27,000</td>
</tr>
<tr>
<td>Br</td>
<td>390</td>
<td>25,600</td>
</tr>
<tr>
<td>SCN</td>
<td>400</td>
<td>25,000</td>
</tr>
<tr>
<td>SeCN</td>
<td>395</td>
<td>25,300</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>22,200 sh. (\dagger)</td>
</tr>
<tr>
<td>I</td>
<td>440</td>
<td>22,700</td>
</tr>
<tr>
<td></td>
<td>520</td>
<td>19,200 sh.</td>
</tr>
</tbody>
</table>

\(\dagger\) sh., shoulder
(the latter being a shoulder); \([\text{Pd(AA)(SeCN)}_2]\), 2126 and 2120 cm\(^{-1}\). The infrared spectra of these complexes is complicated by strong aromatic absorptions in the respective \(v_{CS}\) and \(v_{CS\theta}\) regions so that these weak absorptions could not be determined.

It appears that the S-bonded species, \([\text{Pd(AA)(SCN)}_2]\), is the only product obtained by several different synthetic procedures. For example, by carrying out the reaction of \(\text{Pd(SCN)}_4^{2-}\) with AA at approximately 100° with immediate quenching in an ice/water bath one obtains the same colored solution and product as is obtained performing the synthesis at room temperature. The infrared spectrum of the product prepared at higher temperature (two strong peaks at 2120 and 2111 cm\(^{-1}\)) is identical to that prepared at room temperature. Also, the same spectrum is obtained when \([\text{Pd(AA)(SCN)}_2]\), prepared at room temperature, is recrystallized from hot DMF/ETOH. That is, there is apparently no tendency for the complex to isomerize to the N-bonded form.

By mixing an ethanolic solution of \(\text{Pd(SCN)}_4^{2-}\) with a dichloromethane solution of 1,2-bis(diphenylphosphino)ethane (PP), an initial orange precipitate is obtained. However, a light yellow product, \([\text{Pd(PP)(CNS)}_2]\) is obtained after stirring the mixture for 12 hours and then recrystallizing. The molecular weight of \([\text{Pd(PP)(CNS)}_2]\) is 850 in chloroform (621 calculated for the monomer). Its molar conductance value in acetone is 1.8 cm\(^2\)/ohm-M.
The spectrochemical series, as determined from the first electronic absorption band of the \([\text{Pd}(\text{PP})\text{X}_2]\) complexes (Tables 44 and 45) is: \(\text{Cl}^- \approx \text{CNS}^- > \text{Br}^- > \text{I}^-\). In addition, the extinction coefficient for the thiocyanate complex is similar to that of the halogen derivatives. Two S-bonded or two N-bonded thiocyanate groups can be eliminated on the basis of \(A_{\text{max}}\) of the electronic absorption spectrum. Thus suggests that one N-bonded and one S-bonded CNS\(^-\) may be present in this complex also; i.e., \([\text{Pd}(\text{PP})(\text{NCS})(\text{SCN})]\).

This formulation is also substantiated by the infrared spectrum of this complex which shows two different peaks (Nujol mull), one at 2118 cm\(^{-1}\) (sharp) and one at 2095 cm\(^{-1}\) (broad); see Fig. 37a. This same type spectrum is also observed in dichloromethane (2123 and 2087 cm\(^{-1}\)), so the split peaks are not due to a solid state phenomenon (Fig. 37b).

On the basis of the \(\pi\)-bonding argument, one would have expected that both thiocyanate groups would be N-bonded in this complex. A possible explanation may involve steric interaction between the angular M-SCN groups and the four bulky phenyl groups on the ligand. Alternatively, the 1,2-bis(diphenylphosphino)ethane ligand may somehow lie on a borderline in terms of electronic properties and the stable thiocyanate complex involves one group bonded through nitrogen and one bonded through sulfur.

Although a definitive reason for the nature of the thiocyanate bonding in \([\text{Pd}(\text{PP})(\text{NCS})(\text{SCN})]\) cannot be offered on the basis
of this investigation, it is of interest to note that Bertini and Sabatini have recently published (22) a somewhat similar result with 4,4'-dimethylbipyridine. This ligand contains two
Figure 37. Infrared spectra of $[\text{Pd(PP)(NCS)(SCN)}]$ in $\nu_{CN}$ region, (a) Nujol mull (b) CH$_2$Cl$_2$ solution.
similar nitrogen donors, and yet on the basis of infrared spectrum, it appears to contain one N-bonded and one S-bonded thiocyanate group \([\text{Pd}(\text{LL})(\text{NCS})(\text{SCN})]\).

The possibility of an equilibrium between S- and N-bonding is ruled out since, on the basis of infrared spectra, the same complex is obtained at approximately 100° as at room temperature. A light orange Magnus type salt \([\text{Pd}(\text{PP})_2]\text{[Pd}(\text{SCN})_4]\) appears to be formed at 0°, judging from the similarity of its electronic absorption spectrum (Nujol mull) with that of \(\text{Pd}(\text{SCN})_4^2\). The infrared spectrum of this orange isomer shows peaks at 2105 cm\(^{-1}\), v.s.; 2111 cm\(^{-1}\), s.; and 2118 cm\(^{-1}\), n. (Fig. 38).

A selenocyanate derivative of PP is formed if the ligand is dissolved in hot n-butanol instead of dichloromethane. This light orange product also appears to be a Magnus salt; i.e., \([\text{Pd}(\text{PP})_2]\text{[Pd}(\text{SeCN})_4]\). The infrared spectrum in the CN region (Nujol mull) is complicated. Peaks were observed at (cm\(^{-1}\)) 2057 w., sh.; 2068 w.; 2101 s.; 2116 s., s.; 2123 sh.; and 2129 v.w. (Fig. 39). The electronic spectrum of this complex (Nujol mull) shows two peaks at 535 μm and 420 μm (Fig. 40), analogous to \(\text{Pd}(\text{SCN})_4^2\) (33) but at weaker energy. This complex decomposes at 150-151° without prior change in color.
Figure 38. Infrared spectrum of \([\text{Pd(PP)}_2][\text{Pd(SCN)}_4]\) in \(\nu_{\text{CN}}\) region (Nujol mull).
Figure 32: Infrared spectrum of $\left[\text{Pd}(\text{PP})_2\right]\left[\text{Pd(SeCN)}_4\right]$ in $\nu_{CN}$ region (Nujol mull).
Figure 40. Electronic absorption spectrum $[\text{Pd(PP)}_2]\text{[Pd(SeCN)}_4]\text{]}$ (Nujol mull).
APPENDIX

Preparation of zinc(II) perchlorate hexahydrate, \([\text{Zn(H}_2\text{O)}_6]\text{ClO}_4\). Zinc oxide, 8.1 g. (0.1 mole), was heated on a steam bath for 45 min. with perchloric acid (0.18 mole, 15.5 ml. of a 70% solution). Distilled water (100 ml.) was added and the slurry was filtered to remove excess zinc oxide. The filtrate was concentrated and the white crystals of zinc(II) perchlorate hexahydrate were dried over \(\text{P}_4\text{O}_{10}\) in vacuo for several days. Yield, 15.0 g. (45%).

Preparation of potassium tetranitratopalladate(II), \(\text{K}_2[\text{Pd(NO}_3)_4]\) (78). To palladium metal (5.0 g., 0.047 mole) was added 400 ml. of concentrated nitric acid and five drops of concentrated hydrochloric acid. The reaction mixture was heated gently on a steam bath to effect dissolution of the metal. The resulting solution was filtered and 9.5 g. (0.094 mole) of potassium nitrate was added with stirring. The excess nitric acid was then evaporated nearly to dryness on a steam bath; the crystalline red-orange product was collected and dried over \(\text{P}_4\text{O}_{10}\) in vacuo for 24 hours. Yield, 19.8 g. (97.5%).

Preparation of tris-(o-diphenylarsinophenyl)antimony, \(\text{Sb}[\text{C}_6\text{H}_4\text{AsS}_2]_3\). To a cooled (0-5°) solution of o-lithiodiphenylarsino)benzene in 250 ml. of ethyl ether (prepared as described earlier) was added 4.56 g. (0.02 mole) of antimony...
trichloride in 50 ml. of diethyl ether over a period of 20 minutes. A yellow-orange slurry resulted. The reaction mixture was refluxed for 20 minutes, cooled, and then hydrolyzed with 100 ml. of distilled water (a dilute acid wash would be better). The mixture was filtered, and the solid was washed subsequently with water, ethanol, and ether. A white product which weighed 12.3 g. after drying over P$_4$O$_{10}$ in vacuo for 24 hours, was obtained. A sample of 1 g. was recrystallized for analysis by dissolution in 15 ml. of dichloromethane followed by filtration of the cloudy solution. The dichloromethane solution was subsequently evaporated to yield a white, crystalline product, m.p. 212-214°.

**Anal.** Calcd. for C$_{54}$H$_{42}$As$_3$Sb:

C, 62.52; H, 4.08%.

Found: C, 62.25; H, 4.19%.

Preparation of tris(3-dimethylaminopropyl)phosphine, $P(\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_3$. Employing the usual Grignard techniques, 9.0 g. of magnesium (0.37 mole) in 40 ml. of tetrahydrofuran was activated by the addition of a small amount of 1,2-dibromoethane through the reflux column. After initiation, 41.1 g. (0.338 mole) of 3-chloropropyl(dimethyl)amine in 80 ml. of tetrahydrofuran was added dropwise at such a rate to maintain reflux. The Grignard solution was refluxed for an additional 45 minutes and then filtered through glass wool under nitrogen into another reaction flask. After cooling this solution with dry ice/acetone, trimethylphosphite in 60 ml. of tetrahydrofuran was added over a
period of 40 minutes. The reaction was then allowed to warm to
room temperature with vigorous stirring. A gray, viscous product
was obtained after refluxing the mixture for 30 minutes. After
cooling the reaction mixture, hydrolysis was accomplished by
addition of an acid solution containing 67 ml. of concentrated
hydrochloric acid and 250 ml. of distilled water. Two layers
were present after hydrolysis, the aqueous layer being acidic
to litmus paper. The aqueous layer was separated and 200 ml. of
other together with 160 g. of a 25% aqueous sodium hydroxide
solution was added, with stirring, under nitrogen. The ether
layer was separated and added to ether washes of the aqueous
phase. The organic phase was then washed with 50 ml. of 25%
sodium hydroxide solution, separated, and dried over sodium
sulphate. The solvent was then flash distilled under nitrogen
and the residual liquid was heated for two hours at less than
1 mm pressure with an oil bath (pot temperature, 140°)
Rauhut (290) states that \( P(CH_2CH_2CH_2NH_2)_3 \) has a boiling point
of about 150° at less than 1 mm of pressure. A pale, straw
colored liquid remained (yield, 16.8 g., 68% of theory).

Attempts to prepare an oxide or sulfide derivative of this
ligand were unsuccessful. A reaction with excess methyliodide
was carried out under nitrogen employing ether as solvent
yielded a white precipitate.

\textbf{Anal. Calcd. for } L^4\text{MeI, } C_{19}H_{48}I_4N_3P:\n\text{C, 26.62; H, 5.64; N, 4.90%.}
\text{Calcd. for } L^3\text{MeI, } C_{18}H_{45}I_3N_3P:\n\text{C, 30.22; H, 6.34; N, 5.88%.}
\text{Found: C, 30.25; H, 6.83; N, 5.87%.
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