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DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Jeanette Riker Nappier, B.S., M.S.

* * * * *

The Ohio State University
1973

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INTRODUCTION

Since the beginning of time man has been under the influence of metal complexes containing macrocyclic ligands. They are a vital part of man himself as well as much of the living matter which surrounds him. It was not until recently, however, that man became aware of the nature of these substances. Consequently, this has become an active area of research.

The investigation of metal complexes containing macrocyclic ligands has been approached in two different manners. The first one, mainly employed by those in biology or biochemistry, involves isolation and characterization of the complexes found in nature. Chemists, on the other hand, have tended to approach the problem by synthesizing macrocyclic complexes and studying their behavior. These synthetic macrocycles may be simple copies of natural systems or they may impose the design of natural systems on those not occurring naturally.

The following is a brief discussion of the synthetic approach to the study of macrocyclic systems. Included are examples of early and recent work in this field which are intended to familiarize the reader with the basic principles of synthetic macrocycle research. Several reviews\(^1,2,3\) are recommended for a more detailed account of this area.
As early as the 1930's chemists were investigating the synthesis of metal phthalocyanines (1) which, because of their intense colors and chemical inertness, were important as pigments and dyes. Many methods have been used to prepare the phthalocyanine ligand both free and as its metal complexes. 9-Cyanobenzamide\(^4\) (2) and phthalonitrile (3)\(^5\) have been cyclized catalytically to produce free phthalocyanine. These molecules, as well as 1,3-diiminoisindoline (4) and phthalic anhydride (5)\(^6\), have been condensed in the presence of metal ions under various conditions to form metal complexes of phthalocyanine. Several review articles which give a
more detailed account of these systems are available.⁶,⁷

It was discovered later that many variations of the basic phthalocyanine ring could be achieved by including other condensable molecules in the reaction and by allowing metal ions to participate in these reactions. For instance, the reaction of 1,3-diiminoisoindoline (⁴) with 2,6-diaminopyridine in boiling butanol yields macrocycle (6),⁸ which is one of the class of hemiporphoryrazines.

By changing the conditions of this reactions, and introducing a metal ion into the reaction, macrocycle (7) is formed.⁹ The
preparation of this molecule was shown to involve a template reaction between a metal complex of 2,6-bis-(1-iminoisoindoline-3-ylidene- amino)pyridine (8) and 1,3-diiminoisoindoline (4). This reaction is

\[
\begin{array}{c}
\text{NH} \\
\text{H} \\
\text{N} \\
\text{N} \\
\text{H} \\
\text{NH}
\end{array}
\]

(8)

a good illustration of the effect produced by judicious introduction of metal ions into a particular system, since macrocycle (7) is not formed when 2,6-bis-(1-iminoisoindoline-3-ylideneamino)pyridine (8) and 1,3-diiminoisoindoline were heated without a metal ion. The product of this reaction is macrocycle (6).

The orientation influence that a metal ion exerts during the synthesis is referred to as the coordination template effect.\(^3\) The kinetic template effect refers to the steric arrangement of the reacting species and the thermodynamic template effect refers to the perturbing influence on an existing equilibrium to increase the yield of the desired product.

A great deal of the new synthetic macrocycle work is based on the use of the coordination template effect. Often molecules which do not react or react only very slowly can be induced to react
satisfactorily in the presence of a metal ion. In some systems side reactions such as linear polymerization can be greatly reduced by the inclusion of a metal ion, thereby increasing the yield of the desired macrocycle. A few examples of the role of metal ions in the new synthetic macrocyclic systems will now be discussed.

Perhaps the first of the new synthetic macrocyclic complexes was discovered when Curtis\textsuperscript{10} dissolved tris-(ethylenediamine)nickel(II) perchlorate in acetone. The color of the solution slowly changed from blue-violet to yellow. Two extremely stable isomeric macrocyclic compounds (9) and (10) were isolated from this solution as their perchlorate salts.\textsuperscript{11} Although the mechanism of this reaction is still being elucidated,\textsuperscript{2} two molecules of acetone condensed between the coordinated diamine groups giving rise to the cyclic structure.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{diagram}
\caption{Structures of macrocyclic complexes (9) and (10).}
\end{figure}

Similar reactions occur between tris(rac-1,2-diaminopropane)-nickel(II) perchlorate and tris(1,3-diaminopropane)nickel(II) perchlorate and acetone, but cyclic products are not obtained from the reaction of the bis(diamine)nickel(II) complexes with acetone. Attempts have been made to cyclize tris(ethylenediamine)nickel(II)
with aldehydes and ketones other than acetone, but the only other macrocyclic product was obtained with methyl ethyl ketone after many weeks at 100°C.2

Copper(II) complexes of macrocycles (9) and (10) can be obtained by reacting bis(ethylenediamine)copper(II) with acetone in the presence of additional ethylenediamine.12 A Co(II) complex of macrocycle (10) has also been prepared by the reaction of tris(ethylenediamine)cobalt(II) with acetone in the presence of 1,1,1-trifluoroacetone. This compound is more easily prepared by the reaction of the free macrocycle·2HClO₄ with cobalt(II) carbonate.13 The perchlorate adduct of macrocycle (10) is obtained from the reaction of the mono-hydroperchlorate of ethylenediamine and acetone.14

One of the most popular methods that has been used in the preparation of nitrogen containing macrocycles is the Schiff base reaction. This reaction involves the condensation of a primary amine with an aldehyde or ketone. Since this reaction proceeds via nucleophilic attack by the amine nitrogen on the carbonyl carbon, its efficiency is greatly enhanced by coordination of the carbonyl oxygen to a positive center such as a metal cation. This reaction can fail, however, by coordination of the amine, since association with a positive center reduces its nucleophilic character.

During an investigation of metal complexes of 2,6-diacetylpyridine and its derivatives, Curry15 discovered that the reaction
between NiCl₂, 2,6-diacetylpyridine, and 3,3'-diaminodipropylamine in a water-ethanol mixture produced a six-coordinate, tetragonal nickel(II) complex of macrocycle (11), CR, by a metal ion induced Schiff base reaction. The CR macrocycle was among the first of the new synthetic macrocycles to be studied extensively as a ligand in coordination compounds. Four, five, and six-coordinate complexes of CR were prepared with Ni(II). The structure of the five-coordinate, approximately square pyramidal Ni(CR)Br₂·H₂O shown in Figure 1 was proven by an X-ray structural determination. The crystal is composed of "macrocyclic planes" connected by NH...Br-Ni linkages. The water molecule is located between these planes and is hydrogen bonded to both bromides.

Figure 1. Structure of Ni(CR)Br₂·H₂O.
Several Co(II) compounds of the type Co(CR)X+(X = Cl, Br, I, NO₃, NCS) and Co(CR)A²⁺ (A = NH₃, py, H₂O) have been isolated.¹⁸ They are low-spin, 5-coordinate complexes and have electronic spectra similar to those of the trigonal-bipyramidal CoX(QP)+ (X = Br¹⁹, NO₃⁺). This macrocycle has also been condensed around Cu(II)³ and Zn(II).¹⁸ The copper reaction leads to the isolation of the Cu(CR)X⁺ cation, while Zn(CR)I⁺ is the product of the reaction with zinc.

The CR macrocycle has two C=N bonds as a result of the Schiff base condensation. It has been found that these imine linkages can be fairly easily reduced in complexes of CR to produce complexes of macrocycle (12), CRH. For example, the hydrogenation of Ni(CR)(ClO₄)₂ with H₂/PtO₂ results in the formation of Ni(CRH)(ClO₄)₂.²¹ Many isomers of Ni(CRH)(ClO₄)₂ are possible due to the presence of assymmetric carbon and nitrogen atoms in the ligand. The meso and racemic stereoisomers resulting from the presence of two assymmetric carbon atoms have been isolated and identified²¹ as have two of the
configurational isomers arising from the amine nitrogen atoms.\textsuperscript{22}

Treatment of \textit{Co(CR)Br}$_2$H$_2$O with sodium borohydride in the presence of an alkyl halide leads to the isolation of the cobalt(III) cation RCo(CR)Br$^+$, however.\textsuperscript{23} This reaction probably involves the production of a 5-coordinate Co(I) intermediate by sodium borohydride. This indicates the ease of reduction of the Co(II) compared with Ni(II), since the reaction of Ni(CR)(ClO$_2$)$_2$ with excess sodium borohydride gives rise to Ni(CRH)(ClO$_4$)$_2$.

Although neither CR nor CRH has been prepared in the absence of a metal ion, CRH can be removed from Ni(II) by sodium cyanide in an aqueous medium.\textsuperscript{21} The free CRH obtained in this manner has been used to prepare Co(III) complexes of the type [Co(CRH)X$_2$]ClO$_4$ (X = Cl, N$_3$, NCS, NO$_2$, and CN) and [Co(CRH)Y$_2$](ClO$_4$)$_3$ (Y = H$_2$O and $\frac{1}{2}$ en).\textsuperscript{24} These complexes are shown by electronic spectra and conductance to be six-coordinate and approximately tetragonal. \textit{Cis} and \textit{trans} isomers as well as various stereochemical configurations have been isolated and identified.

The macrocycle CR can also be oxidized\textsuperscript{3} by dissolving the complex Ni(CR)(ClO$_4$)$_2$ in concentrated nitric acid and then warming. The resultant orange solution gives a complex of the tri-imine ligand (13).
A Schiff base reaction in the presence of a metal ion has also been used to condense \( \alpha \)-aminobenzaldehyde into macrocycles (14), TRI, and (15), TAAB. \(^{25,26,27}\) Although \( \alpha \)-aminobenzaldehyde readily condenses in the presence of acid, forming a trimer (16) and a tetramer (17), among other products, no macrocycles are detected in the absence of a metal ion. \(^{28}\) Heating the trimer with nickel nitrate in ethanol, however, produces a nickel complex of TRI suggesting that macrocycle formation is a metal induced rearrangement of the trimer (14). \(^{28}\)
Both TRI and TAAB complexes are formed when α-aminobenzaldehyde is condensed in the presence of nickel(II).\textsuperscript{28,27} Condensation in the presence of Cu(II) gives only Cu(TAAB)\textsuperscript{2+},\textsuperscript{26} illustrating the stereoselectivity of Cu(II). Both square planar, [Ni(TAAB)](BF\textsubscript{4})\textsubscript{2}, and tetragonal, [Ni(TAAB)(H\textsubscript{2}O)]I, complexes of Ni(II) have been isolated with TAAB.\textsuperscript{26} Six-coordinate complexes of the type [Ni(TRI)(H\textsubscript{2}O)\textsubscript{3}](NO\textsubscript{3})\textsubscript{2} and [Ni(TRI)\textsubscript{2}](NO\textsubscript{3})\textsubscript{2}·H\textsubscript{2}O are formed with Ni(II) and TRI.\textsuperscript{27}

When α-aminobenzaldehyde is condensed in the presence of Co(II) evidence for both TRI and TAAB complexes has been found.\textsuperscript{30} Oxidation of the TRI complexes has led to the isolation of the meso and racemic forms of the Co(III) complex, [Co(TRI)\textsubscript{2}](NO\textsubscript{3})\textsubscript{3}·2H\textsubscript{2}O.

As with CR, the imino linkages in a nickel complex of TAAB can be reduced by catalytic hydrogenation over platinum oxide to give complex (18).\textsuperscript{3} The Ni(TAAB)\textsuperscript{2+} complex also reacts with ethoxide, methoxide, and hydroxide ions to produce complexes of structure (19).\textsuperscript{31} Reaction with acid converts these complexes back to Ni(TAAB)\textsuperscript{2+}. 
Attempts to reduce the imine linkages in Cu(TAAB)$^{2+}$ with H$_2$/PtO$_2$ have led to the reduction of the copper ion instead and Cu(TAAB)$^+$ can be isolated from these solutions.$^3$ The copper complex has also been prepared electrochemically as have Ni(TAAB)$^+$ and Ni(TAAB)$^0$. These complexes may also be viewed as the Cu$^{2+}$ and Ni$^{2+}$ derivatives of the aromatic TAAB$^{2-}$ ligand, an analog of phthalocyanine.

Not all of the new synthetic macrocyclic ligands contain exclusively nitrogen donors. Complexes of macrocycle (20) can be prepared by the condensation of ethylene diamine with 1,4-bis-(2-formylphenyl)-1,4-dithiabutane (21) in the presence of nickel(II).$^{33}$
A sexadentate macrocycle (22) can also be isolated as its nickel(II) or cobalt(II) complex from the reaction of 1,4-bis-(2-formylphenyl)-1,4-dithiabutane (21) and 1,2-bis-(2-aminophenylthio)ethane (23) in the presence of Ni(ClO$_4$)$_2$ or Co(ClO$_4$)$_2$. Schiff base condensations have been used to form macrocycles (22) and (23); in addition, it is possible to bridge two coordinated mercaptide groups. For instance, α,α'-dibromo-o-xylene has been reacted with 2,3-pentane-dione-bis-mercaptopoethyliminenicke(lII) (32) to give the complex Ni(PEX)$_2^+$ (24).
Reactions to bridge two mercaptide groups producing a sulfur containing macrocycle have also been used in the absence of metal ions. Rosen and Busch reacted sodium with 1,4,8,11-tetrathiaundecane to produce the dimercaptide (25); this was mixed with 1,3-dibromopropane, and \( \alpha,\alpha'-\text{dibromo-o-xylene} \) using high dilution techniques to give TTP (26) and TTX (27), respectively. Low-spin, square planar complexes of the type \([\text{Ni}(L)](\text{BF}_4)_2\) were prepared with both thioether donor macrocycles. High-spin, tetragonal complexes, \(\text{Ni}(\text{TTP})X_2\) \((X = \text{NCS, Cl, Br, I})\), have also been characterized. The free macrocycle is displaced from these nickel complexes by class A solvents such as water or ethanol.

The macrocycle (28) containing eight sulfur donors has also been isolated from the reaction of (25) with 1,3-dibromopropane.
Nickel(II) complexes with metal to ligand ratios of 2:1 and palladium and platinum complexes of 4:1 ratios have been isolated with this macrocycle.

Several macrocycles containing four sulfur atoms and fewer than 14 members in the ring have been prepared. No complexes of these macrocycles have been isolated in which all of the sulfur atoms lie in the equatorial plane of a metal ion. For instance, TTC (29) reacts

with Ni(BF$_4$)$_2$ to form the complex [Ni$_2$(TTC)$_3$](BF$_4$)$_4$ (30), in which two
of the macrocycles are folded and the third bridges the two nickel ions. It appears, therefore, that a 14-membered macrocycle is necessary to form a planar structure in this type of system.

In addition to sulfur and nitrogen donor macrocycles, several macrocycles have been prepared which contain oxygen donors. Perhaps the best known of these are the "crown" ethers prepared by Pederson. These are cyclic polyethers containing 9 to 60 atoms and including 3 to 20 oxygen atoms in the ring. They were prepared by several methods in yields of up to 80% without the use of high dilution techniques. The "crown" ethers form 1:1, 3:2, and 2:1 complexes with many of the "hard" metal ions such as the alkali and alkaline earth ions.

Whereas macrocyclic ligands containing nitrogen, sulfur, and oxygen donors have been prepared and characterized, no macrocycle containing phosphorus or arsenic can be found in the literature. The reason appears to be a lack of viable synthetic routes. No easy method, such as the Schiff base reaction, has been discovered for formation of a cyclic phosphorus or arsenic containing ligand in the presence of a metal. The literature, moreover, is almost void of any investigations of reactions of coordinated phosphines or arsines; such knowledge is needed if the coordination template effect is to be used.

One attempt to form an all phosphorus donor macrocycle using classical phosphorus synthetic chemistry in the absence of a metal
ion has been reported.\textsuperscript{39} King, et al. reacted 1,2-bis(vinylphenylphosphino)ethane with 1,2-bis(phenylphosphino)ethane, but no macrocyclic product was identified.

The problem of preparing a macrocyclic ligand containing phosphorus or arsenic can be approached from several directions. One approach is to investigate high dilution reactions which may lead to cyclic products. The free radical reaction between 1,2-bis(vinylphenylphosphino)ethane and 1,2-bis(phenylphosphino)ethane and similar free radical reactions may be tried at high dilution. The reaction between metal phosphides and dihaloalkanes could also be tried at high dilution. Macrocycle (31), for instance, may result from a high dilution reaction of the dilithium salt of 1,3-bis(phenylphosphino)propane with 1,2-dichloroethane. Experience has shown, however, that macrocycle formation in the absence of a metal ion is

![Diagram of Macrocycle (31)](image-url)
most often accomplished in only very low yields even when high
dilution techniques are used. Thus, the above reactions do not
seem especially promising at this time.

Another approach to this problem is to use the coordination
template effect to aid the formation of a macrocyclic product. The
reactions mentioned above, for example, may be performed in the
presence of metal ions in attempts to obtain cyclic ligands. The
drawback to this method, of course, is the lack of research on the
reactions of coordinated phosphines or arsines. It is unknown how
a coordinated secondary phosphine or arsine would react. A
significant breakthrough has recently appeared in this area, however.
A coordinated diphenylphosphine was treated with butyl lithium to
produce a coordinated phosphide; the latter was realkylated as shown
in the following reaction.\(^{40}\)

\[
\begin{align*}
\text{BuLi} & \quad \text{THF} \\
M(\text{CO})_5(\text{PPh}_2\text{H}) & \quad \rightarrow \\
M(\text{CO})_5(\text{PPh}_2\text{Li}) & \quad \rightarrow \\
M(\text{CO})_5(\text{PPh}_2\text{CH}_3) + \text{LiI}
\end{align*}
\]

\[
M = \text{Cr} \ (67\%) \\
M = \text{Mo} \ (52\%) \\
M = \text{W} \ (67\%)
\]

Suitable modifications of this reaction may make the synthesis of
polyphosphine macrocycles feasible.

A third method of approaching a phosphorus or arsenic
containing macrocycle involves using well developed template methods
to close the macrocyclic ligand and substituting phosphorus or arsenic
donors at the positions not critical to the closing reaction. Of
course, the macrocycle resulting from this approach will not contain
all phosphorus or arsenic donors, but will contain some sulfur or
nitrogen donors. The most critical step in an approach of this kind
becomes design of the phosphorus or arsenic containing molecule. It
must mimic the behavior of the molecule in the known reaction
sufficiently so that the closing reaction is feasible.

For example, the reaction to bridge coordinated mercaptides has
been demonstrated by the reaction of α,α'-dibromo-α-xylene with
2,3-pentanedione-bis-mercaptoethylimine nickel(II) (32) to give the

\[
\text{Ni(PEX)_{2}^{2+}}
\]

macrocyclic complex Ni(PEX)_{2}^{2+} (34). If phosphorus or arsenic atoms
could be substituted in a similarly designed system then a phos-
phorus- or arsenic-sulfur macrocycle would result. This has been
attempted in an arsenic-sulfur system. The tetradentate arsenic-
sulfur ligands 1,3-bis[phenyl(o-thiomethylphenyl)arsino]propane (C_{3})
and 1,2-bis[phenyl(o-thiomethylphenyl)arsino]ethane (C_{2}) (33) were

\[
\begin{align*}
\text{SCH} & \text{CH}_{2} \text{As(CH}_{2} \text{)}_{n} \text{As} & n = 2, C_{2} \\
\text{As} & \text{CH}_{2} \text{SCH} & n = 3, C_{3}
\end{align*}
\]
prepared. It has been established\textsuperscript{42} that a methylthioether which is coordinated to a transition metal is capable of undergoing a demethylation reaction in the presence of a suitable leaving anion to produce a coordinated mercaptide. These ligands are, therefore, capable of having the required structure for a mercaptide bridging reaction similar to that in which Ni(PEX)\textsuperscript{2+} is produced. The next requirement is that the ligands C\textsubscript{2} and C\textsubscript{3} must act as tetradentate ligands toward one metal ion. Unfortunately this requirement has not been met to date. Complexes of the type Pd(C\textsubscript{n})\textsubscript{X}\textsubscript{2} and Pd\textsubscript{2}(C\textsubscript{n})\textsubscript{2}X\textsubscript{4} in which the ligand acts as a bidentate, Pd\textsubscript{2}(C\textsubscript{n})\textsubscript{2}X\textsubscript{2}\textsuperscript{2+} in which it is a tridentate, and Pd\textsubscript{2}(C\textsubscript{n})\textsubscript{2}\textsuperscript{4+} in which it is a bridged tetradentate have all been isolated, but no successful macrocycle precursors have been found.

The importance of synthesizing a macrocyclic ligand containing phosphorus or arsenic donors is becoming increasingly clear as our knowledge of the properties of cyclic ligands and of phosphorus and arsenic chemistry increases. Experiments have shown\textsuperscript{3} that the in-plane ligand field strength is greater in macrocyclic systems than in noncyclic systems having the same donor sets. One possible reason for the increased ligand field is that the constraints of the macrocyclic ring reduce the flexibility in the resultant complex, thereby forcing the donors closer to the metal ion. Figgis\textsuperscript{43} has shown that, among other things, ligand field strength is a function of metal-donor distance.
Ligand field strength is also dependent on the type of donor involved in coordination. Since phosphines and arsines are "strong field" ligands, a macrorcyclic complex with these donors should have a higher in-plane ligand field than is known at the present time. The orbital splitting resulting from this high in-plane field would promote the formation of low-spin, 4- or 5-coordinate, planar or square pyramidal complexes with low energy filled orbitals. Such complexes may be active catalysts in a properly chosen system.
STATEMENT OF PROBLEM

The purpose of this investigation was to design and synthesize a phosphorus containing macrocyclic ligand and characterize its transition metal complexes. The coordination template effect was to be used in the synthesis, but reactions involving classical phosphorus chemistry or high dilution techniques were to be avoided in the macrocycle closing step.

Although some investigation of the reactions of coordinated phosphines was to be done, the main method of approaching this problem was to design and synthesize phosphorus containing compounds which could be cyclized via well known template reactions. The first attempt in this area was the design and preparation of 1,3-bis-(2-methylthiobenzylphenylphosphino)propane (DISPAR) (34).
This tetradeionate ligand is similar to the arsenic-sulfur tetradentates $C_2$ and $C_2$ (33) which had been prepared earlier for making an arsenic-sulfur macrocycle, but DISPAR contains longer and more flexible linkages between donor atoms. Palladium(II) complexes with DISPAR were to be prepared and cyclization reactions similar to those used for Ni(PEX)$^{2+}$ (24) were to be attempted.

Another system which was based on macrocycle formation via use of the Schiff base reaction was then to be investigated. The tridentate ligand bis(3-aminopropyl)phenylphosphine (PN$_2$) was to be prepared and condensed with 2,6-diacetylpyridine to produce 2,12-dimethyl-7-phenyl-3,11,17-triaza-7-phosphabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (PN$_3$) (35).

![Diagram of PN$_3$](image)

The macrocycle PN$_3$ is similar to the all nitrogen donor macrocycle CR (11), so similar complexes were to be prepared for a comparison of the effect of a phosphorus donor in a macrocyclic system. The results of this investigation are reported in this dissertation.
EXPERIMENTAL

A. Reagents

Standard reagent grade materials were used in the syntheses without further purification. Benzene, diethyl ether and various petroleum solvents were dried using freshly pressed sodium wire. Reagent grade acetonitrile and nitromethane were stored over molecular sieves (Linde, Baker, 4A) for at least 24 hrs prior to use. Tetrahydrofuran was dried over CaSO₄ and then distilled from LiAlH₄. Pyridine and allyl amine were distilled from sodium hydroxide. Recrystallization from a water-ethanol mixture was used to purify 2,6-diacetylpyridine. Phosphines from Pressure Chemical Company and other special reagents were used as received.

B. Physical Measurements

1. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, and M-H-W Laboratories, Garden City, Michigan.

2. Conductivity measurements were obtained on ~ 10⁻³ M solutions using an International Instruments Inc.; Model RC-16B2 conductivity bridge and a Fisher Scientific Products Co. cell (k = 0.1037). In calculating the molar conductance, corrections were made for initial solvent conductance.
3. Electronic absorption spectra were obtained using a Cary Model 14 spectrometer. Solution spectra were taken using matched 0.10 and 1.0 cm cells in spectral grade chloroform, dichloromethane, acetonitrile, or methanol. Solid state spectra were obtained as Nujol mulls suspended on filter paper both in dry air at ambient temperature (~24°C) and immersed in liquid nitrogen (77°K) in a quartz dewar.

4. Infrared spectra were obtained from 4000 to 400 cm⁻¹ on a Perkin-Elmer Model 337 grating spectrophotometer and, for more precise measurements, on a Beckman IR-9 spectrophotometer. Solid samples were run as Nujol, hexachlorobutadiene, or fluorocarbon mulls between KBr plates or as KBr pellets. Liquid samples were run "neat" between KBr plates or in 0.1 mm KBr cells.

5. Magnetic susceptibility determinations were performed on a Faraday balance assembled in this laboratory. The primary parts of this balance are a Cahn #2000 RG Electrobalance equipped with a Sargent Model-SR millivolt recorder and a Varian V-4004 four inch electromagnet system. The operation of this system has been previously described. Diagnomagnetic corrections for the complexes were made using standard values. The following Pascal constants were calculated for the ligands reported in this work: PN₂, -167.2 10⁻⁶ cgsu mole⁻¹; PN₃, -227.4 10⁻⁶ cgsu mole⁻¹; PN₃H, -289.7 cgsu mole⁻¹.

6. Mass spectral data were obtained by Mr. Richard Weisenberger with an AEI MS-902 mass spectrometer operating at ca. 8 or 70 ev.
Heptacosfluorotributylamine was used as an internal standard.

7. Proton magnetic resonance spectra were taken on Varian Associates A-60, A-60A, HA-100, and Jeol MH-100 spectrophotometers. The chemical shift values are reported in \( \tau \) relative to TMS as an internal standard.

8. Melting points were determined using a hot stage microscope and are reported uncorrected as degrees Centigrade (°C).

C. General Experimental Procedures

The phosphines used in this study are, for the most part, air sensitive and of undetermined, but assumed high toxicity. Many of the organic compounds reported here which contain sulfur were found to be powerful skin irritants. Caution is, therefore, advised in the use of these compounds.

Standard inert atmosphere techniques\textsuperscript{46} were followed throughout this study. Nitrogen, deoxygenated and dried by passing through a hydrogen reduced, copper oxide column (BTS catalyst, manufactured by Badische-Aniline und Soda-Fabrik), followed by a \( \text{P}_2\text{O}_{10} \) column was used to carefully flush all equipment prior to use. All solvents were routinely degassed by refluxing under nitrogen or purging with bubbling nitrogen.
D. Preparation of 1,3-Bis(2-methylthiobenzylphenylphosphino)propane (DISPAR)

1. Methyl o-(methylthio)benzoate

\[
\begin{align*}
\text{COH} & \quad \xrightarrow{\text{MeOH, H}^+} \quad \text{COCH}_3 \\
\text{SH} & \quad \xrightarrow{\text{OCH}_3} \\
\text{CH}_3-C & \quad \xrightarrow{\text{CH}_3} \\
& \quad \xrightarrow{\text{OCH}_3}
\end{align*}
\]

To a solution of 100g (0.652 mol) of o-mercaptobenzoic acid in 500 ml of methanol, which had been acidified with 1 ml of concentrated hydrochloric acid, was added 173.2g (1.304 mol) of 2,2-dimethoxypropane. The resulting solution was refluxed for 60 hrs before removing all but 100 ml of solvent by distillation. The resulting brown solution was made basic with about 100 ml of aqueous sodium hydroxide. Then 184g (1.304 mol) of methyl iodide was added and the reaction was allowed to proceed at room temperature until the VPC indicated that all of the \( \text{C}_6\text{H}_4(\text{COCH}_3)\text{SH} \) had reacted, about 3 hrs. A brown oil separated during the reaction. The reaction mixture was then heated, causing the brown oil to dissolve. On cooling white, needle-like crystals precipitated from the reaction mixture. Yield of methyl o-(methylthio)benzoate, 36.5g (31.7%). M. pt., 65°C.\(^{47}\)
2. 2-Methylthiobenzyl alcohol

\[
\begin{align*}
\text{CH}_3&\text{CO}_\text{OCH}_3 \quad \text{LiAlH}_4 \quad \text{CH}_2\text{OH} \\
\text{SCH}_3 & \quad \text{SCH}_3 \\
\end{align*}
\]

To a suspension of 13.6 g (0.358 mol) of lithium aluminum hydride in 350 ml of ether was added slowly a solution of 33 g (0.214 mol) of methyl o-(methylthio)benzoate in 300 ml of ether. The resulting mixture was refluxed for 11 hrs. It was then hydrolyzed slowly with 35 ml of water. The inorganic salts were removed by filtration, leaving an ether solution of the product. The ether was removed by evaporation and the product was vacuum distilled ( b. pt., 100°C/0.3 torr). Yield of 2-methylthiobenzyl alcohol, 23.8 g (72%).

3. 2-Methylthiobenzyl chloride

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{SOCl}_2 \quad \text{CH}_2\text{Cl} \\
\text{SCH}_3 & \quad \text{SCH}_3 \\
\end{align*}
\]

A solution of 23.8 g (0.154 mol) of 2-methylthiobenzyl alcohol and 24 ml (0.298 mol) of pyridine in 50 ml of benzene was added to a solution of 20.2 ml (0.280 mol) of thionyl chloride in 200 ml of benzene. The resulting light orange solution was refluxed for 1 hr. An orange oil separated during the reflux period and on cooling it solidified. The reaction mixture was hydrolyzed with 50 ml of water.
causing the orange solid to dissolve. The organic layer was separated from the water layer and the solvents were removed from it. The orange liquid which remained was vacuum distilled (b. pt., 76°C/0.3 torr). Yield of 2-methylthiobenzyl chloride, 16.2 g (61%).

Caution: The compound 2-methylthiobenzyl chloride is very irritating to the skin.

4. 1,3-Bis(phenylphosphino)propane

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

To a solution of 106 g (0.963 mol) of phenylphosphine in 600 ml of dry benzene was added 10 g (0.246 mol) of potassium. The reaction mixture was heated to reflux causing an orange solid to begin appearing. The reaction mixture was then refluxed for 7½ hrs during which time the solid turned from orange to yellow. The solvents were removed through a frit attached to the bottom of the flask. The yellow potassium phenylphosphide which remained was washed with 100 ml of benzene.

The potassium phenylphosphide was combined with 500 ml of benzene and the mixture was brought to reflux. The heating was discontinued and 13 g (0.0643 mol) of 1,3-dibromopropane was allowed to drop into the reaction mixture over a one hr period. The heat of
reaction caused the reaction mixture to continue refluxing. After
the addition was completed, the reaction mixture was refluxed for
6 hrs, causing the solid to become pale yellow. The reaction mixture
was cooled and the liquid phase was separated from the pale yellow
solid by filtration. The benzene and a small amount of phenylphos-
phine were removed from the product by distillation. The product, a
colorless liquid, was then vacuum distilled (b. pt., 167°/0.5 torr).

The pale yellow solid which remained after the liquid phase
was removed was combined with 500 ml of benzene; the mixture was
then brought to reflux and the heat was removed. Small amounts of
1,3-dibromopropane were added to the reaction mixture until the
solid just turned white; about 4 g (0.02 mol) of 1,3-dibromopropane
were required. The resulting mixture was refluxed for 3 hrs, cooled
and then the liquid phase was separated by filtration. The benzene
and phenylphosphine were removed by distillation and the product was
vacuum distilled. Total yield of 1,3-bis(phenylphosphino)propane,
19.3 g (60%).

5. 1,3-Bis(2-methylthiobenzylphenylphosphino)propane (DISPAR)
A solution of 12.8g (0.0474 mol) of 1,3-bis(phenylphosphino)-
propane in 100 ml of dry ether was cooled to 0°C. A 72 ml (0.115
mol) portion of n-butyl lithium in hexane was slowly added to the
resulting solution. A yellow color developed and deepened as the
solution was warmed to room temperature and stirred for one hr. Then
16.2g (0.0942 mol) of 2-methylthiobenzyl chloride in 100 ml of ether
was slowly added. The solution became dark yellow and a yellow-orange
precipitate appeared. The reaction mixture was stirred at room
temperature for 45 min and then refluxed for one hr. The color
darkened during the reflux period. The mixture was cooled and then
hydrolyzed with a mixture of 70 ml of saturated aqueous ammonium
chloride and 12 ml of 1 M HCl. After hydrolysis there remained a
cloudy white ether layer, a clear water layer, and a yellow solid.
The ether and water layers were removed from the reaction flask and
separated from one another. The yellow solid was washed from the
reaction flask with benzene, in which it was soluble, but it has
not been further characterized. The solvents were removed from the
ether layer in vacuo, leaving a cream colored oil. The oil was
dissolved in benzene and run through a Grade III alumina column under
nitrogen. The solvents were pumped from the eluted benzene solution
leaving a cream colored oil. Yield of DISPAR, 11.5g (46%).

A stock solution of the product was prepared by combining it
with enough dry benzene to give 100 ml of solution (4.63 ml/mole).
A crystal of benzophenone was added to the stock solution to inhibit
free radical oxidation of the ligand.
Attempts to prepare a methyl iodide or benzyl bromide derivative of the oil by refluxing these reagents with the product in acetone resulted in oils which were not further characterized.

E. Preparation of palladium complexes of DISPAR

1. Pd₂(DISPAR)Cl₄

To a warm, filtered solution containing 0.21g (1 mmol) of PdCl₂ and 0.08g (2 mmol) of LiCl in 10 ml of ethanol was added 4.6 ml (1 mmol) of a benzene solution of DISPAR. A yellow precipitate formed immediately and was isolated by filtration. It was recrystallized from a dichloromethane-ethanol solution and dried in vacuo.

Anal. Calcd. for C₃₁H₃₄Cl₄P₂Pd₄S₂: C, 41.96; H, 3.86; Cl, 15.98  
   Found: C, 42.06; H, 4.12; Cl, 15.79.

2. Pd₂(DISPAR)Br₄

To 20 ml of a filtered solution containing 0.42g (2 mmol) of PdCl₂, 0.16g (4 mmol) of LiCl, and 0.70g (8 mmol) of LiBr in ethanol was added 1 mmol of DISPAR in benzene. An orange precipitate resulted immediately and it was isolated by filtration. The product was dissolved in a dichloromethane-ethanol solution and the dichloromethane was slowly removed, causing an orange solid to form. The solid was isolated by filtration and dried in vacuo over P₄O₁₀ at 100°C.

Anal. Calcd. for C₃₁H₃₄Br₄P₂Pd₄S₂: C, 38.83; H, 3.57; Br, 33.34  
   Found: C, 37.14; H, 3.85; Br, 31.15.
3. \( \text{Pd}_2(\text{DISPAR})\text{I}_4 \)

A solution of 0.21 g (1 mmol) of \( \text{PdCl}_2 \) and 0.08 g (2 mmol) of \( \text{LiCl} \) in 10 ml of ethanol was stirred with 0.665 g (5 mmol) of \( \text{LiI} \) for 20 min and then filtered. A 1 mmol portion of a benzene solution of DISPAR was added, causing a dark red oil to separate. The solvents were removed from the solution and the oil which remained was dissolved in dichloromethane. A dark red precipitate was obtained on the addition of hexane to this solution. This solid was isolated by filtration and vacuum dried.

\textbf{Anal.} Calcd. for \( \text{C}_{33}\text{H}_{34}\text{I}_4\text{P}_2\text{Pd}_2\text{S}_2 \): C, 29.71; H, 2.74; I, 40.98.

\text{Found: C, 28.31; H, 2.64; I, 41.98.}

4. \( \text{Pd}_2(\text{DISPAR})(\text{SCN})_4 \)

A solution of 0.21 g (1 mmol) of \( \text{PdCl}_2 \) and 0.08 g (2 mmol) of \( \text{LiCl} \) in 10 ml of ethanol was warmed and stirred with 0.41 g (5 mmol) of \( \text{NaSCN} \). The resulting solution was filtered into 9.2 ml (2 mmol) of a benzene solution of DISPAR. The solvents were removed from the resultant orange solution to give an orange solid. The solid was dissolved in hot ethanol and precipitated on cooling this solution. The orange solid was isolated by filtration, recrystallized from an ethanol-dichloromethane solution, and dried in vacuo.

\textbf{Anal.} Calcd. for \( \text{C}_{33}\text{H}_{34}\text{N}_2\text{P}_2\text{Pd}_2\text{S}_2 \): C, 46.00; H, 3.98; S, 14.88.

\text{Found: C, 46.07; H, 3.90; S, 14.94.}
5. Attempted preparation of \([\text{Pd(DISPAR)}]_2(\text{BF}_4)\_2\)

A solution of 1 g of NOBF\(_4\) in 50 ml of acetonitrile was stirred with 1 g of finely divided palladium metal at 100 torr for 12 hrs. The excess palladium was removed by filtration giving a yellow solution of Pd(BF\(_4\))\(_2\) in acetonitrile.

A 10 ml portion of this solution was treated with 1 mmol of DISPAR. The solution turned from yellow to orange as the DISPAR was added. The solvents were removed on a rotary evaporator leaving an orange oil. The orange oil was dissolved in nitromethane and the resulting solution was allowed to evaporate slowly, resulting in a brown oil. The oil was pumped to dryness and then stirred with ether, producing a brown, hygroscopic solid. The solid was isolated by filtration and dried in vacuo. Warming this compound in reducing solvents such as alcohols or DMF produces palladium metal.

F. Attempted preparation of nickel(II) complexes of DISPAR

Many attempts were made to obtain nickel(II) complexes of DISPAR. Solutions of NiX\(_2\)·xH\(_2\)O (X = Cl, Br, I, BF\(_4\), PF\(_6\), and ClO\(_4\)) in alcohols, DMF, dehydrating solvents such as 2,2-dimethoxypropane and acetic anhydride, and Ni(glyme)Br\(_2\) in THF were added in a 1:1 ratio to benzene stock solutions of DISPAR. The resulting solutions ranged in color from red or brown to green, depending on solvent and concentration; however, no characterizable solid product could be isolated from any of these solutions.
G. Preparation of 3-mercaptopropylphenylphosphine

\[
\text{PhPH}_2 + \text{BuLi} \rightarrow \text{PhPHLi} + \text{BuH}
\]

To a 12.5 g (0.114 mol) portion of phenylphosphine in 400 ml of dry petroleum ether was added 1.47 ml (0.227 mol) of 1.6 M BuLi in hexane, causing a yellow precipitate to form immediately. The mixture was refluxed for one hr and then cooled to room temperature. The solvents were removed by filtration through a frit in the bottom of the Grignard flask and the yellow solid Li₂PPh was washed with 100 ml of petroleum ether. A 400-ml portion of dry ether was then added to the precipitate, followed by 12.5 g (0.114 mol) of phenylphosphine. A yellow solution of lithium phenylphosphide was produced via an exothermic reaction. After stirring the solution for 15 min, 11.1 ml (0.227 mol) of trimethylene sulfide was added, causing a light yellow precipitate to separate. The mixture was refluxed for 7 hrs, allowed to cool, and stored under nitrogen overnight. It was then hydrolyzed with 19.6 ml of concentrated HCl and 50 ml of water. The water layer was removed and then the ether layer was washed with 50 ml of water and dried over CaSO₄. The CaSO₄ was separated and the ether was removed to give a colorless liquid. This product was vacuum distilled and the fraction which
boils at 131°C/3 torr was collected. Yield of 3-mercaptopropylphenylphosphine, 28g (67%).

H. Reaction of HPhP(CH₂)₃SH with Ni(glyme)Br₂

To a solution of 0.60g (2 mmol) of Ni(glyme)Br₂ in 25 ml of freshly distilled THF was added 0.74g (4 mmol) of HPhP(CH₂)₃SH. The solution immediately became red and after removal of some of the THF under a stream of nitrogen, a red crystalline product precipitated from solution. It was isolated by filtration, washed with ether, and dried in vacuo.

A 0.2g sample of the red crystalline product obtained in the above reaction was mixed with 4 ml of allyl bromide and a small amount of azobisisobutynitrile. The reaction mixture was heated (bath temp. 110°C) for 8 hrs, resulting in a green oil. The oil was dried in vacuo for 12 hrs. An identical green oil is obtained when 1 ml of dry toluene is included in the reaction mixture.

I. Reaction of HPhP(CH₂)₃SH with palladium(II)

1. Li₂PdBr₄ + HPhP(CH₂)₃SH

A solution of 2 mmol of Li₂PdCl₄ and 0.70g (8 mmol) of LiBr in 20 ml of ethanol was warmed for ½ hr and then filtered. To the resulting solution was added 0.37g (2 mmol) of HPhP(CH₂)₃SH, causing an orange precipitate to form. The precipitate was isolated by filtration, recrystallized from a dichloromethane-ethanol solution, and dried under vacuum.
Anal. Calcd. for C_{18}H_{24}Br_2P_2Pd_2S_2: C, 29.17; H, 3.18; Br, 21.57.

\[ \text{[Pd(PhHP(CH_2)_3S)Br]_2} \]

Found: C, 25.45; H, 2.99; Br, 24.49.

2. Li_2PdCl_4 + HPhP(CH_2)_3SH

To a warm, filtered solution of 2 mmol of Li_2PdCl_4 in 20 ml of ethanol was added 0.37 g (2 mmol) of HPhP(CH_2)_3SH. An orange precipitate formed immediately. The solution was cooled and the precipitate was isolated by filtration and dried in vacuo. Due to its virtual insolubility in common organic solvents this compound has not been further characterized.

3. Attempted preparation of Pd(HPhP(CH_2)_3S)_2

To a deaerated solution of 0.29 g (1 mmol) of Na_2PdCl_4 in 10 ml of ethanol was added 0.37 g (2 mmol) of HPhP(CH_2)_3SH. An orange precipitate formed immediately but dissolved as the addition was completed. The solution was filtered and the solvents were removed under nitrogen. The orange oil which remained was induced to solidify by stirring it with diethyl ether. A crystalline compound was obtained by dissolving the orange powder in nitromethane and then allowing the nitromethane to slowly evaporate.

4. 2HPhP(CH_2)_3SH + Cl(CH_2)_3Cl + Na_2PdCl_4

A mixture of 0.74 g (4 mmol) of HPhP(CH_2)_3SH, 0.12 ml (2 mmol) of 1,3-dichloropropane and 0.58 g (2 mmol) of Na_2PdCl_4 in 50 ml of deaerated chloroform was prepared. This mixture was stirred overnight, refluxed five hours, and filtered. An orange solid was
isolated by evaporation of the solvents from the resultant orange solution. The nmr and electronic spectra of the solid compound are identical to the compound in 3., which is believed to be Pd(HPPh(CH₂)₃S)₂.

J. Preparation of 3-methylthiopropylphenylphosphine

\[
K + \text{PhPH}_2 \rightarrow KPPhH
\]

\[
KPPhH + \begin{array}{c}
\text{S} \\
\downarrow
\end{array} \xrightarrow{\text{CH₃I}} \text{HPPh(CH₂)₃SCH₃}
\]

To a solution of 4.5 ml (45 mmol) of phenylphosphine in 150 ml of dry, deaerated benzene was added 0.53g (13.5 mmol) of potassium which had been cut into small pieces. The resulting mixture was brought to reflux in a special Grignard flask causing an orange precipitate to form. This mixture was refluxed for a total of 17 hrs during which time the solid changed in color from orange to bright yellow. Then 0.87 ml (12.1 mmol) of trimethylene sulfide was added to the reaction mixture. The resulting mixture was refluxed for 3 hrs causing the solid to change from bright to pale yellow. A 0.75 ml (12.1 mmol) portion of methyl iodide was then added to the refluxing mixture. The yellow precipitate disappeared and a white one immediately replaced it. The resulting mixture was refluxed for 15 min and then cooled to room temperature. The white solid was separated from the colorless solution by filtration through a frit in
in the bottom of the Grignard flask. The solvents were removed from this solution in vacuo leaving a colorless liquid. It was vacuum distilled and the fraction boiling at 119°C/1.5 torr was collected. Yield of 3-methylthiopropylphenylphosphine, 1.2g (50%).

K. Attempted preparation of 1,2-bis(3-mercaptopropylphenylphosphino)ethane

\[
\text{HPhP(CH}_2\text{)}_2\text{PPhH} + \text{BuLi} \rightarrow \text{LiPhP(CH}_2\text{)}_2\text{PPhLi}
\]

\[
\text{LiPhP(CH}_2\text{)}_2\text{PPhLi} + 2 \text{S} \rightarrow \text{EtOH}
\]

To a solution of 5g (20.3 mmol) of HPhP(CH\(_2\))\(_2\)PPhH in 120 ml of dry, deaerated ether was slowly added 25.4 ml (40.6 mmol) of 1.6M BuLi in hexane. The resulting yellowish-brown solution was refluxed for two hrs. A 3g (40.6 mmol) portion of trimethylene sulfide in 20 ml of ether was then added to the solution causing a yellow precipitate to form in an exothermic reaction. The solvents were then removed through a frit in the bottom of the Grignard flask. A 100 ml portion of deaerated, anhydrous ethanol was then added to the yellow solid to give a colorless solution.

An attempt was made to isolate this compound as its palladium(II) complex by combining the above solution with 10 mmol of Li\(_2\)PdCl\(_4\) in 100 ml of ethanol. The product of this reaction is an oily, very insoluble, dark brown material. It is apparently
polymeric and has not been further characterized.

In another attempt to prepare a metal complex of the product of this reaction, Ni(glyme)Br$_2$ in THF was added to the ethanol solution resulting from this reaction. A red solution and a dark red intractable oil resulted. An IR of the red oil indicated that it was contaminated with ionic OH$^-$. An attempted purification by column chromatography on florisil was made. At least three distinct fractions were isolated with benzene, acetone, and ethanol elution, respectively. The NMR and infrared spectra of these fractions are so similar that they appear to be different stages of polymerization. No solid product could be obtained from either of the three fractions.

The reaction between LiPhP(CH$_2$)$_2$PPhLi and trimethylene sulfide was attempted once again using p-dioxane as the solvent. In this reaction a yellow p-dioxane adduct of LiPhP(CH$_2$)$_2$PPhLi precipitates after the addition of butyl lithium to HPhP(CH$_2$)$_2$PPhH. This mixture was refluxed for 2 hrs before the addition of 2 equivalents of trimethylene sulfide. The yellow precipitate dissolved during the addition of trimethylene sulfide giving a pale yellow solution, which was refluxed for 5 hrs. In contrast to ether, the product of the reaction with trimethylene sulfide appears to be soluble in p-dioxane.

An attempt was made to isolate a nickel derivative of the product in the p-dioxane; although a reaction does occur with nickel tetrafluoroborate, only a tarry substance was isolated. The
p-dioxane solution was reacted with benzyl bromide also, but no characterizable product could be isolated from this reaction. An attempt to make a sulfide derivative of the product of the benzyl bromide reaction also failed to yield a characterizable product.

**Caution:** Contact of any of the above solutions with the author's skin produced itchy blisters.

**L. Preparation of bis(3-aminopropyl)phenylphosphine (PN₂)**

\[
\text{PhPH}_2 + \text{CH}_2=\text{CH}-\text{CH}_2\text{NH}_2 \xrightarrow{\text{ATBN}} \text{PhP}((\text{CH}_2)_3\text{NH}_2)_2
\]

A 5g (0.0454 mmol) portion of phenylphosphine was combined with 8 ml (0.0908 mol) of allylamine and 0.2g of azobisisobutyril-nitrile. The mixture was slowly heated to 140°C and held there for 10 hrs. After cooling the solution the volatile materials were removed in vacuo. The remaining colorless liquid was vacuum distilled and the fraction obtained at 125°C/0.65 torr was collected. Yield of PN₂, 9g (82%).

**M. Preparation of [Ni(PN₂)Cl]PF₆**

To a deaerated solution of 0.24 g (1 mmol) of NiCl₂·6H₂O in 20 ml of ethanol was added 0.25 ml (1 mmol) of PN₂. The resulting red-orange solution was stirred for ½ hr and then heated. An ethanol solution of excess NH₄PF₆ was then added and about half of the solvents were removed. A red-orange, crystalline precipitate was
obtained on cooling. It was isolated by filtration and dried
in vacuo over P₄O₁₀.

Anal. Calcd. for C₁₂H₂₁ClF₆N₂NiP₂: C, 31.10; H, 4.57; Cl, 7.65.
  Found:  C, 30.92; H, 4.70; Cl, 7.43.

N. Preparation of nickel(II) complexes of 2,12-dimethyl-7-phenyl-
3,11,17-triaza-7-phosphabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-
pentaene (PN₃)

1. [Ni(PN₃)Cl]PF₆

A solution of 0.24 g (1 mmol) of NiCl₂·6H₂O and 0.185 g (1 mmol)
of NaPF₆·H₂O in 20 ml of ethanol was stirred for 15 min and then
filtered. The resulting solution was deaerated and 0.16 g (1 mmol) of
2,6-diacetylpyridine was added. After stirring for 15 min the
solution was heated and 0.25 ml (1 mmol) of PN₂ was introduced. The
resulting purple solution was refluxed for 1 hr and then cooled. The
purple crystalline product, which had precipitated out of the
solution, was collected. It was recrystallized from an acetone-ethanol
mixture and dried in vacuo over P₄O₁₀ at 100°C overnight.

Anal. Calcd. for C₂₁H₂₆ClF₆N₃NiP₂: C, 42.71; H, 4.44; Cl, 6.00.
  Found:  C, 42.47; H, 4.25; Cl, 6.22.

2. [Ni(PN₃)Br](PF₆)

A solution of 0.27 g (1 mmol) of NiBr₂·3H₂O and 0.16 g (1 mmol)
of 2,6-diacetylpyridine was stirred for ½ hr. To this was added
0.25 ml (1 mmol) of PN₂ causing an immediate color change from light
green to purple. The purple solution was refluxed for 1.5 hrs, filtered, and reheated. A warm ethanol solution containing excess NH₄PF₆ was added. As the solution cooled a slow precipitation of purple crystals occurred. They were isolated by filtration, recrystallized from an acetone-ethanol solution, and dried in vacuo over P₄O₁₀ at 100°C.


3. [Ni(PN₃)I]PF₆

To a solution of 0.29 g (p mmol) of Ni(NO₃)₂·6H₂O in 20 ml of ethanol was added excess sodium iodide causing an immediate color change from green to yellow. The solution was stirred for 10 min and then filtered. A 0.16 g (1 mmol) sample of 2,6-diacetylpypyridine was added and the resulting solution was stirred for 1.5 hr. Then 0.25 ml (1 mmol) of PN₂ was added causing the solution to turn purple immediately. The purple solution was refluxed for 2 hrs and then filtered into an ethanol solution of excess NH₄PF₆. The volume of solvent was reduced and, on cooling, a purple crystalline product appeared. It was isolated by filtration, recrystallized from an acetone-ethanol mixture, and dried in vacuo over P₄O₁₀ at 100°C.

4. **[Ni(PN₃)](PF₆)₂**

An acetone-ethanol solution of [Ni(PN₃)Cl]PF₆ was warmed in the presence of excess NH₄PF₆. Evaporation of some of the acetone gave a brown crystalline solid. The solid was isolated by filtration, recrystallized from an acetone-ethanol solution, and dried in vacuo over P₄O₁₀ at 100°C.

**Anal. Calcd.** for C₂₁H₂₆F₁₂Ni₃P₃: C, 36.02; H, 3.74; P, 13.27.

**Found:** C, 35.92; H, 3.73; P, 13.03.

---

0. Attempted preparation of cobalt(II) and (III) complexes of 2,12-dimethyl-7-phenyl-3,11,17-triaza-7-phosphabicyclo[11.3.1]-heptadeca-1(17),2,11,13,15-pentaene (PN₃)

1. Attempted preparation of [Co(PN₃)Cl]PF₆

A solution of 0.24g (1 mmol) of CoCl₂·6H₂O and 0.185g (1 mmol) of NaPF₆·H₂O in 20 ml of ethanol was stirred for 15 min and then filtered. A 0.16g (1 mmol) portion of 2,6-diacetylpypyridine was added to the filtrate and the resulting solution was stirred for 15 min. A 0.25 ml (1 mmol) sample of PN₂ was then introduced causing a red solution and precipitate to form immediately. This mixture was refluxed for 1 hr during which time it turned green. The mixture was cooled and a dark green solid was isolated by filtration, washed with ethanol and ether, and dried in vacuo.

**Anal. Calcd.** for C₂₁H₂₆ClCoF₆N₃P₂: C, 42.69; H, 4.44; Cl, 6.00.

[Co(PN₃)Cl](PF₆)
2. Attempted preparation of $[\text{Co}(\text{PN}_3)\text{Br}_2]\text{Br}$

Two different methods to prepare this compound have been tried. The first attempt began with the preparation of a solution of 0.22 g (1 mmol) of CoBr$_2$ and 0.16 g (1 mmol) of 2,6-diacylpyridine in 35 ml of ethanol and 15 ml of methanol. This solution was warmed and 0.25 ml (1 mmol) of PN$_2$ was added causing the solution to become red. After a 1 hr reflux period the solution had become green. Then a few drops of aqueous HBr and excess LiBr were added and air was bubbled through the resulting warm solution for 45 min. The solution was then allowed to cool and a red crystalline precipitate appeared. It was isolated by filtration, washed with ethanol, and dried in vacuo.

The second attempt, which was done in pure ethanol, was carried out in the same manner as the first attempt except a few drops of bromine were added as the oxidizing agent instead of using air. The product was a red-brown solid, which was isolated by filtration, washed with ethanol and ether, dried in vacuo and analyzed for C, H, and Br.

$\text{Anal. Calcd. for } C_{21}H_{26}Br_3CoN_3P: \ C, 38.94; \ H, 4.05; \ Br, 36.64.$

$\text{Found: } C, 32.52; \ H, 3.87; \ Br, 40.07.$
Preparation of nickel(II) complexes of 2,12-dimethyl-7-phenyl-3,11,17-triaza-7-phosphabicyclo[11.3.1]heptadeca-1(17),13,15-triene (PN₃H)

1. \([\text{Ni}(\text{PN₃H})](\text{PF₆})₂\) produced by reduction with \(\text{NaBH}_4\)

A solution of 0.48 g (2 mmol) of \(\text{NiCl}_2·6\text{H}_2\text{O}\) and 0.32 g (2 mmol) of 2,6-diacetylpyridine in 25 ml of ethanol was stirred for \(\frac{1}{2}\) hr. To this was added 0.50 ml (2 mmol) of \(\text{PN}_2\). The resulting red solution was refluxed for 2 hrs and then cooled. An ethanol solution of excess \(\text{NaBH}_4\) was added slowly with stirring. The resulting black mixture was stirred overnight and then filtered. To the filtrate was added an ethanol solution of excess \(\text{Ni}_4\text{PF}_6\). The resulting dark solution was heated under a nitrogen steam causing some of the solvents to evaporate. As the volume of solution was reduced, a yellow precipitate came out of solution. It was isolated by filtration and recrystallized from an acetone-ethanol mixture. The infrared spectrum of the freshly recrystallized material indicates that acetone is still present. Drying in vacuo over \(\text{P}_4\text{O}_{10}\) at 100°C for 48 hrs or longer is required to remove this acetone.

**Anal. Calcd.** for \(\text{C}_{21}\text{H}_{30}\text{F}_{12}\text{N}_3\text{NiP}_3\): C, 35.82; H, 4.29; P, 13.20.

**Found:** C, 35.76; H, 4.14; P, 12.98.

2. \([\text{Ni}(\text{PN₃H})I](\text{PF₆})₂\)

An excess of an ethanol solution of sodium iodide was added to a solution of 0.5 g of the yellow form of \([\text{Ni}(\text{PN₃H})](\text{PF₆})₂\) in 10 ml
of an acetone-ethanol solution. The acetone was removed by a stream of nitrogen causing rose colored crystals to form. They were recrystallized from an acetone-ethanol mixture, and dried in vacuo over P₄O₁₀ at 100°C.

**Anal. Calcd. for C₂₁H₃₀F₆IN₃NiP₂:**
C, 36.74; H, 4.41; I, 18.50.

**Found:** C, 36.86; H, 4.67; I, 18.41.

3. **[Ni(PN₃H)](PF₆)₂ produced by reduction with H₂/PtO₂**

Forty ml of a saturated solution of [Ni(PN₃Cl)](PF₆) in acetone was stirred with a small amount of activated charcoal and then filtered. This was combined with 0.1g of PtO₂ catalyst in a Parr bomb. The solution was stirred under 80 psi of H₂ for 4 hrs causing it to change in color from purple to dark brown. The solution was then filtered and an ethanol solution containing excess NH₄PF₆ was added. The resulting solution was filtered again and allowed to set for three days. During this time red-brown crystals formed. They were isolated by filtration, washed with ethanol, and dried in vacuo.

Q. **Attempted preparation of [Rh(PN₃H)](PF₆)**

In order to determine if an interaction between Rh(I) and 2,6-diaceetylpyridine suitable for condensing PN₃ occurs, a solution of 0.25 mmol of Rh(COD)Cl₂ in dichloromethane was added to an ethanol solution of 1 mmol of 2,6-diaceetylpyridine. The resulting yellow solution was stirred for 10 min and then the dichloromethane was blown off under a nitrogen stream. The only material recovered by
this method was Rh(COD)Cl₂, which was identified by nmr and infrared spectra.

In an attempt to prepare a Rh(I) complex with PN₃H, a benzene solution of this macrocycle, which was prepared in a manner analogous to that used for the preparation of (S)PN₃H (see below), was added to a benzene solution of [Rh(COD)Cl]₂. An approximate 1:1 stoichiometry was used. No color change occurred on mixing the two solutions, but the resulting solution became red on heating and a red oil separated. Enough ethanol was added to dissolve the oil and the resulting solution was filtered. An ethanol solution of NH₄PF₆ was then added causing the solution to become yellow. Some of the solvents were removed under a stream of nitrogen until a yellow precipitate appeared. The solid was isolated by filtration, recrystallized from an ethanol-benzene mixture, and dried in vacuo over P₄O₁₀ at 100°C.

R. Preparation of [Ni(PN₃H)OH]CN

A 0.5g (0.72 mmol) portion of [Ni(PN₃H)](PF₆)₂ was reacted with 0.25g (5 mmol) of NaCN in 25 ml of water. The mixture was refluxed for 10 min producing an orange precipitate. The solid was isolated by filtration and dried in vacuo at 100°C overnight.


Found: C, 57.82; H, 6.79; N, 11.73.
S. Preparation of (S)PN$_3$H

When the above reaction mixture was allowed to reflux for 2$\frac{1}{2}$ hrs the orange precipitate dissolved giving a yellow aqueous solution. A warm, deaerated solution of 0.32 g (10 mmol) of sulfur in 20 ml of benzene was added to the aqueous solution. The resulting mixture was stirred for 10 min and the layers were separated. Evaporation of the benzene gave a mixture of the desired product and sulfur. This solid mixture was extracted with ether. Slow evaporation of the ether produced off-white crystals of (S)PN$_3$H. A mass spectrum of this material has a parent ion peak at m/e = 387. The only peaks higher than this represent the addition of one and two hydrogens, respectively.

T. Preparation of bis(3-oxobutyl)phenylphosphine

\[
\begin{align*}
\text{PhPH}_2 & \quad \text{CH}_3\text{CCH}=&\text{CH}_2 & \quad \text{AIBN} & \quad \text{PhP}((\text{CH}_2)_2\text{CCH}_3)_2 \\
\end{align*}
\]

A 1.1g (10 mmol) portion of phenylphosphine and a small amount of azobisisobutylnitrile were placed in a 50-ml, 3-necked flask. It was lowered into an oil bath which had been heated to 110$^\circ$C. Immediately a 1.4g (10 mmol) portion of vinyl methyl ketone was added through a serum stopper in the flask. The reaction mixture was maintained at 110$^\circ$C for 10 min and was then allowed to cool to room temperature. It was stored under vacuum for 24 hrs, leaving an oily solid. Yield of bis(3-oxobutyl)phenylphosphine, 1.5g (60%).
U. Reaction of bis(3-oxobutyl)phenylphosphine with aniline

A 0.5 g (2 mmol) portion of bis(3-oxobutyl)phenylphosphine was warmed and stirred with 0.36 g (4 mmol) of aniline. The volatile materials were removed in vacuo at 100°C. The product of this reaction was a heavy oil.
RESULTS AND DISCUSSION

A. Attempts to Obtain a Phosphorus Containing Macrocycle

1. a. The Phosphorus-Sulfur Donor Tetradequate Ligand,

\[ \text{1,3-Bis(2-methylthiobenzylphenylphosphino)propane,} \]

DISPAR

The initial attempt at the preparation of a phosphorus
containing macrocycle was based on a known nitrogen-sulfur system,
Ni(PEX)\(^{2+}\) (36).\(^{34}\) The objective of the problem was to design a
tetradequate ligand similar to PE (37) in which the imine nitrogen

\[
\begin{align*}
\text{(36)} & & \text{(37)}
\end{align*}
\]

atoms were replaced by phosphines and to make complexes in which this
tetradequate is coordinated to a single metal ion. The phosphorus-
sulfur tetradequate ligand could then be closed by reacting the
coordinated mercaptide groups with \(\alpha,\alpha'-\text{dibromo-\(\alpha\)-xylene}\) or a
dihaloalkane.

This approach has been tried\(^{41}\) in an arsenic-sulfur system.
The tetradequate ligands \(\text{C}_2\) and \(\text{C}_3\) (38) have been prepared and
complexes of these ligands have been isolated. No complexes in which all four donor atoms in these ligands were coordinated to a single metal ion could be found, however. Since a compound of this type is a necessary intermediate in macrocycle formation, this system did not lead to an arsenic-sulfur macrocycle. It was believed that perhaps the short, inflexible o-phenylene linkage between the arsenic and sulfur atoms was responsible for the bridging ligands in all of the compounds in which sulfur was coordinated.

The tetradeutate ligand synthesized for this study, DISPAR, (39) is analogous to \( C_3 \) except the phosphorus and sulfur atoms in DISPAR are connected by benzyl linkages, which are longer and more flexible than the o-phenylene linkages in the arsenic-sulfur ligand,
$C_3$. This ligand design should allow the thiomethyl group to coordinate to the same metal as the phosphorus and eliminate $Y\overline{SCH_3}$ ($Y = As, P$) bridging, which was seen in the complexes of $C_3$. The synthetic route used in preparing this ligand is described in detail in the experimental section and is summarized here.

Although the sulfur containing intermediates have been prepared in the literature, no characterization data is reported on them. The infrared and nmr data on these compounds which was collected in this study are given in Table 1. It should be noted that these compounds may produce an irritation on contact with the skin.
TABLE 1
CHARACTERIZATION DATA FOR THE SULFUR CONTAINING INTERMEDIATES
IN THE PREPARATION OF DISPAR

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR(^a)</th>
<th>NMR(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OH-3360</td>
<td></td>
</tr>
<tr>
<td>[Image]</td>
<td>C(_6)H(_5)-3060</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH(_3)-2930</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C(_6)H(_5)-1450, 748</td>
<td></td>
</tr>
<tr>
<td>[Image]</td>
<td>CH(_3)-7.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH(_2)-5.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C(_6)H(_5)-2.80</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Some characteristic absorptions are reported in cm\(^{-1}\).

\(^b\) Measured on CCl\(_3\)D solutions; reported in \(\tau\).
Since DISPAR is a cream colored oil no analytical data were obtained on it. Attempts to prepare solid organic derivatives of this ligand with methyl iodide and benzyl bromide also produced oils which were not further characterized.

The infrared spectrum of DISPAR is shown in Figures 2 and 3. Peaks which are assigned to methyl, methylene, and phenyl groups, as well as the absence of a P=O peak, all indicate that the spectrum is consistent with the assigned structure. The nmr spectrum of this phosphorus-sulfur tetradoentate in CDCl₃ is given in Figure 4. The multiplet in the 2.6 τ region has been assigned to phenyl protons. The benzyl portions are at 6.83 τ and the methyl protons are responsible for the peaks at 7.58 τ. These peaks integrate in a 5.5:1:1.8 ratio. The ratio expected for the DISPAR structure is 4.5:1.1:1.5; the experimental values indicate that some phenyl containing impurities may be present in the sample. The impurities also contain methylene groups and the methylene groups connecting the two phosphorus atoms cannot be distinguished from the impurity in the nmr spectrum.

The 70 ev mass spectrum of DISPAR does not contain a parent ion peak at m/e = 532. The highest mass ion which was detected was at m/e = 502. This corresponds to a loss of the methyl groups from both of the thioether groups to give a S-demethylated species. The relative abundance of this peak, however, is less than 1%.

The splitting pattern for the fragments with m/e > 100 and
Figure 2. The Infrared Spectrum of DISPAR Recorded Neat Between KBr Plates.
Figure 3. The Infrared Spectrum of DISPAR Recorded Neat Between KBr Plates.
Figure 4. The nmr Spectrum of DISPAR in CDCl₃.
Figure 5. Major Fragments in the Mass Spectrum of DISPAR.
with relative abundance > 5\% is given in Figure 5. Careful
examination of the fragments allows the structure of DISPAR to be
deduced. The peak at m/e = 105 indicates that there are two
phosphorus atoms connected by a trimethylene bridge in the molecule.
The peak at m/e = 230 coupled with the lack of other peaks in which
phosphorus is attached to any R group other than trimethylene
suggests that each phosphorus is bonded to a phenyl and an
o-methylthiobenzyl group. The attachment of sulfur to both methyl
and benzyl groups is indicated by the peak at m/e = 137.

b. Complexes of Palladium(II) with DISPAR

Palladium(II) complexes of the type Pd₂(DISPAR)X₄ (X = Cl, Br,
I, SCN) were isolated with this ligand even when a large excess of
DISPAR was present. The potentially tetracordinate ligand is acting
as a bidentate toward each of two Pd(II) ions. Some characterization
data on these complexes are given in Table 2. Although the DISPAR
complexes may be regarded as molecular, the conductivity values in
nitromethane suggest some ionic behavior in this solvent.

The infrared spectra of these complexes are very similar to
the infrared spectrum of the free ligand, as would be expected.
The infrared spectrum of a Nujol mull of Pd₂(DISPAR)(SCN)₄ is
representative and is given in Figures 6 and 7. Besides ligand peaks
the infrared spectrum of Pd₂(DISPAR)(SCN)₄ has two C≡N stretching
bands at 2085 and 2118 cm⁻¹ arising from the thiocyanate anions.
These two bands indicate that both N-bonded and S-bonded thiocyanate
is present in the solid state.⁵¹ There may be one N-bonded and one
### TABLE 2

**CHARACTERIZATION DATA FOR THE Pd₂(DISPAR)ₓ₄ COMPLEXES**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>( \lambda_M ) (cm²/ohm-mole)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd₂(DISPAR)Cl₄</td>
<td>Yellow-orange</td>
<td>14.9</td>
</tr>
<tr>
<td>Pd₂(DISPAR)Br₄</td>
<td>orange</td>
<td>30.1</td>
</tr>
<tr>
<td>Pd₂(DISPAR)I₄</td>
<td>red</td>
<td>18.3</td>
</tr>
<tr>
<td>Pd₂(DISPAR)(SCN)₄</td>
<td>orange</td>
<td>b</td>
</tr>
</tbody>
</table>

\(^a\) Measured on 10⁻³ M nitromethane solutions.

\(^b\) Not sufficiently soluble in suitable solvents.
Figure 6. The Infrared Spectrum of \( \text{Pd}_2(\text{DISPAR})(\text{SCN})_4 \) as a Nujol Mull.
Figure 7. The Infrared Spectrum of Pd₂(DISPAR)(SCN)₄ as a Nujol Mull.
S-bonded thiocyanate per palladium or a random mixture of N- and S-bonding.

The only complex which was sufficiently soluble for proton NMR was Pd₂(DISPAR)Br₄. The phenyl protons appeared as a multiplet at 2.58 τ in CDCl₃ and the benzyl protons were found at 6.88 τ in the bromide complex. These peaks occur at nearly identical positions in the spectrum of the uncomplexed DISPAR. The methyl peaks are found at 6.13 τ and are shifted 1.45 ppm downfield on coordination of the thioether. This downfield shift on coordination has been previously observed in palladium(II) complexes of 2-(methylthio)-3,4,5,6-tetrafluorophenyldiphenylphosphine (40), fsp. The methyl resonance of free fsp appears at 7.6 τ. On coordination to palladium(II) the methyl resonance shifts downfield by 0.90 ppm to 6.77 τ in the Pd(fsp)I₂ complex. The trimethylene resonance in Pd₂(DISPAR)Br₄ is broad and is located at 7.4 τ. Due to the low concentration of sample in the nmr of Pd₂(DISPAR)Br₄ no meaningful integration could be obtained.

![Diagram](image-url)
The electronic spectra of the Pd₂(DISPAR)X₄ complexes were recorded in dichloromethane solution and, for X = Cl and I, in the solid state at liquid nitrogen temperature; the data are presented in Table 3. The d-d transitions for the chloride and thiocyanate complexes are obscured by low energy charge transfer bands. The spectrum of the chloride was examined in the solid state at liquid nitrogen temperature, but the d-d transitions were obscured here too. A single d-d band at 25,000 cm⁻¹ (ε = 2100) suggests that the bromide complex has a square planar arrangement of ligands. In this complex it appears that each palladium is coordinated to a single sulfur and phosphorus atom and two bromide ions. Each ligand is, therefore, bridging two palladium ions resulting in the arrangement illustrated in Figure 8.

The electronic spectrum of Pd₂(DISPAR)I₄ in dichloromethane consists of two peaks at 18,870 cm⁻¹ (ε = 1518) and 22,730 cm⁻¹ (ε = 3600) which can be attributed to d-d transitions. The 5-coordinate, trigonal bipyramidal complex, [PdI(QAS)]I also exhibits two absorptions in the visible region at 18,690 cm⁻¹ (ε = 6300) and 26,040 cm⁻¹ (ε = 7530). These two spectra are compared in Figure 9. The similarity of these spectra leads to the conclusion that Pd₂(DISPAR)I₄ is also a 5-coordinate, trigonal bipyramidal complex. Each palladium ion is surrounded by a sulfur and a phosphorus atom from DISPAR and two bridging and one non-bridging iodide ions. An
TABLE 3

THE ELECTRONIC SPECTRAL DATA FOR THE Pd$_2$(DISPAR)$_x$$_4$ COMPLEXES$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solution Spectra$^b$</th>
<th>Solid State Spectra$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$_2$(DISPAR)Cl$_4$</td>
<td>32,100 (13,810)</td>
<td>32,260</td>
</tr>
<tr>
<td>Pd$_2$(DISPAR)Br$_4$</td>
<td>25,000 (2100)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31,300 (11,600)</td>
<td></td>
</tr>
<tr>
<td>Pd$_2$(DISPAR)I$_4$</td>
<td>18,870 (1518)</td>
<td>18,200 (sh)</td>
</tr>
<tr>
<td></td>
<td>22,730 (3600)</td>
<td>20,400 (sh)</td>
</tr>
<tr>
<td></td>
<td>27,000 (14,810)</td>
<td>27,500</td>
</tr>
<tr>
<td>Pd$_2$(DISPAR)(SCN)$_4$</td>
<td>31,300 (11,100)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>33,900 (13,100)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Frequency recorded in cm$^{-1}$, molar extinction coefficients are given in parentheses.

$^b$ Taken on 10$^{-3}$M dichloromethane solutions

$^c$ Recorded at liquid nitrogen temperature, 77°K.
Figure 8. The Proposed Arrangement of Ligands in Pd$_2$(DISPAR)Br$_4$ and Pd$_2$(DISPAR)I$_4$. 
Figure 9. The Electronic Spectra of [PdI(QAS)]I in Methanol (---) and Pd₂(DISPAR)I₄ in dichloromethane (——).
illustration of this arrangement is given in Figure 8. The solid state, liquid nitrogen temperature electronic spectrum of this compound is essentially the same as the spectrum recorded in dichloromethane.

The 70 ev mass spectral data for \( \text{Pd}_2(\text{DISPAR})\text{Cl}_4 \) are given in Table 4. The fragmentation of the complex is similar to that of the free ligand. The complex decomposes in the mass spectrometer, however, and no fragments containing palladium were observed.

Since it appears that DISPAR forms only bridged complexes with palladium(II) in the presence of halide ions, an acetonitrile solution of \( \text{Pd} (\text{BF}_4)_2 \) was prepared by reacting finely divided palladium metal with \( \text{NOBF}_4 \) in acetonitrile. Addition of an equivalent of DISPAR to this solution and removal of solvent gives a brown solid. The infrared spectrum of this solid contains peaks characteristic of DISPAR and a strong absorption at 1070 cm\(^{-1}\) due to the tetrafluoroborate ion. The molar conductivity of this solution in acetonitrile is 310 cm\(^2\)/ohm-mole if a formulation of \( \text{Pd}(\text{DISPAR})(\text{BF}_4)_2 \) is assumed. This value is reasonable for a 2:1 electrolyte and may indicate that DISPAR is coordinated to one metal ion. An electronic spectrum of the acetonitrile solution of \( [\text{Pd}(\text{DISPAR})](\text{BF}_4)_2 \) which was used for the conductivity determination consists of a single shoulder on the charge transfer band at 34,500 cm\(^{-1}\) (\( \varepsilon = 8770 \)). This is consistent with a planar arrangement of ligands around palladium(II).\(^{54} \)
<table>
<thead>
<tr>
<th>m/e</th>
<th>Positive Ion Fragment</th>
<th>% Relative Abundance</th>
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</thead>
<tbody>
<tr>
<td>256</td>
<td>CH$_2$P(CH$_2$)$_3$PCH$_2$(C$_6$H$_4$)SCH$_3$</td>
<td>3</td>
</tr>
<tr>
<td>241</td>
<td>P(CH$_2$)$_3$PCH$_2$(C$_6$H$_4$)SCH$_3$</td>
<td>3</td>
</tr>
<tr>
<td>240</td>
<td>CH$_2$P(CH$_2$)$_3$PCH$_2$(C$_6$H$_4$)S</td>
<td>7</td>
</tr>
<tr>
<td>228</td>
<td>CH$_2$(C$_6$H$_4$)SC$_6$H$_5$</td>
<td>6</td>
</tr>
<tr>
<td>227</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>226</td>
<td>P(CH$_2$)$_3$PCH$_2$(C$_6$H$_4$)S</td>
<td>6</td>
</tr>
<tr>
<td>212</td>
<td>(CH$_2$)$_3$PCH$_2$(C$_6$H$_4$)SCH$_3$ + H</td>
<td>10</td>
</tr>
<tr>
<td>211</td>
<td>(CH$_2$)$_3$PCH$_2$(C$_6$H$_4$)SCH$_3$</td>
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</tr>
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<td>210</td>
<td>(CH$_2$)$_3$PCH$_2$(C$_6$H$_4$)SCH$_3$ - H</td>
<td>10</td>
</tr>
<tr>
<td>194</td>
<td>P(CH$_2$)$_3$PCH$_2$(C$_6$H$_4$)</td>
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</tr>
<tr>
<td>180</td>
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<tr>
<td>165</td>
<td></td>
<td>6</td>
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<tr>
<td>152</td>
<td>PCH$_2$(C$_6$H$_4$)S - H</td>
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<tr>
<td>140</td>
<td>CH$_2$(C$_6$H$_4$)SCH$_3$ + 3H</td>
<td>7</td>
</tr>
<tr>
<td>139</td>
<td>CH$_2$(C$_6$H$_4$)SCH$_3$ + 2H</td>
<td>13</td>
</tr>
<tr>
<td>138</td>
<td>CH$_2$(C$_6$H$_4$)SCH$_3$ + H</td>
<td>100</td>
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<tr>
<td>137</td>
<td>CH$_2$(C$_6$H$_4$)SCH$_3$</td>
<td>29</td>
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</table>
Table 4 (continued)

<table>
<thead>
<tr>
<th>m/e</th>
<th>Positive Ion Fragment</th>
<th>% Relative Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>136</td>
<td>(\text{CH}_2(\text{C}_6\text{H}_4)\text{SCH}_3 - \text{H})</td>
<td>6</td>
</tr>
<tr>
<td>135</td>
<td>(\text{CH}_2(\text{C}_6\text{H}_4)\text{SCH}_3 - 2\text{H})</td>
<td>10</td>
</tr>
<tr>
<td>134</td>
<td>(\text{CH}_2(\text{C}_6\text{H}_4)\text{SCH}_3 - 3\text{H})</td>
<td>7</td>
</tr>
<tr>
<td>128</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>126</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>125</td>
<td>((\text{O})\text{P(\text{C}_6\text{H}_5)} + \text{H})</td>
<td>7</td>
</tr>
<tr>
<td>124</td>
<td>((\text{O})\text{P(\text{C}_6\text{H}_5)})</td>
<td>39</td>
</tr>
<tr>
<td>123</td>
<td>((\text{C}_6\text{H}_4)\text{SCH}_3)</td>
<td>48</td>
</tr>
<tr>
<td>122</td>
<td>\text{C}_6\text{H}_5\text{PCH}_2</td>
<td>6</td>
</tr>
<tr>
<td>121</td>
<td>\text{PCH}_2(\text{C}_6\text{H}_4)</td>
<td>12</td>
</tr>
<tr>
<td>109</td>
<td>\text{C}_6\text{H}_5\text{P} + \text{H}</td>
<td>17</td>
</tr>
<tr>
<td>105</td>
<td>\text{P(\text{CH}_2)_3P} + \text{H}</td>
<td>7</td>
</tr>
</tbody>
</table>

*Analysed for peaks for which m/e > 100 and % relative abundance > 2%.*
Attempts were made to demethylate the ligand in the 
\([\text{Pd(DISPAR)}](\text{BF}_4)_2\) complex in order to form the necessary precursor to a macrocycle. Demethylation reactions are generally performed in reducing solvents such as DMF or an ethanol-DMF mixture. When this compound is brought into contact with reducing solvents, however, a finely divided metal, presumably Pd(0), separated from solution. Apparently \([\text{Pd(DISPAR)}](\text{BF}_4)_2\) is reduced by these solvents. No further work was attempted with this system.

c. Reactions of DISPAR with Nickel(II)

Although thioethers have a greater affinity for palladium(II) and the chance of successful coordination of the thioether groups should be greater with this ion, several attempts were made to isolate nickel(II) complexes of DISPAR. When DISPAR is added to an ethanol solution of NiX\(_2\) (X = Cl, Br, BF\(_4\), PF\(_6\), ClO\(_4\)) which has been dehydrated with 2,2-dimethoxypropane, the solution becomes red immediately, indicating that a reaction has occurred. No solid, characterizable complex was ever isolated from the resultant intractable oils. When the source of nickel was Ni(glyme)Br\(_2\) in THF, a green solution resulted on the addition of DISPAR, but again only an oil was isolated. If this green oil is dissolved in ethanol a red solution results. A red oil which appears to be the same as that obtained from the reaction with NiBr\(_2\) can be isolated from the red solution. Perhaps the various conformers of this flexible ligand and the low affinity of nickel(II) for thioethers
is preventing characterizable complexes from being formed with this ion. No further work was attempted with this system.

2. The Phosphorus-Sulfur Bidentate Ligands, 3-Mercaptopropylphenylphosphine and 3-Methylthiopropylphenylphosphine (PSH and PSMe)

Two ligands, 3-mercaptoethylphenylphosphine (PSH) and 3-methylthiopropylphenylphosphine (PSMe) were synthesized in order to investigate some of the properties of coordinated secondary phosphines. These compounds were prepared by cleaving trimethylene sulfide with phenylphosphide and adding either acid or methyl iodide to the resulting mercaptide. The following equations summarize the reactions.

$$\text{LiPPhH} + \overset{\text{S}}{\text{H}} \rightarrow \text{HP} \text{P(CH}_2\text{)}_3\text{SLi}$$

$$\text{KPPPhH} + \overset{\text{S}}{\text{H}} \rightarrow \text{HP} \text{P(CH}_2\text{)}_3\text{SCH}_3 \quad (\text{PSMe})$$

The infrared spectra of these two ligands are very similar as would be expected. The infrared spectrum of PSH is given in Figures 10 and 11. The peaks at 2560 cm\(^{-1}\) \((w)\) and 2280 cm\(^{-1}\) \((s)\) can be assigned to the SH and PH stretching frequencies, respectively. In the infrared spectrum of PSMe the peak at 2560 cm\(^{-1}\) is completely absent, but otherwise it is nearly identical with that of PSH.

The nmr data on CDCl\(_3\) solutions of these two compounds are summarized in Table 5. The nmr spectrum of PSH consists of two
Figure 10. The Infrared Spectrum of PSH Recorded Neat Between KBr Plates.
Figure 11. The Infrared Spectrum of PSH Recorded Neat Between KBr Plates.
TABLE 5

THE NMR DATA FOR THE BIDENTATE PHOSPHORUS-SULFUR LIGANDS PSH AND PSMe

<table>
<thead>
<tr>
<th>Assignment</th>
<th>PSH</th>
<th>PSMe</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅</td>
<td>2.97</td>
<td>2.64</td>
</tr>
<tr>
<td>PH</td>
<td>d</td>
<td>8.7</td>
</tr>
<tr>
<td>SH</td>
<td>d</td>
<td>--</td>
</tr>
<tr>
<td>SMe</td>
<td>--</td>
<td>8.07</td>
</tr>
<tr>
<td>(CH₂)₂S</td>
<td>d</td>
<td>8.13</td>
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<tr>
<td>PCH₂</td>
<td>d</td>
<td>7.48</td>
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<tr>
<td>JₚH</td>
<td>--</td>
<td>143 Hz</td>
</tr>
<tr>
<td>JₚCH</td>
<td>--</td>
<td>6 Hz</td>
</tr>
</tbody>
</table>

a Reported in τ.
b Taken in CDCl₃ solution with TMS as internal standard.
c Recorded neat and in CDCl₃ solution with TMS as internal standard.
d Included in envelope of peaks centered at ~8 τ.
multiplets centered ca. 2.97 and 8 τ. The multiplet at 2.97 τ can be assigned to the phenyl protons. All other protons in this compound are assumed to be included in the envelope at ~ 8 τ. The two envelopes of peaks integrate in a 5.0:7.1 ratio which is consistent with the structure, HPhP(CH₂)₃SH. The nmr spectrum of PSMe is better defined than that of PSH. The phenyl protons are responsible for the multiplet at 2.64 τ and the triplet at 7.48 τ can be assigned to the methylene protons attached to and split by the phosphorus (JₚCH₂ = 6 Hz). The peak at 8.07 τ can be assigned to the methyl protons and the remaining methylene protons are responsible for the multiplet at 8.13 τ. The exact position of the PH proton is ill defined since one-half of the doublet is partially hidden under the methylene multiplet, but it is located at about 8.7 τ and Jᵢᵢ is about 14.3 Hz. The ratio of phenyl to PCH₂ to methyl to methylene to half of the PH doublet at 9.70 τ is 5.2:2.5:6.7:0.5 as would be expected for this compound.

The 70 ev mass spectrum of PSH, analyzed for all peaks over 5% relative abundance is given in Figure 12 and a fragmentation pattern of this compound is shown in Figure 13. A parent peak at m/e = 184 (5%) is the largest mass fragment observed in the spectrum of PSH. The great stability of the fragment at m/e = 182 as indicated by the high relative abundance suggests the formation in the mass spectrometer of the cyclic structure which is shown in Figure 13. Most of the remainder of the fragments in the mass
Figure 12. The Mass Spectrum of PSH Analyzed to 5% Relative Abundance.
Figure 13. A Fragmentation Pattern for the Major Peaks in the Mass Spectrum of PSH.
spectrum of PSH result from the cleavage of groups from the phosphorus or sulfur atoms of this 5-membered heterocycle. Two peaks at m/e = 154 and 89 in this mass spectrum can be attributed to recombination ions. The peak at m/e = 154 is due to biphenyl formed from the recombination of two phenyl radicals and that at m/e = 89 results from the combination of a phenyl and a carbon radical.

3. Nickel(II) and Palladium(II) complexes with PSH

A phosphorus-sulfur bidentate ligand, HPhP(CH₂)₂SH, which is similar to PSH, except that the phosphorus and sulfur atoms in PSH are bridged by a trimethylene linkage, has been prepared and characterized by Isslieb, et al. They have prepared nickel(II) complexes with this ligand of the type (NiLBr)₂ and NiL₂ in which L represents the mercaptide HPhP(CH₂)₂S⁻. They also suggest that the PH bond in this ligand is sufficiently acidic that it might be broken by a very strong base. Consequently butyl lithium was reacted with (NiLBr)₂ to produce a black crystalline solid which could not be identified. Unfortunately in planning this reaction the minimum of four ligand donors was not conveniently supplied to nickel(II) and apparently a polymeric material has resulted.

In the present work two equivalents of PSH were reacted with an equivalent of Ni(glyme)Br₂ in THF. The red crystalline product of this reaction is assumed to be Ni(HPhP(CH₂)₂S)₂ by analogy with the similar product, Ni(HPhP(CH₂)₂S)₂, isolated from the reaction of
two equivalents of HPhP(CH₂)₂SH with an equivalent of anhydrous NiBr₂. The infrared spectrum of this red material contains peaks which are characteristic of the ligand, except that no S-H or P-H stretching peaks are visible. The absence of a P-H stretching peak in the infrared spectrum of compounds which contain coordinated secondary phosphines has been observed in this lab before (c.f. Appendix B), especially when the metal is not in a low oxidation state, and therefore cannot be taken as evidence that PH is absent.

The pmr spectrum of the red product in CDCl₃-d₆-DMSO consists of a multiplet due to phenyl protons at 2.53 τ and a multiplet due to methylene protons at 7.51 τ. These peaks integrate in a 5.0:5.9 ratio, which is in agreement with the assigned structure. No peaks which could be assigned to the PH protons were detected in the nmr spectrum but this does not rule out their presence in the complex. The low solubility of Ni(HPhP(CH₂)₃S)₂ in a CDCl₃-d₆-DMSO (2:1) mixture, the possibility of being split by both phosphorus atoms, and the relatively small number of PH protons may make them indistinguishable from the baseline in the nmr spectrum. The peaks might also be obscured by the broad phenyl and methylene multiplets.

It is to be noted that this red compound reacts with the CDCl₃-d₆-DMSO mixture after several hours to produce a green crystalline compound. No further work was done with the green compound, but it is not unlikely that a dichloromethylthioether group (CCl₂DS⁻) has been produced.
A proposed structure of Ni(HPhP(CH₂)₃S)₂ is given in Figure 14. This complex could be a macrocycle intermediate if a way to bridge the phosphorus and sulfur could be found. One possible method of doing this would be to react this molecule with an allyl or a vinyl halide. The halide end of the allyl halide should react with the mercaptide to give a thioether. Under proper conditions the double bond could be induced to react with the coordinated secondary phosphine, thus closing the macrocycle.

When the red crystalline compound described above is warmed in allyl bromide in the presence of the free radical initiator AIBN a green insoluble oil is formed. The nmr spectrum of this oil after it has been dried in vacuo consists of a multiplet at 2.21 τ which can be assigned to phenyl protons, a multiplet at 4.52 τ due to vinyl protons, and a multiplet at 7.01 τ assigned to methylene protons. These peaks integrate in a 5.0:3.1:8.2 ratio. This
suggests that a thioether has formed and that the green oil is 
Ni(HPhP(CH₂)₃SCH₂CH=CH₂)₂Br₂. No proton resonances assignable to 
PH protons were detected, but the limited solubility of this 
compound may preclude their observation or they may be obscured by 
some of the multiplets.

It is evident that no macrocyclic products have resulted from 
these reactions. The alkylation of the coordinated mercaptide has 
apparently been completed, but the free radical addition of the 
coordinated secondary phosphine has failed. The possibility that 
coordinated secondary phosphines do not undergo free radical 
additions to carbon-carbon multiple bonds has not been eliminated, 
but this seems unlikely in view of the reactivity of secondary 
phosphine oxides under similar conditions. The extreme insolubility 
of the green oil formed in this reaction might have prevented the 
free radical reaction before it could take place. Attempting the 
reaction under more favorable free radical reaction conditions 
might lead to the desired product. This could be accomplished by 
heating a solution of the red material to 100°C before slowly adding 
a mixture of allyl bromide and AIBN. Vinyl chloride or allyl 
chloride could also be better suited for this reaction than allyl 
bromide.

Several attempts were made to prepare palladium(II) complexes 
with PSH which are analogous to (Ni(HPhP(CH₂)₂S)Br)₂.⁵⁷ As a 1:1 
ratio of PdX₄ = (X=Cl,Br) and PSH were combined in ethanol a very
insoluble orange solid precipitated. The infrared spectrum of this material consists of absorptions characteristic of the ligand, except no PH or SH stretching bands can be detected. However, this doesn't exclude their presence. Nmr spectra could not be obtained on these materials owing to their insolubility.

The electronic spectra were obtained for both the chloride and bromide compounds in dichloromethane. These spectra consisted of two absorptions in the visible region at 29,000 and 32,800 cm⁻¹ for the chloride and 27,600 and 32,800 cm⁻¹ for the bromide. Molar extinction coefficients of 4360 and 7380, respectively, per palladium were calculated for the bromide complex assuming the formula of \((\text{Pd} (\text{HPPH} (\text{CH}_2)_3 \text{S}) \text{Br})_x\). The chloride complex was too insoluble for a similar determination. Assuming that the higher energy band in these two spectra is due to a charge transfer transition, the data suggest that halide ion is bound to a square planar palladium(II) ion.

An elemental analysis for the bromide complex is lower in carbon and higher in bromine than is calculated for the formula \((\text{Pd} (\text{HPPH} (\text{CH}_2)_3 \text{S}) \text{Br})_x\), but no other suitable formula could be deduced. The insolubility of this compound suggests a high molecular weight. It has not been further characterized.

When a second equivalent of PSH is added to the solid resulting from one equivalent of PSH and one equivalent of \(\text{PdCl}_4^-\) in ethanol, the solid dissolves to give an orange solution. An orange
oil results when the solvents are slowly removed from this solution. Recently a solid has been obtained by slow evaporation of a nitromethane solution of this oil. The electronic spectrum of this compound in dichloromethane consists of a single absorption in the visible region at 28,000 cm\(^{-1}\). Assuming this compound to be \(\text{Pd} (\text{HPhP(CH}_2\text{)}_3\text{S})_2\) a molar extinction coefficient of 9260 is calculated. This may be assigned to the \(1\text{A}_{1g} \rightarrow 1\text{E}_g\) transition in a square planar \(\text{Pd(II)}\) if \(D_{4h}\) symmetry is assumed.\textsuperscript{54} It also may be a low energy charge transfer band.

The nmr spectrum of this compound consists of two multiplets at 2.6 \(\tau\) and 8.8-6.9 \(\tau\) which can be assigned to phenyl and methylene protons, respectively. These peaks integrate in a 5.0:7.3 ratio which is reasonable for the compound \(\text{Pd} (\text{HPhP(CH}_2\text{)}_3\text{S})_2\). No \(\text{PH}\) protons could be detected in the nmr of this compound.

This compound does not react with refluxing 1,3-dichloropropane, as evidenced by nmr and electronic spectral data.

4. Attempted Preparation of 1,2-Bis(3-mercaptopropylphenyl-phosphino)ethane (\(\text{P}_2\text{S}_2\text{H}_2\))

In conjunction with attempts to synthesize a macrocyclic ligand by joining two bidentate phosphorus-sulfur ligands in the presence of a metal ion, a route to the synthesis of the tetratentate phosphorus-sulfur ligand \(\text{P}_2\text{S}_2\text{H}_2\) (\textsuperscript{41}) was being investigated. Although this ligand is similar to the DISPAR, \(\text{C}_2\), and \(\text{C}_3\) ligands,
one significant design change has been made. The weakly coordinating terminal thioether groups in DISPAR, C₂, and C₃ have been replaced by highly acidic thiol groups. These thiol groups lose the hydrogen in the presence of a metal ion and coordinate as mercaptides. Having these good donors in the terminal positions of the tetradeutate ligand could allow it to coordinate entirely to one metal ion, thus forming the necessary intermediate for macrocycle production.

The method used to synthesize this phosphorus-sulfur tetradeutate ligand is represented by the following equations:

\[
\text{HPhP(CH}_2\text{)}_2\text{PPhH} + 2 \text{BuLi} \rightarrow \text{LiPhP(CH}_2\text{)}_2\text{PPhLi}
\]

\[
\text{LiPhP(CH}_2\text{)}_2\text{PPhLi} + 2 \begin{array}{c}
\text{S} \\
\end{array} \rightarrow \text{P}_2\text{S}_2\text{H}_2
\]

These reactions were attempted in two different solvents, ether and p-dioxane. The yellow final product of this reaction, which is assumed to be LiS(CH₂)₃PPh(CH₂)₂PPh(CH₂)₃SLi precipitates out of the
ether, but is soluble in p-dioxane. This material is, therefore, more easily purified when ether is used as the solvent. Addition of ethanol to this yellow solid produces a colorless solution, presumably by protonating the dilithium salt. Exposing the yellow solid to air causes a white solid to form. These materials have not been further characterized.

A THF solution of Ni(glyme)Br₂ was also added to a portion of the ethanol solution of the product of the above reaction. A red solution and a dark red, intractable oil resulted. The infrared spectrum of this material contains a sharp peak at 3680 cm⁻¹ which is indicative of hydroxide. Absorptions characteristic of methylene and phenyl groups were also observed in the infrared spectrum of this compound. An attempt was made to purify this compound by passing it through a fluorosil column in benzene. A red fraction was eluted by the benzene, followed by another red fraction eluted by acetone, and a third red fraction eluted by ethanol. A red band which could not be eluted also remained on the column. The infrared spectra of all three oils were very similar and exhibited bands characteristic of methylene and phenyl groups. The hydroxide was removed by the fluorosil column, however. The nmr spectra of the three red oils, obtained in CDCl₃, are similar and consist of a phenyl multiplet at 2.55 τ and a multiplet between 9.3 and 7.15 τ which may be due to methylene protons. Owing to the insolubility of these compounds in CDCl₃ no meaningful integration data could be obtained.
Since all three red oils exhibit similar infrared and nmr spectra, it is assumed that they contain similar ligands. The differences in solubilities, as reflected by the chromatography experiment, may indicate different degrees of polymerization. Before any intelligent comment can be made on these systems, it is necessary to determine the nature of the yellow solid obtained from the reaction between LiPhP(CH₂)₂PPhLi and trimethylene sulfide. An nmr spectrum of the white solid obtained by exposing this yellow solid to the air should indicate whether this reaction has produced the desired tetradeutate or not.

B. The PN₃ Macrocycle

1. Nickel(II) Complex of Bis(3-aminopropyl)phenylphosphine (PN₂)

The tridentate ligand PN₂ (42) was prepared by the free radical addition of phenylphosphine to allyl amine as has been described in the literature. The infrared spectrum of this ligand is shown in Figures 15 and 16. The NH₂ stretching frequencies appear at 3375 and 3290 cm⁻¹ and a broad band due to uncoordinated amine appears at...
850 cm\(^{-1}\). The remainder of the spectrum is in agreement with the structure assigned to this compound, except for the weak band at 2280 cm\(^{-1}\). It is believed that this peak is due to a small amount of C=N impurity remaining from the decomposition of the free radical initiator AIBN used in the preparation of this compound.

The nmr spectrum of PN\(_2\) has been run in CDCl\(_3\); it consists of a phenyl multiplet at 2.60 \(\tau\), a triplet due to the methylene groups attached to phosphorus at 7.38 \(\tau\) (\(J_{PC}\) = 4 Hz), a multiplet due to the other methylene groups at 8.42 \(\tau\), and a NH\(_2\) singlet at 8.99 \(\tau\). These peaks integrate in a 5.1:4.0:7.9:3.9 ratio which is consistent with the structure that has been assigned to PN\(_2\).

Mixing PN\(_2\) with a warm ethanol solution of nickel(II) chloride and excess ammonium hexafluorophosphate gives, on cooling, red-orange crystals of [(Ni(PN\(_2\))Cl)](PF\(_6\)). The infrared spectrum of this complex (Nujol mull) is given in Figures 17 and 18. The NH\(_2\) stretching modes are at lower frequencies in this compound than in the free ligand, indicating that the amine groups are coordinated. There are four bands in the N-H stretching region of [Ni(PN\(_2\))Cl]PF\(_6\) which indicates that the symmetric and assymetric modes of both NH\(_2\) groups are coupled in this complex.

The electronic spectrum of [Ni(PN\(_2\))Cl]PF\(_6\) in acetonitrile consists of a single absorption at 21,600 cm\(^{-1}\) (\(\epsilon = 260\)) indicating a square planar arrangement of ligands around nickel(II). This
Figure 15. The Infrared Spectrum of PN\textsubscript{2} Recorded as a Liquid in 0.01 mm KBr Cells.
Figure 16. The Infrared Spectrum of FN₂ Recorded as a Liquid in 0.01 mm KBr Cells.
Figure 17. The Infrared Spectrum of $[\text{Ni(PN}_{2}\text{)}\text{Cl}]\text{PF}_{6}$ as a Nujol Mull.
Figure 18. The Infrared Spectrum of [Ni(PN₃)Cl]PF₆ as a Nujol Mull.
absorption may be assigned as the $^1A_1 \rightarrow ^3B_2 (d_{xz} \rightarrow d_{x^2-y^2})$ transition, assuming approximately planar symmetry. The spectrum of this compound has a single peak at 22,200 cm$^{-1}$ in the solid state at liquid nitrogen temperature.

The molar conductivity of a 10$^{-3}$M acetonitrile solution of [Ni(PN$_2$)Cl]$PF_6$ is 128 cm$^2$/ohm-mol, which is indicative of a 1:1 electrolyte. Thus, the structure shown in Figure 19 is proposed for this compound.

![Proposed structure of Ni(PN$_2$)Cl$^+$](image)

Figure 19. Proposed structure of Ni(PN$_2$)Cl$^+$.

The magnetic moment of [Ni(PN$_2$)Cl]$PF_6$ is 0.66 B.M. at 24$^\circ$. This is reasonable for a low spin nickel(II) complex of this type. The small residual moment is due to temperature independent paramagnetism.

The approach toward synthesizing a phosphorus containing macrocycle to be used in this section is based on the macrocycle, CR (43). Complexes of CR were prepared by the reaction of

\[
\begin{align*}
N & N \\
H & \\
N & N
\end{align*}
\]

(43)

\(\gamma,\gamma'-\text{diaminodipropylamine with 2,6-diacyetylpyridine in the presence of nickel(II). Since PN₂ (42) is similar to }\gamma,\gamma'-\text{diaminodipropylamine, it was believed that the Schiff base condensation of this compound with 2,6-diacyetylpyridine would produce the desired phosphorus containing macrocycle, PN₃ (44).}

The addition of PN₂ to an ethanol solution of NiX₂ \((X = \text{Cl, Br, I})\) and 2,6-diacyetylpyridine causes the formation of a purple solution. Addition of excess \(\text{NH₄PF₆}\) to these solutions leads to the
isolation of purple complexes of the type $[\text{Ni}(\text{PN}_3)X]\text{PF}_6$ when $X = \text{Br}$ or $\text{I}$; when $X = \text{Cl}$ the brown $[\text{Ni}(\text{PN}_3)](\text{PF}_6)_2$ was formed. The purple complex, $[\text{Ni}(\text{PN}_3)\text{Cl}]\text{PF}_6$, could be isolated by using "NiCl($\text{PF}_6$)" as the original source of nickel(II). These complexes are only slightly soluble in water, alcohols, or less polar organic solvents. They are moderately soluble in acetone and reasonably soluble in acetonitrile, DMF, and DMSO.

Some characterization data for these complexes are presented in Table 6. Conductivity values for the $[\text{Ni}(\text{PN}_3)X]\text{PF}_6$ complexes in acetonitrile are $140-148 \text{ cm}^2/\text{ohm-mol}$ and are reasonable for 1:1 electrolytes in this solvent. The halide ion, therefore, is coordinated as a fifth ligand in this solvent. The molar conductivity of $[\text{Ni}(\text{PN}_3)](\text{PF}_6)_2$ is $286 \text{ cm}^2/\text{ohm-mol}$ in acetonitrile, indicating that this compound is a 2:1 electrolyte.
## TABLE 6
CHARACTERIZATION DATA FOR SOME NICKEL(II) COMPLEXES OF PN₃

<table>
<thead>
<tr>
<th>Complex</th>
<th>Color</th>
<th>$\Lambda_M^a$</th>
<th>$\mu_{\text{eff}}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni(PN}_3\text{)Cl}]\text{PF}_6$</td>
<td>Purple</td>
<td>144</td>
<td>0.52</td>
</tr>
<tr>
<td>$[\text{Ni(PN}_3\text{)Br}]\text{PF}_6$</td>
<td>Purple</td>
<td>140</td>
<td>1.57</td>
</tr>
<tr>
<td>$[\text{Ni(PN}_3\text{)I}]\text{PF}_6$</td>
<td>Purple</td>
<td>148</td>
<td>0.54</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7BPF%7D_6">\text{Ni(PN}_3\text{)}</a>_2$</td>
<td>Brown</td>
<td>286</td>
<td>0.80</td>
</tr>
</tbody>
</table>

$^a$ Measured on $10^{-3}\text{M}$ acetonitrile solutions, cm²/ohm-mol.

$^b$ B.M.
The infrared spectrum of \([\text{Ni}(\text{PN}_3)\text{Cl}]\text{PF}_6\) is representative of these complexes and is given in Figures 20 and 21. The absence of peaks which could be assigned to NH$_2$ or C=O and the presence of a weak peak at 1620 cm$^{-1}$ which is assigned to C=N stretching frequency all indicate that a complex of PN$_3$ has been isolated.

The electronic spectra of these PN$_3$ complexes have been recorded on the same acetonitrile solutions used for conductivity measurements and on dichloromethane solutions of \([\text{Ni}(\text{PN}_3)X]\text{PF}_6\) \((X = \text{Br}, \text{I})\). The solid state electronic spectra of these compounds have also been recorded at liquid nitrogen temperature. These spectral data are shown in Table 7.

The spectra of the \([\text{Ni}(\text{PN}_3)X]\text{PF}_6\) complexes in acetonitrile or dichloromethane consist of two or three bands in the visible region, the lowest energy band having a larger molar extinction coefficient than the one of next higher energy. The spectra in acetonitrile are compared in Figure 22. This spectral shape is consistent with a trigonal bipyramidal arrangement of ligands around nickel(II). Although the true microsymmetry of these compounds is Cs, their electronic spectra can be described in terms of C$_{3v}$ symmetry if it is assumed that the splitting of the degenerate E levels in C$_{3v}$ is small. This situation is illustrated in Figure 23. If a ligand field of C$_{3v}$ symmetry is considered, two spin allowed transitions, $^1A_1 \rightarrow ^1E'$ and $^1A_1 \rightarrow ^1E''$, can be expected; the
Figure 20. The Infrared Spectrum of $[\text{Ni(PN}_3\text{)}\text{Cl}]\text{PF}_6$ as a Nujol Mull.
Figure 21. The Infrared Spectrum of $[\text{Ni(PN}_3\text{)}\text{Cl}]\text{PF}_6$ as a Nujol Mull.
TABLE 7
THE ELECTRONIC SPECTRAL DATA FOR NICKEL(II) COMPLEXES OF PN₃ AND PN₃H

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solution a,b</th>
<th>Solid State c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₃CN</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Ni(PN₃)Cl</a></td>
<td>17,400(4780)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30,800(3000)sh</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Ni(PN₃)Br</a></td>
<td>19,100(3700)</td>
<td>19,100(3750)</td>
</tr>
<tr>
<td></td>
<td>29,000(2700)</td>
<td>29,000(2600)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Ni(PN₃)I</a></td>
<td>19,300(5700)</td>
<td>18,500(6200)</td>
</tr>
<tr>
<td></td>
<td>28,200(3100)sh</td>
<td>28,200(3000)sh</td>
</tr>
<tr>
<td></td>
<td>32,300(7000)sh</td>
<td>32,300(7000)sh</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Ni(PN₃)</a>₂</td>
<td>22,700(1700)</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td>30,800(3310)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Ni(PN₃H)</a>₂</td>
<td>24,100(220)</td>
<td>d</td>
</tr>
<tr>
<td>Compound</td>
<td>Solution</td>
<td>Solid State</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------</td>
<td>-------------</td>
</tr>
<tr>
<td></td>
<td>CH$_3$CN</td>
<td>CH$_2$Cl$_2$</td>
</tr>
<tr>
<td><a href="PF$_6$">Ni(PN$_3$H)$_2$I</a></td>
<td>22,700(220)sh</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td>27,800(1470)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a* Reported in cm$^{-1}$ with molar extinction coefficients in parentheses.

*b* Measured on 10$^{-3}$ M solutions.

*c* Recorded at liquid nitrogen temperature, 77$^\circ$K.

*d* Insoluble.
Figure 22. The Electronic Spectra of [Ni(PN₃)ₓ]PF₆ (X = Cl, Br, I) in Acetonitrile Solution.
\[ \begin{align*}
\text{C}_{3v} & \\
& \uparrow \quad - \quad d_{z^2} \quad A_1 \\
& \uparrow \quad - \quad d_{xz}, d_{yz} \quad E' \\
& \downarrow \quad - \quad d_{x^2-y^2}, d_{xy} \quad E''
\end{align*} \] 
\[ \begin{align*}
\text{C}_5 & \\
& \uparrow \quad - \quad d_{z^2} \\
& \downarrow \quad - \quad d_{xz}, d_{yz} \\
& \downarrow \quad - \quad d_{x^2-y^2}, d_{xy}
\end{align*} \]

Figure 23. d-Orbital Energy Levels for C\(_{3v}\) and C\(_{5}\) Microsymmetries.

\( ^1A_1 \to ^1E'' \) transition is more intense. The first two transitions which have been recorded, therefore, can be assigned to the \( ^1A_1 \to ^1E' \) and \( ^1A_1 \to ^1E'' \) transitions, respectively; the transition which appears at 32,300 cm\(^{-1}\) in the iodide complex is assigned as a charge transfer band. The spectra of the bromide and iodide complexes were recorded in dichloromethane, a poorly coordinating solvent, and are identical to the corresponding spectra taken in acetonitrile. This indicates that interactions of acetonitrile with the five-coordinate bromide and iodide complexes is negligible.

Although \([\text{Ni(PN}_3\text{)](PF}_6\text{)}_2\) is a 2:1 electrolyte in acetonitrile, its electronic spectrum in this solvent is extremely similar to that of the five-coordinate, trigonal bipyramidal \([\text{Ni(PN}_3\text{)]X]PF_6\) complexes. This is probably due to coordination of acetonitrile as a fifth ligand. Unfortunately this compound is not soluble in non-coordinating solvents so no solution spectrum of a four-coordinate species could be obtained.
Solid state spectra of all the PN₃ complexes have been recorded at liquid nitrogen temperature. The spectra of the [Ni(PN₃)ₓ]PF₆ complexes are compared in Figure 24. These spectra of the solid complexes recorded at liquid nitrogen temperature are significantly different from the spectra obtained on the [Ni(PN₃)ₓ]PF₆ complexes in acetonitrile or dichloromethane solutions. The spectra of the solids are unlike typical spectra of compounds known to possess trigonal bipyramidal or square pyramidal geometries. They do resemble the solid state spectrum of [Ni(CR)Br]Br·H₂O, however, and a comparison is shown in Figure 25. The geometry of [Ni(CR)Br]Br·H₂O is known from an X-ray structure determination to be a distorted square pyramid.¹⁷ This structure is represented in Figure 26. Pending an X-ray structural determination of [Ni(PN₃)ₓ]PF₆, a distorted square pyramidal coordination geometry is assigned to the nickel ion in these complexes in the solid state.

The solid state spectrum of [Ni(PN₃)](PF₆)₂ at liquid nitrogen temperature is shown in Figure 27. It consists of three shoulders at 18,200, 27,000 and 31,200 cm⁻¹ and resembles the spectra of the five-coordinate [Ni(PN₃)ₓ](PF₆) complexes more than a typical four-coordinate nickel(II) spectrum. The affinity of this complex for a fifth ligand has already been demonstrated by its electronic spectrum in acetonitrile; consequently, possibly water from the liquid nitrogen bath is coordinated to this compound as a fifth ligand.
Figure 24. The Electronic Spectra of $[\text{Ni(PH}_3\text{)}X]\text{PF}_6$ ($X = \text{Cl, Br, I}$) in the Solid State at Liquid Nitrogen Temperature.
Figure 25. The Solid State Spectra of [Ni(CR)Br]Br·H₂O (---) at Room Temperature and [Ni(PN₃)Cl]PF₆ (-----) at Liquid Nitrogen Temperature.
Figure 26. The Structure of $[\text{Ni(CR)}\text{Br}]\text{Br}_2\cdot\text{H}_2\text{O}$. 
Figure 27. The Electronic Spectrum of \([\text{Ni(PN}_3\text{)}]_2(\text{PF}_6)_2\) in the Solid State at Liquid Nitrogen Temperature.
The nickel(II) complexes are diamagnetic; the magnetic moments calculated from data taken at several field strengths are recorded in Table 6. These small residual moments are typical of low-spin nickel(II) complexes and is due to temperature independent paramagnetism.\textsuperscript{45} The nickel(II) complexes of the $N_4$ nitrogen donor macrocycle, CR (45), are paramagnetic and have a tetragonal arrangement of ligands, except for a series of diamagnetic compounds containing the $[\text{Ni(CR)}\text{Br}]^+$ cation and a water molecule.\textsuperscript{16} The higher ligand field strength of phosphine in the PN$_3$ complexes, therefore, has resulted in diamagnetic, five-coordinate complexes with nickel(II).

The nmr spectra of these complexes are consistent with a macrocyclic structure. The nmr spectrum of $[\text{Ni(PN}_3\text{)}\text{I}](\text{PF}_6)$ in d$_6$-DMSO is typical and is shown in Figure 28. The singlet at 7.25 $\tau$ can be assigned to the methyl groups, which do not appear to be coupled to other protons. The multiplet between 2.6 and 2.2 $\tau$ can be assigned to phenyl protons and that between 1.6 and 1.2 $\tau$ to protons on the pyridine ring. These two multiplets integrate in a 5.0:3.0 ratio. The remaining resonances in this spectrum can be assigned to the methylene groups connecting nitrogen and phosphorus.

3. Attempts to Prepare Cobalt(II) and Cobalt(III) Complexes of 2,12-Dimethyl-7-phenyl-3,11,17-triaza-7-phosphabicyclo-[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (PN$_3$)

An attempt was made to prepare $[\text{Co(PN}_3\text{)}\text{Cl}](\text{PF}_6)$ by treating
Figure 28. The nmr Spectrum of $[\text{Ni} (\text{PN}_3) \text{I}] (\text{PF}_6)$ in $d_6$-DMSO.
"CoCl(PF₆)" with 2,6-diacetylpyridine in ethanol followed by an addition of PN₂. A red solution and precipitate which formed after the addition of PN₂ became green during a one hour reflux period and a green solid was isolated from this reaction. The infrared spectrum of a Nujol mull of this compound is identical to that of [Ni(PN₃)Cl]PF₆ which is shown in Figures 20 and 21. This strongly suggests that the PN₃ macrocycle has been formed in this reaction. The presence of the PF₆⁻ anion is also confirmed by the infrared spectrum.

The solid state electronic spectrum of this compound consists of absorptions at 7250, 8400, 13700, 15300, 16000, and 16400 cm⁻¹. This is consistent with known four- and five-coordinate Co(II) spectra. A six-coordinate Co(II) compound would not contain low energy, low intensity bands at 7250 and 8400 cm⁻¹ as is seen in this compound.

An elemental analysis of this compound shows it to be lower in carbon and hydrogen and higher in chlorine than would be expected for [Co(PN₃)Cl]PF₆. It may be a mixture of compounds with Co(PN₃)²⁺ and Co(PN₃)Cl⁺ cations and PF₆⁻ and CoCl₄²⁻ anions.

Dissolving this green material in acetonitrile or alcohols gives a red-orange solution. This could be due to a geometry change around cobalt or to a reaction with trace amounts of oxygen which might have been in the solvents. The materials in these solutions have not been characterized.

Two different methods to prepare cobalt(III) complexes of the PN₃ macrocycle have been tried. In both attempts CoBr₂ was
stirred with an equivalent of 2,6-diacetylpypyridine in alcohol and then an equivalent of PN$_2$ was added. The solution became red immediately on the addition of PN$_2$, but after a one hour reflux period the color had changed to green. Two methods of oxidation were attempted on this green solution. In the first attempt, a few drops of aqueous HBr and an excess of LiBr were added and air was bubbled through the resulting warm solution. On cooling a red crystalline solid was isolated. The infrared spectrum of this compound indicates that the macrocycle PN$_3$ has been formed.

The molar conductivity of this solid in methanol is 136 cm$^2$/ohm-mol assuming a formulation of [Co(PN$_3$)Br$_2$]Br. This value is higher than would be expected for a 1:1 electrolyte in this solvent. An aqueous solution gave a conductivity value, based on this formula, of 395 cm$^2$/ohm-mol. This resembles a value which would be expected for a 4:1 electrolyte rather than the 3:1 electrolyte, [Co(PN$_3$)(H$_2$O)$_2$]Br$_3$ which should form from [Co(PN$_3$)Br$_2$]Br in aqueous solution.

The electronic spectrum of this compound in methanol contains three bands at 19600sh, 21500 sh, and 28600 cm$^{-1}$. This resembles the spectrum of a six-coordinate cobalt(III) complex with trans arrangement of bromide ligands.$^{24}$

A reaction to oxidize the green solution, which was assumed to be Co(PN$_3$)Br$_2$, with bromine was also attempted. Addition of a few drops of bromine to the green solution produced an immediate
red-brown precipitate which was isolated and dried. The infrared spectrum of this compound indicates that the macrocycle PN3 has been formed. The molar conductivity of this solid in methanol is 124 cm²/ohm-mol if a formulation of [Co(PN3)Br₂]Br is assumed. This value is considerably higher than the values of 90-103 cm²/ohm-mol reported for macrocyclic complexes of the type [Co(CRH)X₂]ClO₄ in this solvent.²⁴ The analysis of this compound is higher in bromine and lower in carbon and hydrogen than would be expected for [Co(PN3)Br₂]Br.

C. The PN₃H Macrocycle


   The imine linkages in several all nitrogen donor macrocycles have been reduced by such reagents as NaBH₄ and PtO₂/H₂.²¹ Meso and racemic isomers have been isolated from the NaBH₄ reduction of the macrocycle, CR (43), which is similar to the PN₃ macrocycle. Since its nickel(II) complexes are based on a square planar arrangement of CR and PN₃ is not arranged in a planar manner around nickel(II), it was interesting to investigate the reduction products of complexes of PN₃ with NaBH₄ and PtO₂/H₂.

   Addition of NaBH₄ to an ethanol solution of Ni(PN₃)Cl₂, prepared in situ by the reaction of NiCl₂ with 2,6-diacetylpypyridine and PN₂, produces a black solution in an exothermic reaction. Addition of an ethanol solution of NH₄PF₆ to this solution and
removal of some of the solvents causes the separation of a yellow crystalline precipitate. The infrared spectrum of this compound is given in Figures 29 and 30. The peak at 3225 cm⁻¹ which is due to the NH stretch indicates that the macrocycle PN₃ has been reduced to give a complex of PN₃H, whose structure is shown in Figure 31.

An elemental analysis of this yellow solid indicates that it is [Ni(PN₃H)](PF₆)₂. Reaction of this compound with sodium iodide in an acetone-ethanol mixture leads to a rose colored crystalline material whose infrared spectrum is nearly identical to that of [Ni(PN₃H)](PF₆)₂, and the elemental analysis reveals this compound to be [Ni(PN₃H)I](PF₆). If [Ni(PN₃H)](PF₆)₂ is refluxed with NaCN in water an orange solid can be isolated. The infrared spectrum of this compound is given in Figures 32 and 33, and shows that the ligand PN₃H is still present in this material. However, no hexafluorophosphate is present as indicated by the absence of a strong absorption at 850 cm⁻¹ and peaks 3375 cm⁻¹ and 2100 cm⁻¹ indicate the presence of OH and CN in this compound. An elemental analysis of this orange material suggests that it is [Ni(PN₃H)OH]CN. Some characterization data for these nickel(II) complexes of PN₃H is presented in Table 8.

Molar conductivity values for [Ni(PN₃H)](PF₆)₂ and [Ni(PN₃H)OH]CN in acetonitrile are 286 and 129 cm²/ohm-mol respectively, which are reasonable values for 2:1 and 1:1 electrolytes, respectively. The value of 171 cm²/ohm-mol observed for [Ni(PN₃H)I](PF₆) in a 10⁻³M acetonitrile solution is higher than the values recorded for most
Figure 29. The Infrared Spectrum of [Ni(PN₃H)](PF₆)₂ as a Nujol Mull.
Figure 30. The Infrared Spectrum of $[\text{Ni(PN}_3\text{H)}](\text{PF}_6)_2$ as a Nujol Mull.
Figure 31. A nickel(II) Complex of PN$_3$H.
Figure 32. The Infrared Spectrum of \([\text{Ni(PN}_3\text{H)}\text{OH}]\text{CN}\) as a Nujol Mull.
Figure 33. The Infrared Spectrum of [Ni(PH$_2$H)OH]CN as a Nujol mull.
TABLE 8
SOME CHARACTERIZATION DATA FOR COMPLEXES OF PN₃H WITH Ni(II)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>$\Lambda_M \text{ cm}^2/\text{cm} \cdot \text{mol}^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="PF%E2%82%86">Ni(PN₃H)</a>₂</td>
<td>Yellow</td>
<td>286</td>
</tr>
<tr>
<td>[Ni(PN₃H)I]PF₆</td>
<td>Rose</td>
<td>171</td>
</tr>
<tr>
<td>[Ni(PN₃H)OH]CN</td>
<td>Orange</td>
<td>129</td>
</tr>
</tbody>
</table>

*aRecorded on 10⁻³M acetonitrile solutions.*
1:1 electrolytes in this solvent. This suggests some ionization of the iodide ion in this complex to form [Ni(PN₃H)]²⁺ cation in this solvent.

The electronic spectra of acetonitrile solutions and of the solid complexes which have been collected on these complexes of PN₃H are presented in Table 7. The electronic spectrum of [Ni(PN₃H)](PF₆)₂ both in acetonitrile solution and in the solid state at liquid nitrogen temperature consists of a single absorption at 24,100 cm⁻¹. The molar extinction coefficient is 220 obtained in acetonitrile solution, and suggests a square planar nickel(II) complex.

The electronic spectrum of [Ni(PN₃H)I]PF₆ in acetonitrile consists of a peak at 22,700 cm⁻¹ (ε = 220) and at 27,800 cm⁻¹ (ε = 1470). This suggests that the five-coordinate complex of the reduced macrocycle, PN₃H, prefers a square pyramidal ligand arrangement. This is in contrast to the unreduced PN₃ complexes which contain a trigonal bipyramidal ligand arrangement in solution. The solid state spectrum of [Ni(PN₃H)I]PF₆ at liquid nitrogen temperature consists of three transitions at 19,400(sh), 23,500 and 27,600 cm⁻¹. This spectrum is illustrated in Figure 34.

The magnetic moments of [Ni(PN₃H)](PF₆)₂ and [Ni(PN₃H)I]PF₆ are 0.71 and 0.44 B.M., respectively; these values are typical of diamagnetic nickel(II) complexes. Recently Sacconi has discussed the dependence of the spin state of the metal ion in five-coordinate
Figure 34. The Electronic Spectrum of [Ni(PN₃H)I]PF₆ in the Solid State at Liquid Nitrogen Temperature.
complexes on the nature of the donor atoms. Ligand donor sets were ordered according to the sum of their individual nucleophilic reactivity constants, \( n \), which is related to the polarizability and \( \pi \)-bonding properties of the nucleophiles. \[^{55}\] A good correlation between \( \Sigma n \) and spin state was demonstrated. The cross over point from high to low spin complexes for nickel(II) was about \( \Sigma n = 25.5 \). The \( \Sigma n \) calculated for \([\text{Ni}(\text{PN}_3\text{H})\text{I}]\text{PF}_6\) is 23.51. Although this is well within the high spin range, the complex is diamagnetic. The diamagnetism of \([\text{Ni}(\text{PN}_3\text{H})\text{I}]\text{PF}_6\) suggests that a macrocyclic arrangement of ligands produces a sufficiently strong field to cause electron pairing on nickel(II) when it would otherwise not be predicted. The geometry of the ligands, therefore, as well as the type of donor atoms must be considered when attempting to predict the spin state of the metal.

An nmr spectrum of \([\text{Ni}(\text{PN}_3\text{H})](\text{PF}_6)_2\) has been obtained in \( d_6 \)-DMSO and is shown in Figure 35. The data is summarized in Table 9. The doublet at 8.50 ppm can be assigned to the two methyl groups in \( \text{PN}_3\text{H} \). They are equivalent and split by the proton on the neighboring carbon with \( J_{\text{CHCH}} = 7 \text{ Hz} \). The spin-spin coupling constant was determined by running the spectrum of the same sample of \([\text{Ni}(\text{PN}_3\text{H})](\text{PF}_6)_2\) in \( d_6 \)-DMSO at both 60 and 100 MHz. A separation of 7 Hz between the two peaks of the doublet was observed at both field strengths. The equivalence of the methyl groups in \( \text{PN}_3\text{H} \) suggests that this ligand is in the meso form as shown in
Figure 35. The nmr Spectrum of \([\text{Ni(PN}_3\text{H)}](\text{PF}_6)_2\) in \(d_6\)-DMSO.
### TABLE 9

**NMR DATA FOR [Ni(PN$_3$H)](PF$_6$)$_2$**

<table>
<thead>
<tr>
<th>Chemical Shift</th>
<th>Description</th>
<th>Assignment</th>
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<tr>
<td>8.90</td>
<td>broad</td>
<td>c</td>
</tr>
<tr>
<td>8.50</td>
<td>doublet$^d$</td>
<td>CH$_3$</td>
</tr>
<tr>
<td>8.10</td>
<td>broad</td>
<td>c</td>
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<tr>
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<td>singlet</td>
<td>acetone</td>
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<tr>
<td>7.60</td>
<td>multiplet</td>
<td>c</td>
</tr>
<tr>
<td>7.30</td>
<td>multiplet</td>
<td>N-CH$_2$</td>
</tr>
<tr>
<td>5.85</td>
<td>multiplet</td>
<td>c</td>
</tr>
<tr>
<td>5.50</td>
<td>broad</td>
<td>amine NH</td>
</tr>
<tr>
<td>2.4-2.6</td>
<td>multiplet</td>
<td>phenyl</td>
</tr>
<tr>
<td>1.5-2.0</td>
<td>multiplet</td>
<td>pyridine</td>
</tr>
</tbody>
</table>

$^a$ Obtained in d$_6$-DMSO solution

$^b$ Reported in $\tau$ with TMS as an internal standard.

$^c$ Undetermined

$^d$ $J = 7$ Hz
Figure 36. The spike at 8.07 τ in the nmr of this compound has been shown to be due to acetone by adding a small amount of acetone to the nmr tube and observing an increase in the relative amount of this peak. The multiplets at 2.65 - 2.40 τ and 2.0 - 1.5 τ can be assigned to phenyl and pyridine ring protons, respectively. They integrate in a 5.2:3.0 ratio as would be expected. If a small amount of D2O is added to this nmr sample the broad peak at 5.50 τ decreases to about 1/3 its original intensity and a water peak appears at 6.75 τ. This peak, therefore, can be assigned to the amine protons which exchange with the D2O. Some of the broadening of the peak at 7.30 τ disappears when the amine protons are exchanged with deuterium. On this basis this peak is assigned to the methylene groups attached to the amines. The remaining peaks
in the nmr of this compound are unassigned.

When \([\text{Ni}(\text{PN}_3\text{H})\text{Cl}]\text{PF}_6\) is reduced with \(\text{PtO}_2/\text{H}_2\) and excess ammonium hexafluorophosphate is added a red-brown solid can be isolated. The nmr spectrum of this compound in \(\text{d}_6\)-DMSO is identical with that of the yellow \([\text{Ni}(\text{PN}_3\text{H})](\text{PF}_6)_2\) indicating that the meso isomer of \(\text{PN}_3\text{H}\) has also formed under these conditions. The infrared spectrum of this compound is identical to that of \([\text{Ni}(\text{PN}_3\text{H})](\text{PF}_6)_2\), except the bands at 850 and 560 cm\(^{-1}\) which can be assigned to the \(\text{PF}_6^-\) anion are considerably less intense in the red-brown compound. This indicates that the red-brown compound is the five-coordinate \([\text{Ni}(\text{PN}_3\text{H})\text{Cl}]\text{PF}_6\) complex. No further characterization on this compound has been done. These experiments indicate that the trigonal bipyramidal cation, \([\text{Ni}(\text{PN}_3\text{H})\text{Cl}]^+\) is reduced preferentially to the meso \(\text{PN}_3\text{H}\) complex.

2. **Formation of (S)PN\(_3\)H**

Refluxing \([\text{Ni}(\text{PN}_3\text{H})](\text{PF}_6)_2\) in water with an excess of sodium cyanide for two to three hours gives rise to a pale yellow solution. Extraction of this solution with a benzene solution containing sulfur gave (S)PN\(_3\)H. Evaporation of the benzene and extraction of the remaining solid with diethyl ether yields the pure (S)PN\(_3\)H. The infrared spectrum of this compound is shown in Figures 37 and 38. The NH stretching absorption is broad and appears at \(\approx 3400\) cm\(^{-1}\). As expected, this band is at higher frequency in (S)PN\(_3\)H than in
Figure 37. The Infrared Spectrum of (S)PN₃H as a Nujol mull.
Figure 38. The Infrared Spectrum of (S)PN₃H as a Nujol mull.
[Ni(PN₃H)](PF₆)₂ (νₐₕ = 3225 cm⁻¹). The absorption at 585 cm⁻¹, which is not present in the infrared spectrum of [Ni(PN₃H)](PF₆)₂ (see Figure 30), has been assigned to the P=S stretching mode. The remainder of the infrared spectrum of (S)PN₃H is similar to that of [Ni(PN₃H)](PF₆)₂ except for the absence of peaks due to the PF₆⁻ anion in the (S)PN₃H spectrum.

The proton nmr spectrum of (S)PN₃H was taken in CDCl₃ and is shown in Figure 39. The phenyl and pyridine multiplets are somewhat overlapping and are in the 3.20-2.64 τ and 2.64-2.20 τ regions, respectively. The doublet at 8.80 τ is due to the methyl protons which are coupled to the hydrogen on the adjacent carbon atoms (Jₗ=CH = 7 Hz). The peak at 7.80 τ is assigned to the amine proton. Addition of a drop of D₂O to this nmr sample causes this peak to disappear and a water peak to appear at 5.50 τ. The remainder of this spectrum is unassigned.

The 70 ev mass spectrum of (S)PN₃H has been obtained and the data are shown in Table 10. A parent peak with 100% relative abundance is observed at m/3 = 387. The remainder of the fragments given in this table are in agreement with the assigned structure.

3. Attempted Preparation of [Rh(PN₃H)](PF₆)

In order to condense the PN₃ macrocycle around Rh(I), it is necessary that some interaction occur between this ion and 2,6-diacetylpyridine. A dichloromethane solution of [Rh(COD)Cl]₂ was added, therefore, to an ethanol solution of 2,6-diacetylpyridine.
Figure 39. The nmr Spectrum of (S)PN₃H in d₆-DMSO.
TABLE 10

MASS SPECTRAL DATA OF \((S)PN_3H\)

<table>
<thead>
<tr>
<th>m/e</th>
<th>% relative abundance</th>
<th>Fragment</th>
</tr>
</thead>
<tbody>
<tr>
<td>389</td>
<td>8</td>
<td>((S)PN_3H)</td>
</tr>
<tr>
<td>388</td>
<td>26</td>
<td>((S)PN_3H - 2H)</td>
</tr>
<tr>
<td>387</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>385</td>
<td>10</td>
<td>((S)PN_3H - 2H)</td>
</tr>
<tr>
<td>299</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>258</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>256</td>
<td>76</td>
<td>((S)PhP((CH_2)_3NH_2)_2)</td>
</tr>
<tr>
<td>238</td>
<td>11</td>
<td>((S)PhP((CH_2)_3(NCH_2)_3))</td>
</tr>
<tr>
<td>224</td>
<td>18</td>
<td>((S)PhP((CH_2)_3)_2)</td>
</tr>
<tr>
<td>194</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>192</td>
<td>74</td>
<td>(PhP((CH_2)_3)_2)</td>
</tr>
<tr>
<td>183</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>162</td>
<td>16</td>
<td>(\text{PhCCH}_3)</td>
</tr>
<tr>
<td>160</td>
<td>67</td>
<td>&quot; - 2H</td>
</tr>
<tr>
<td>149</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>136</td>
<td>9</td>
<td>(\text{CCH}_2\text{CH}_3)</td>
</tr>
<tr>
<td>135</td>
<td>49</td>
<td>&quot; - H</td>
</tr>
</tbody>
</table>

\[\text{Diagram of molecule} \]
Table 10 (continued)

<table>
<thead>
<tr>
<th>m/e</th>
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<th>Fragment</th>
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<td>52</td>
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<td>76</td>
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</tr>
<tr>
<td>64</td>
<td>100</td>
<td><img src="chart6.png" alt="Fragment" /></td>
</tr>
</tbody>
</table>

*70 ev, analyzed for m/e>8%.
Removal of the dichloromethane led to the isolation of a yellow solid. This solid was shown by proton nmr and infrared spectra to be \([\text{Rh(COD)}\text{Cl}]_2\) indicating that no strong interaction between this Rh(I) complex and 2,6-diacetylpyridine occurred under these conditions. No further attempts to condense the PN₃ macrocycle around Rh(I) were tried.

The PN₃H macrocycle has been removed from Ni(II) with cyanide ion and can be extracted into benzene. A benzene solution of PN₃H obtained in this manner was combined with a benzene solution of \([\text{Rh(COD)}\text{Cl}]_2\). On heating a red oil came out of solution. It was dissolved in an ethanol-benzene mixture and was combined with an ethanol solution of ammonium hexafluorophosphate; this caused a yellow solution to form. A yellow solid was isolated on removal of some of the solvents. The infrared spectrum of this yellow compound is identical to that of \([\text{Ni(PN₃H)}]_2(\text{PF₆})_2\) which is shown in Figures 29 and 30. This suggests that it is \([\text{Rh(PN₃H)}]_2(\text{PF₆})_2\). The molar conductivity value calculated for this compound in acetonitrile assuming the formulation above is 110 cm²/ohm-mole. This value is lower than would be expected for a one to one electrolyte in acetonitrile, which suggests that this sample may be contaminated with a nonelectrolyte such as \([\text{Rh(COD)}\text{Cl}]_2\). No further characterization data has been obtained on this complex.

D. Bis(3-oxobutyl)phenylphosphine (PO₂)

Since the modification of the CR system to produce the
phosphorus containing macrocycle PN$_3$ has worked so well with nickel(II), it was hoped that further modifications of this system would allow a second phosphorus to be substituted in CR. Specifically the molecule bis(3-oxobutyl)phenylphosphine, PO$_2$, (45) was prepared

\[
\begin{align*}
\text{PO}_2
\end{align*}
\]

(45)

with the intention of substituting it for the 2,6-diacetlypyridine used in the preparation of CR or PN$_3$. The following reaction to form a macrocyclic ligand containing two phosphorus and two nitrogen donors is proposed.

The compound PO$_2$ was prepared by a free radical reaction between phenyl phosphine and vinyl methyl ketone in the presence of the free radical initiator AIBN. The infrared spectrum of PO$_2$
is shown in Figures 40 and 41. The strong absorption at 1720 cm\(^{-1}\) indicates that a carbonyl group is present in this compound. However, the absorption at \(\sim 3450\) cm\(^{-1}\) suggests that some enol form of this diketone may be present. The other absorptions in the infrared spectrum of this compound are consistent with the proposed structure except the weak peak at 2280 cm\(^{-1}\). This is most likely due to impurities in the sample resulting from the decomposition of the free radical initiator, AIBN.

The proton nmr spectrum of PO\(_2\) in CDCl\(_3\) which is shown in Figure 42 is also consistent with the structure proposed for this compound. It consists of a multiplet at 2.90 \(\tau\) which is due to the phenyl protons, a singlet at 7.99 \(\tau\) which can be assigned to the methyl protons, and a multiplet between 9.0 and 7.2 \(\tau\) which is due to the methylene protons. The phenyl to alkyl proton peaks integrate in a 5:13.9 ratio, nearly the expected 5:14 value. The absence of resonances in the 5 \(\tau\) region indicates that no vinyl methyl ketone starting material remains in this sample.

A 70 ev mass spectrum has been obtained on PO\(_2\) and is shown in Figure 43. A parent ion peak at m/e = 250 is the largest fragment observed in this spectrum. The most intense peak in this spectrum is m/e = 42 and is assigned to the CH\(_2\)CO fragment. The remaining fragments shown in Table 11 are reasonable for a compound with the structure which has been assigned to PO\(_2\).

In order to investigate the ability of PO\(_2\) to form Schiff bases, it was reacted with aniline. The proton nmr spectrum of the
Figure 40. The Infrared Spectrum of $\text{PO}_2$ Recorded Neat Between KBr Plates.
Figure 41. The Infrared Spectrum of P02 Recorded Neat Between KBr Plates.
Figure 42. The nmr Spectrum of PO₂ in CDCl₃.
Figure 43. The Mass Spectrum of P\textsubscript{02} Analyzed to 10\% Relative Abundance.
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<th>Positive fragment</th>
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<td>PO₂</td>
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<td>CH = CHCPPhCH₂CH₂COCH₃</td>
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<td>207</td>
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<td>PO₂ - CH₃CO</td>
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<tr>
<td>204</td>
<td>23</td>
<td></td>
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<td>193</td>
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<td>PO₂ - CH₃C, OH</td>
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<td>PO₂ - CH₃C, H₂O</td>
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Table 11 (continued)

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Table 11 (continued)

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<td>42</td>
<td>100</td>
<td>CH₂CO</td>
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<td></td>
</tr>
<tr>
<td>40</td>
<td>33</td>
<td></td>
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</tbody>
</table>

*70 ev spectrum, relative abundances > 10%.
product of this reaction was taken in d$_6$-DMSO. It consists of two broad multiplets at 2.8 $\tau$ and 8.0 $\tau$ and a broad peak at 5.44 $\tau$. The phenyl region integrates in a 1:1.5 ratio to the remainder of the spectrum. This indicates that only one aniline group has reacted with each PO$_2$. The peak at 5.44 $\tau$ may indicate the presence of vinyl protons in the product.

The mass spectrum has been obtained on the product of the reaction between PO$_2$ and aniline. The data analyzed for percent relative abundance > 10% is shown in Table 12. The largest fragments are clustered around m/e = 307 indicating the presence of only one aniline group in the product if it is assumed that the basic framework of PO$_2$ has remained intact. Two possible structures, (46) and (47), are worth considering for this compound. The broad peak at 5.44 $\tau$ in the proton nmr of this compound make structure (46) the most likely.
<table>
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<th>m/e</th>
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<td>206</td>
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Table 12 (continued)

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<td>54</td>
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<td>105</td>
<td>16</td>
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<tr>
<td>100</td>
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</table>
APPENDIX A
REATIONS OF NICKEL(II) AND PALLADIUM(II) WITH
BIS(2-(METHYLTHIO)-3,4,5,6-TETRAFLUOROPHENYL)PHENYLPHOSPHINE, fdsp

Introduction

In previous work$^{52,60}$ the author prepared the tridentate phosphorus-sulfur ligand fdsp (48). It was shown to behave as a bidentate ligand in complexes of the type Pd(fdsp)X$_2$ (X = Cl, Br, I, SCN), in which the phosphorus and only one sulfur are coordinated to the palladium. Two complexes of the general formula [Pd(fdsp-CH$_3$)X]$_2$ (X = Cl, SCN) were also isolated. In these complexes the methyl has been removed from one thioether group leaving a coordinated mercaptide anion. These compounds have been shown to be dimers and mass spectral evidence indicates that bridging mercaptide groups are present.

150
Reported here is some further work on this system including the preparation of $M(fdsp-\text{CH}_3)_2$ ($M = \text{Ni}, \text{Pd}$) and the solid state electronic spectra of $\text{Pd}(fdsp)X_2$ ($X = \text{Cl}, \text{I}$) at liquid nitrogen temperature. An infrared study of the effect of solvent on the mode of thiocyanate bonding in the complex $\text{Pd}(fdsp)(\text{SCN})_2$ is also presented.

**Experimental**

**A. General Procedures**

The ligand, $fdsp$, and its complexes were prepared as previously reported. All organic solvents and other reagents were the best commercial grades and were used without additional purification. The characterization measurements were performed as described in the main body of this dissertation.

**B. Preparation of the Complexes**

1. **Ni($fdsp$-\text{CH}_3)_2**

A solution of 0.30g (2 mmol) of NaI and 0.366g (1 mmol) of $\text{Ni(Clo}_4)_2\cdot6\text{H}_2\text{O}$ in ethanol was combined with a solution of 1.00g (2 mmol) of $fdsp$ in warm ethanol. After refluxing the solution for 15 min and reducing the volume of solvent, a green powder precipitated. The product was collected on a filter, washed with hot ethanol, and dried \textit{in vacuo}.

\textbf{Anal.} Calcd. for $C_{38}H_{16}F_{16}NiP_2S_4$: C, 44.51; H, 1.57; S, 12.51.

\textit{Found:} C, 44.28; H, 1.61; S, 12.55.
2. \( \text{Pd(fdsp-CH}_3\text{)}_2 \)

A 0.360 g (0.5 mmol) sample of \( \text{Pd(fdsp)(SCN)}_2 \) was combined with 0.250 g (0.5 mmol) of fdsp in 18 ml of ethanol and 2 ml of \( \text{N,N-dimethylformamide} \). The solution was refluxed for 0.5 hr; after the solution cooled to room temperature, an orange solid separated. The complex was collected on a filter and recrystallized from an ethanol-dichloromethane solution.

\text{Anal. Calcd. for } C_{30}H_{16}F_6P_2PdS_4: \text{ C, 42.53; H, 1.50; S, 11.95.}

\text{Found; C, 42.36; H, 1.75; S, 12.23.}

\text{Results and Discussion}

Complexes of the type \( \text{M(fdsp-CH}_3\text{)}_2 \) (\( \text{M = Ni, Pd} \)) are isolated with nickel(II) or palladium(II) in the presence of a suitable leaving group such as iodide or thiocyanate. These complexes are formed when a coordinated thioether in fdsp loses a methyl group to produce the corresponding mercaptide. It is interesting to note here that although complexes of fdsp could be isolated with Pd(II), no complexes of fdsp which were not demethylated could be isolated with Ni(II).

The electronic spectral data for these compounds, along with their other characterization data, appears in Table 13. Traces of the spectra are given in Figures 44 and 45. Comparison of these spectra with that of the square planar \( \text{Ni(fsp-CH}_3\text{)}_2 \), \text{which has maxima at } 16,400 \text{ cm}^{-1} (\varepsilon = 141) \text{ and } 24,000 \text{ cm}^{-1} (\varepsilon = 5180) \text{, indicates}
# TABLE 13

**CHARACTERIZATION DATA FOR THE COMPLEXES M(fdsp-CH₃)₂**

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<thead>
<tr>
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<th>Pd(fdsp-CH₃)₂</th>
<th>Ni(fdsp-CH₃)₂</th>
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</thead>
<tbody>
<tr>
<td><strong>color</strong></td>
<td>orange</td>
<td>green</td>
</tr>
<tr>
<td><strong>λₘ (cm²/ohm-mole)ᵃ</strong></td>
<td>0.01</td>
<td>0.42</td>
</tr>
<tr>
<td><strong>electronic spectrumᵇ</strong></td>
<td>19,880(126)</td>
<td>16,000(113)</td>
</tr>
<tr>
<td></td>
<td>26,600(7942)</td>
<td>25,100(5542)</td>
</tr>
<tr>
<td><strong>proton magnetic</strong></td>
<td>CH₃ — 8.25 (\tau)</td>
<td>d</td>
</tr>
<tr>
<td><strong>resonanceᶜ</strong></td>
<td>C₆H₅ — 2.42 (\tau)</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ Measured on \(~10^{-3}\)M nitromethane solutions

ᵇ Energy in \(\text{cm}^{-1}\); molar extinction coefficients are given in parentheses; measured on \(~10^{-3}\)M chloroform solutions

ᶜ Measured in \(\text{d}\)-chloroform solution.

ᵈ Not determined.
Figure 44. The Electronic Spectrum of Ni(fdsp-CH₃)₂ in CH₂Cl₂.
Figure 45. The Electronic Spectrum of Pd(fdsp-CH₃)₂ in CH₂Cl₂.
that these compounds also possess square planar structures.

Assuming an approximate $D_{4h}$ symmetry the low energy band in these two spectra can be assigned to the $^1A_{1g} \rightarrow ^1E_g$ transition.\textsuperscript{54} The high extinction coefficient of the higher energy band suggests that it is a charge transfer band. A similar band in the electronic spectrum of the square planar complex $[\text{Ni(sp)}_2](\text{ClO}_4)_2$ has also been assigned as a charge transfer band.\textsuperscript{61}

Due to insolubility in suitable solvents the nmr of $\text{Ni(fdsp-CH}_3)_2$ was not obtained. The nmr of $\text{Pd(fdsp-CH}_3)_2$ is interesting, but not totally understood. As can be seen in Table 14, both phenyl protons at 2.42 $\tau$ and methyl protons at 8.25 $\tau$ are observed. On the basis of the other known compounds of fdsp and fdsp-CH$_3$, the methyl resonance is shifted further upfield than would be predicted.\textsuperscript{52,60} The methyl resonance position for free fdsp is 7.59 $\tau$. In the case of $\text{Pd(fdsp)(SCN)}_2$, coordination of one of the thiomethyl groups shifts the methyl resonance downfield to 7.09 $\tau$. The single methyl resonance in this compound is explained by a rapid exchange of the coordinated and uncoordinated thiomethyl groups. If this compound is demethylated, the methyl resonance of the resulting compound, $[\text{Pd(fdsp-CH}_3](\text{SCN})]_2$, appears at 7.42 $\tau$. This is near the resonance position found for free fdsp, as would be expected, since the thiomethyl group which remains in this compound is uncoordinated. The two thiomethyl groups which remain
in the square planar complex, Pd(fdsp-CH₃)₂, are also uncoordinated and their methyl resonance would be predicted to appear near 7.59 τ. The resonance at 8.25 τ can only be explained at this time by assuming that the steric requirements of the molecule force the methyl groups to be held in such a position so as to be shielded by another part of the molecule resulting in a substantial upfield shift.

The solid state electronic spectra at liquid nitrogen temperature for the complexes Pd(fdsp)ₓ₂ (X = Cl, I) are given in Figures 46 and 47. In addition to the maxima at 20,600 and 25,200 cm⁻¹ which are also observed in the solution spectrum of the iodide compound, a low energy shoulder at 19,000 cm⁻¹ is observed. The spectrum of the chloride compound consists of a single maximum 26,700 cm⁻¹ and is identical to that of a chloroform solution of this compound.

In a study of the effects of solvent on the mode of thiocyanate bonding in Pd(AsPh₃)₂(SCN)₂ and Pd(AsPh₃)₂(NCS)₂ Burmeister has found that S-bonding is favored when the solvent polarity is high and N-bonding is favored when it is low. The isomers are distinguished by their characteristic νCN bands (S-bonded, 2119 cm⁻¹, s, sp; N-bonded, 2089 cm⁻¹, s, br). In similar experiments with Pd(II) complexes of phosphorus donors, however, Li and Meek have obtained the opposite results. The infrared experiments done in solvents of various polarities with
Figure 46. The Electronic Spectrum of Pd(fdsp)Cl₂ in the Solid State at Liquid Nitrogen Temperature.
Figure 47. The Electronic Spectrum of Pd(fdsp)I₂ in the Solid State at Liquid Nitrogen Temperature.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Group</th>
<th>$\nu_{\text{max}}$ (cm$^{-1}$)</th>
<th>A/CNS $10^4$ cm$^{-2}$ M$^{-1}$</th>
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<td>2082</td>
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<td></td>
<td></td>
<td>2117</td>
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<td>Acetone + 1% DMF</td>
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<td></td>
<td>2117</td>
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<td>b</td>
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<tr>
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<td>2116</td>
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</table>

*a* Measured on ~ $10^{-2}$M solutions.

*b* Not determined.
Pd(\(\text{fdsp}\))(\(\text{CNS}\))\(_2\) are reported in Table 14. The solvents are divided into two groups, A and B, according to the method of Burmeister.\(^{62}\) Group A solvents exhibit generally larger dipole moments, dielectric constants, and internal pressures than do Group B solvents.

Integrated intensities of the \(\text{C}=\text{N}\) peak have been calculated by the Ramsay method of direct integration,\(^{64}\) i.e.

\[
A = K \ln(\frac{I_0}{I_{\text{max}}}) \frac{v_{1/2}^a}{bc}
\]

where \(A\) is the integrated intensity, \(b\) is the cell thickness, \(c\) is the concentration of the solution, \(\ln(\frac{I_0}{I_{\text{max}}})\) is the apparent peak intensity, \(v_{1/2}^a\) is the apparent band width at peak half height, and \(K\) is the Ramsay constant (1.57). The integrated intensities obtained in this manner for N-bonded thiocyanate have been found to be 2-8 times larger than for S-bonded thiocyanates.

The results on Pd(\(\text{fdsp}\))(\(\text{CNS}\))\(_2\) conform with those obtained by Li and Meek, i.e., the greater occurrence of N-bonded thiocyanate was found with the more polar solvents and vice versa. In each case N-bonded thiocyanate is formed in solution whereas only S-bonded thiocyanate is found in the solid state spectrum of this compound.
THE REACTIONS OF NICKEL(II) AND PALLADIUM(II)
WITH SECONDARY PHOSPHINES

Introduction

Although the reactions of tertiary phosphines with Ni(II) and Pd(II) have been fairly thoroughly studied, similar reactions between Ni(II) and Pd(II) and secondary and primary phosphines have been, for the most part, neglected. Several reasons can be cited for this neglect. First, primary and secondary phosphines are more difficult to handle than are tertiary phosphines and are less readily available commercially. Second, their reactions may also not be as straightforward due to their greater ability as reducing agents. For instance, it has been shown that reactions of palladium halides with two or four equivalents of diphenylphosphine give several types of halogen containing palladium(II) complexes of diphenylphosphine. The reaction of tetrachloropalladate ion with excess diphenylphosphine in ethanol, however, produces a product which contains no halogen. This product was originally formulated as Pd(PHPh_2)_2(PPh_2)_2, but has recently been shown to be the palladium(0) compound, Pd(PHPh_2)_4. The palladium(II) starting material was reduced by the excess diphenylphosphine to produce the palladium(0) product.
Their potential as reducing agents, however, is but one characteristic which makes metal complexes with primary and secondary phosphine ligands worth investigating. The smaller size of these ligands may also make available complexes which were prohibited by the steric requirements of larger alkyl and aryl groups in tertiary phosphines. The most promising characteristic of primary and secondary phosphines as ligands, however, lies in the potential acidity of the P-H group. In a carefully chosen system the hydrogen attached to phosphorus can be removed by a base and the phosphide which is produced can be alkylated. This has been recently demonstrated with complexes of metal carboxyls and secondary phosphines. The following is a typical reaction.

\[
\begin{align*}
M(CO)_5(PPh_2H) & \xrightarrow{BuLi, THF} M(CO)_5(PPh_2)Li \\
& \xrightarrow{CH_3I} M(CO)_5(PPh_2CH_3) + LiI
\end{align*}
\]

\[
M = Cr \ (67\%) \\
M = Mo \ (52\%) \\
M = W \ (67\%)
\]

A suitable modification of this reaction may allow new and unusual phosphine ligands to be synthesized while coordinated in metal complexes.

The purpose of this investigation was to generate a secondary phosphide coordinated to nickel or palladium and then alkylate it,
generating a coordinated tertiary phosphine. Although this goal was not attained, several interesting reactions were discovered, an understanding of which will bring one closer to achieving the original goal.

Experimental

A. General Procedures

All syntheses were carried out under an atmosphere of dry nitrogen and all solvents were deaerated with nitrogen prior to use. Absolute ethanol, sodium tetrachloropalladate obtained from Engelhard Industries, butyl lithium in hexane, and the phosphines obtained from Pressure Chemical Co. were used without further purification. Ni(diphos)Br₂ was prepared according to the method described in the literature.⁶₈ Methyl iodide and 1,2-dibromoethane were dried over molecular sieves for 24 hrs before using. Characterization measurements were performed as described in the main body of this thesis.

B. Preparation of the Complexes

1. \([\text{Pd}(\text{PPh}_3\text{H})_4](\text{SO}_3\text{F})_2\)

To a filtered solution of 0.29g (1 mmol) of Na₂PdCl₄ in 20 ml of ethanol was added 0.74g (4 mmol) of diphenylphosphine. The resulting red solution was quickly filtered and 0.22g (2 mmol) of CH₃SO₃F was added. A yellow crystalline material separated slowly. It was collected by filtration, washed with ether, and dried in vacuo.
2. \([\text{Pd(PPh}_2\text{H)}_4]\)\((\text{BF}_4)_2\)

This compound was prepared in a manner analogous to the above compound using 5 ml of 48% HBF₄ solution in place of CH₃SO₃F.

**Anal. Calcd. for C₄₂H₄₀F₂P₂PdO₆S₂:**  C, 54.94; H, 4.23; S, 6.11; P, 11.80.

**Found:**  C, 54.71; H, 4.44; S, 5.95; P, 11.57.

3. **The reaction of Ni(diphos)Br₂ with lithium diphenylphosphide and methyl iodide**

To a solution of 0.372g (2 mmol) of diphenylphosphine in 10 ml of dry, deaerated THF was added 1.25 ml (2 mmol) of butyl lithium in hexane, resulting in the immediate formation of an orange solution. After stirring the orange solution for about 15 min, 0.53g (1 mmol) of Ni(diphos)Br₂ in 25 ml of THF was added causing a dark green air sensitive solution to form. This solution was refluxed for one hr and then cooled. A 0.125 ml (2 mmol) portion of methyl iodide was then added and the resulting solution was refluxed for one hr. On cooling, the solution appeared purple in color and a white precipitate was present. The precipitate was removed by filtration and some of the solvent was removed from the purple solution. After several hrs a dark red crystalline
precipitate appeared in the purple solution. It was isolated by filtration and dried in vacuo. Both solid state and solution electronic spectra have been used to identify the product as Ni(diphos)I₂.

4. The reaction of Ni(diphos)Br₂ with lithium diphenylphosphide and 1,2-dibromoethane

This reaction was identical to the above reaction except 0.09 ml (1 mmol) of 1,2-dibromoethane was added instead of methyl iodide. The product which was isolated was shown by an electronic spectrum to be Ni(diphos)Br₂.

5. The reaction of Ni(BF₄)₂·6H₂O and HPhP(CH₂)₃PPhH

To a deaerated solution of 0.68 g (2 mmol) of Ni(BF₄)₂·6H₂O in 20 ml of ethanol was added 1.04 g (4 mmol) of HPhP(CH₂)₃PPhH. The color of the solution changed immediately from green to red and a red oil appeared. After about an hour the red oil began to slowly dissolve and a gas was evolved. A yellow-orange precipitate then began coming out of solution. It was collected by filtration and dried in vacuo.

Results and Discussion

The careful reaction of 4 equivalents of diphenylphosphine with tetrachloropalladate in the presence of HBF₄ or CH₃SO₃F leads to the formation of tetrakis(diphenylphosphine)palladium(II). The electronic spectra of these compounds in the solid state or in dichloromethane solution consist of a single shoulder on the charge transfer band at about 27,600 cm⁻¹, indicating a square planar
arrangement of ligands. The electronic spectrum of these compounds in other solvents such as ethanol or acetonitrile rapidly changes from one which resembles the solid state spectrum to one which is identical to the spectrum of Pd(HPPh₂)₄ in these solvents.

The decomposition of these palladium(II) compounds in acetonitrile and nitromethane is also seen in the molar conductivity taken in these solvents. Freshly prepared solutions of [Pd(HPPh₂)₄](SO₃F)₂ and [Pd(HPPh₂)₄](BF₄)₂ give molar conductivities of 240 and 265 cm²/ohm-mole in acetonitrile, respectively, indicating 2:1 electrolytes. Values of 127 and 155 cm²/ohm-mol, respectively in nitromethane are also consistent with 2:1 electrolytes. These molar conductivities decrease with time, indicating decomposition. The decrease is more rapid in the case of the fluorosulfonate anion.

The infrared spectra of these compounds contain a very weak P-H stretch at about 2300 cm⁻¹. This is in sharp contrast to the infrared spectrum of Pd(HPPh₂)₄ which has a strong P-H stretch at 2280 cm⁻¹. Anion peaks due to tetrafluoroborate at 1065 cm⁻¹ and fluorosulfonate at 1285, 582, 569, and 425 cm⁻¹ can be assigned in the respective compounds. Peaks at 1082 and 768 cm⁻¹ which are characteristic of the fluorosulfonate anion are covered by ligand peaks.⁶⁹

The 70 ev mass spectrum of [Pd(HPPh₂)₄](SO₃F)₂ has been compared with that of Pd(HPPh₂)₄ in Figure 48. The two spectra are virtually identical with the exception of peaks originating from the
Figure 48. The Mass Spectra of \([\text{Pd}(\text{HPPH}_2)_4](\text{SO}_3\text{F})_2\) (top) and \(\text{Pd}(\text{HPPH}_2)_4\) (bottom).
fluorosulfonate ion. The relative percent abundances of the ions in the spectrum of Pd(HPPh₂)₄ are greater with respect to PPh (m/e = 108, 100%) than in the spectrum of the corresponding Pd(II) compound.

No meaningful nmr spectra of these compounds can be obtained due to decomposition in solvents in which they are sufficiently soluble.

The isolation of a square planar palladium(II) complex with diphenylphosphine may indicate that an intermediate of this type is involved in the reduction of palladium(II) with diphenylphosphine to give Pd(HPPh₂)₄.

The reactions of lithium diphenylphosphide with Ni(diphos)Br₂ leads to the production of a dark green, air sensitive product. Although this product has not been characterized, it is believed to be Ni(diphos)(PPh₂)₂. If this is indeed the intermediate, then it appears that reaction of this compound with alkyl halides leads to alkylation of the coordinated phosphide followed by displacement of the resulting tertiary phosphine by halide. In the reaction with methyl iodide an intermediate of the type [Ni(diphos)(PPh₂CH₃)₂]I₂ may be formed. The methyldiphenylphosphine ligands may then be displaced by the iodide ions to give Ni(diphos)I₂, the characterized product of this reaction. A similar reaction may occur with 1,2-dibromoethane to produce Ni(diphos)Br₂.
An alternate mechanism for this reaction involves the production of a Ni(0) intermediate. This mechanism appears to be operating in the reaction of what was reported to be Pd(HPPh₂)(PPh₂)₂ with methyl iodide. It was postulated that the product of this reaction, [PdI(PPh₂)(HPPh₂)]₂, was formed by reaction of the methyl group with one PPh₂ group in Pd(PPh₂)₂(HPPh₂)₂ followed by displacement of CH₃PPh₂ by iodide ion and loss of a diphenylphosphine group. It is now known, however, that what was thought to be Pd(PPh₂)₂(HPPh₂)₂ is the Pd(0) compound, Pd(HPPh₂)₄. A mechanism involving an initial oxidative addition of methyl iodide to Pd(HPPh₂)₄ can now be proposed:

\[
Pd(HPPh₂)₄ + CH₃I \xrightarrow{-2HPPh₂} \xrightarrow{CH₃} Pd(HPPh₂)₂ \xrightarrow{-CH₄} \]

\[
[PdI(PPh₂)(HPPh₂)]₂
\]

If a nickel(0) intermediate is involved in the above reactions, a mechanism involving oxidative addition of methyl iodide can be postulated as follows:

\[
Ni(diphos)(HPPh₂)₂ + CH₃I \xrightarrow{-2HPPh₂} \xrightarrow{CH₃} Ni(diphos)
\]

\[
+ CH₃I \xrightarrow{-C₂H₆} Ni(diphos)I₂
\]
With this mechanism, however, one must account for the production of Ni(diphos)(HPPh₂)₂ from Ni(diphos)Br₂ and lithium diphenylphosphide. This does not seem reasonable at the present time.

Two modifications of this reaction may prove to be very interesting. First, the use of an alkylating agent such as CH₃SO₂F which doesn't contain a coordinating anion may lead to isolation of a compound which contains a methyl group. Identification of the atom to which the methyl group is attached, i.e., Ni or P, should help identify the mechanism involved.

Second, it would be instructive to use LiPhP(CH₂)₂PPhLi in the place of LiPPh₂ in this reaction. If initial alkylation of the phosphorus atom is involved, diphos would be the less basic of the two bidentate ligands and should be displaced by the halide ions. Isolation and identification of Ni(CH₃PhP(CH₂)₂PPhCH₃)I₂ should be accomplished most readily.

The reaction between an ethanol solution of Ni(BF₄)₂·6H₂O and 1,3-bis(phenylphosphino)propane is poorly understood at the present time. The initial red product of this reaction slowly reacts with the evolution of a gas. An attempt was made to trap this gas and identify it by its mass spectrum. The mass spectrum of the gas was identical to that of the background, except the peak at m/e = 2 was increased in intensity. This indicates that the gas which is evolved is hydrogen. The insolubility of this compound has prevented its further characterization.
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