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LOW-SPIN TRANSITION METAL COMPLEXES OF A FLEXIBLE
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TRIDENTATE PHOSPHORUS LIGAND

DISSERTATION

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

by

John Charles Cloyd, Jr., B.A.

* * * * *

The Ohio State University
1970

Approved by

Advisor
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Studies in Coordination Chemistry. Professor Devon W. Meek
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INTRODUCTION

Transition metal coordination compounds\(^1\) occupy a unique and necessary niche in man's environment. Where would we be if there were no cobalt atom in vitamin B\(_{12}\). Chemists, most without the glint of anthropomorphism suggested above, have spent long years in the experimental and theoretical study of these types of compounds. One, among many, of the properties of transition metal complexes is their almost infinite variety of colors, which stimulates the chemist's intellect more than his psyche. It was soon discovered that for a complex, M\(_n\)L\(_p\), different colors were often associated with different values of \(n\). For this simplistic case, values of 4 and 6 for \(n\) are most amenable to theoretical interpretation of experimental results. The subject of this thesis is pentacoordination (\(n=5\)), and whereas the colors of these types of compounds are often more striking than others, the solution of the associated theoretical equations is most difficult. Consequently, more emphasis must be given to experimental evaluation.
This discussion will be concerned mainly with those examples of pentacoordination involving Ni(II) and Co(II) with either mono- or polydentate ligands containing Group VA and Group VIA donor atoms and anionic species such as the halogens, cyanide, thiocyanate, etc. Five-coordinate compounds involving metals in low oxidation states and noninnocent\textsuperscript{2} ligands are not readily amenable to ligand field interpretation and will not be of primary importance in this discussion. The heavier members of the cobalt and nickel triads will be considered where the preceding criterion is met, or where a comparison will be instructive.

Pentacoordinate 3d\textsuperscript{7} and 3d\textsuperscript{8} complexes can exhibit spin state isomerism.* In general, five-coordinate complexes containing ligands with the donors P, As, and cyanide are low spin; complexes containing O and N donors are high spin; complexes with S, Se, and halide ion may be either low or high spin. However the above classification is too inclusive to be rigorous. In an effort to find a qualitative means of differentiating between low and high spin complexes, Sacconi\textsuperscript{3} has suggested using either the overall electronegativities ($\Sigma_x$) or

* The phrase, spin state isomerism, as used in this discussion indicates the existence of both high and low spin species for a particular pentacoordinate complex. Pentacoordinate 3d\textsuperscript{n} configurations other than n= 7 or 8 may exhibit this phenomenon also, but they are not germane to the discussion.
overall nucleophilic reactivity constants ($\Sigma_{n,0}$). Thus, the $\Sigma_x$ and/or $\Sigma_{n,0}$ values for the donor atom set of a five-coordinate complex are computed and compared with the $\Sigma_x$ or $\Sigma_{n,0}$ values for a number of other complexes. A fairly definitive range is found for both $\Sigma_x$ and $\Sigma_{n,0}$ that tends to separate high and low spin Ni(II) and Co(II) complexes.

The existence of spin isomerism presents few problems in detection, since the existence of one or the other may be verified by determining the magnetic susceptibility of the compound. However, the assignment of a pentacoordinate complex as either trigonal bipyramidal (TBP) or tetragonal pyramidal (TP) is more difficult (Figure 1). Whether the

![Diagram of TBP and TP geometries](image)

**Figure 1.** The trigonal bipyramidal (TBP) and tetragonal pyramidal (TP) geometries. For an explanation of the angles adopted, see reference 23.

**TBP**

(Six) $\angle L_A-M-L_b = 90^\circ$
(three) $\angle L_e-M-L_e = 120^\circ$
(one) $\angle L_A-M-L_A = 180^\circ$

**TP**

(four) $\angle L_A-M-L_B = 100^\circ$
(four) $\angle L_B-M-L_B = 88^\circ$
(two) $\angle L_B-M-L_B = 160^\circ$
complex adopts the TBP or TP geometry seems to be governed by several factors, but the three most important appear to be the steric restrictions, any unique structural rigidity, and pi-bonding abilities of the ligand (restricting ourselves to those donors considered above). The steric considerations are most obvious; the ligand may inherently possess a geometry which forces the metal to adopt one of the two geometries. For example, Venanzi's QP (QP is tris(o-diphenylphosphinophenyl)phosphine) ligand, which possesses a trigonal symmetry, imposes its structure upon the \([\text{Co}(\text{QP})\text{Cl}]^+\) complex. A good pi-bonding ligand should favor the formation of a TP over a TBP, since pi-bonding is thought to be more important in the former geometry.\(^2\) Other factors to consider are (1) ligand-ligand repulsion, (2) crystal field stabilization energy (CFSE), and (3) crystal packing effects. With respect to (1), a TBP is more stable than a regular TP (i.e., one in which the apical to basal ligand-metal bond angle, \(I_a-M-I_b\), is 90°). When \(I_a-M-I_b\) is opened to ~100°,\(^6\) the resulting TP is only slightly less stable than the TBP.\(^7\) The CFSE, factor (2), for a TBP is only slightly less than the CFSE for the regular TP.\(^7\) Factor (3) is more difficult to assess quantitatively, and its relative contribution to the stabilization of either geometry may be as important as ligand steric constraints or pi-bonding factors (i.e., consider Ni(CN)\(_5^{-3}\)).\(^8\) However, if packing effects induce a geometry that is different in
the solid state from that in solution, comparison of the electronic spectra in the solid and solution states would indicate the change in geometries. These preceding factors will be considered in the discussion of the following pentacoordinate complexes, which have appeared in the recent literature.

A preliminary report on high spin \([\text{Ni}[(\text{CH}_3)_3\text{AsO}]_5]\)\(_2\)\(\text{ClO}_4\), containing five equivalent donors, shows the structure to be intermediate between a TBP and a TP. Steric bulkiness of the ligands is considered to be the main reason for the distortion.

Goedkin, et al., found that complexes of the composition \(\text{MC}_3(L^+)L'\), where \(L' = \text{H}_2\text{O}\) or \(\text{NH}_3\), \(M = \text{Co(II)}\) or \(\text{Ni(II)}\), and \(L^+ = [N(\text{CH}_2\text{CH}_2)_3-\text{NCH}_3]^+\), were high spin TBP's. An X-ray structural analysis confirmed this geometry, with the three chlorine atoms occupying the trigonal plane, and \(L'\) and \(L^+\) occupying the apical positions. Packing effects undoubtedly played a part in the isolation of \([\text{Ni}_2\text{Cl}_8]^4^-\) and \([\text{NiCl}_4(\text{ROH})]^2^-\) (\(R = \text{CH}_3\) and \(\text{C}_2\text{H}_5\)) by the same authors, who used the large divalent cations, \([\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{NH}]^2^+\) and \([\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2)_2\text{NCH}_3]^{2^+}_\text{H}\). Through spectral and magnetic data, the divalent anion was shown to be high spin, five-coordinate, whereas the tetravalent anion was considered to possess a high spin, five-coordinate, binuclear structure utilizing chlorine bridges.

A series of five-coordinate \(\text{ML}_2\text{X}_2\) complexes have been isolated, where \(M = \text{Co(II)}, \text{Ni(II)}, \text{Pd(II)},\) and \(\text{Pt(II)}\), \(\text{L}=9\)-alkyl-9-phosphafluorenes,
and X=halide or cyanide. Preliminary X-ray structural data\textsuperscript{13} indicate that these NiL\(_3\)(CN)\(_2\) complexes possess a distorted TP structure. This is compatible with the bulkiness of this phosphine, but is nevertheless somewhat striking because cyanide preferentially occupies the apical positions of a TBP in other complexes of the NiL\(_3\)(CN)\(_2\) type. The other Ni(II) and Co(II) complexes are presumed to have the same stereochemistry. The TBP structure assumed for the Pd(II) and Pt(II) complexes is consistent with the observation that pentacoordinate Pd(II) complexes\textsuperscript{14} are usually more TP than TBP than their Ni(II) counterparts, presumably as a result of increased crystal field effects. Palladium(II) and platinum(II) complexes containing N,N'-disubstituted thio- or seleno-ureas of the formulation [ML\(_4\)X]\(^+\), (X=halogen), have been isolated and possess a TP structure as indicated\textsuperscript{15} by spectral studies.

Several authors\textsuperscript{16-23} have studied the formation of the pentacoordinate species M(PR\(_3\))\(_3\)X\(_2\), where M=Co(II) or Ni(II), X=halogen or cyanide, and R=alkyl or aryl. The complexes are TBP in general, as deduced from X-ray structural and/or electronic spectral investigations, although there are some exceptions. The reaction\textsuperscript{18} between NiX\(_2\) and P(CH\(_3\))\(_3\) produces NiL\(_2\)X\(_2\), NiL\(_3\)X\(_2\), [NiL\(_3\)X]Y, or NiL\(_4\)X\(_2\) (Y=C\(_{10}\)\(_4\)\(^-\)) depending on the anion X. Subsequently, Chastain and co-workers\textsuperscript{17}
made an extensive study of the spectral properties of Ni[P(CH₃)₃]₂Br₂ and concluded that it is a distorted TBP. Two papers¹⁸,¹⁹ reported the formation of the distorted TBP's Ni₃(CN)₂, where L=RₚₙP(OR)₃⁻-n and n=0⁻³, R'=C₆H₅, R=C₆H₅ or alkyl. Distorted TBP structures were suggested on the basis of electronic and infrared spectral measurements with the cyanides occupying the apical positions. It is interesting to note that Ni₃(CN)₂ was not isolated when L=P(C₆H₅)₃,¹⁸ whereas the corresponding complex with L=P(OC₆H₅)₃¹⁹ apparently does not dissociate in solution.

Alyea and Meek²⁰ investigated the formation of Ni₃X₂ from NiL₂X₂ and excess L; L is C₆H₅P(CH₃)₂ or C₆F₅P(CH₃)₂, X is halogen, cyanide, thiocyanate, or nitrite. They found that TBP Ni₃X₂ complexes were formed when L=C₆H₅P(CH₃)₂; however, when L=C₆F₅P(CH₃)₂ only X=cyanide gave a pentacoordinate complex. Dissociation constants for the reaction

Ni₃L₂X₂ + L → Ni₃L₃X₂

in dichloromethane solution showed that the ability to form pentacoordinate complexes depended on the anion, and decreased in the order CN⁻>Br⁻>Cl⁻>NO₂⁻>NCS. The inability of C₆F₅P(CH₃)₂ to form corresponding pentacoordinate complexes was interpreted in terms of its different electronic and steric requirements. A similar stability study²¹ was made for the reaction

Ni(PR₃)₂(CN)₂ + PR₃ → Ni(PR₃)₃(CN)₂

and it was found that the stability of the pentacoordinate species
decreased in the order \( \text{CsH}_5 \text{P(C}_2\text{H}_5)_2 \gg (\text{CsH}_5)_2\text{PC}_2\text{H}_5 > \text{P(C}_2\text{H}_5)_3 > \text{P(n-C}_4\text{H}_9)_3 > \text{P(n-C}_3\text{H}_7)_3 \). The structural assignments in the equilibrium constant studies\(^{20,21}\) were confirmed by Stalick and Ibers through X-ray structural determinations. Both \( \text{Ni[CsH}_5\text{P(OC}_2\text{H}_5)_2\text{]_3(CN)_2} \)\(^{22}\) and \( \text{Ni[CsH}_5\text{P(CH}_3)_2\text{]_3(CN)_2} \)\(^{23}\) possess a slightly distorted TBP structure (Figure 2), and the former complex is more distorted than the latter.

![Figure 2](image-url)

**Figure 2.** The structures of (a), \( \text{Ni[CsH}_5\text{P(OC}_2\text{H}_5)_2\text{]_3(CN)_2} \); and (b), \( \text{Ni[CsH}_5\text{P(CH}_3)_2\text{]_3(CN)_2} \); reproduced from references 22 and 23. Note that the major difference between the two structures resides in the three P-Ni-P equatorial angles.
The structure of NiBr$_3$[C$_6$H$_5$P(CH$_3$)$_2$]$_2$·0.5NiBr$_2$[C$_6$H$_5$P(CH$_3$)$_2$]$_2$·C$_6$H$_5$ is interesting not only because it contains both Ni(II) and Ni(III), but because the NiBr$_3$[C$_6$H$_5$P(CH$_3$)$_2$]$_2$ unit is a fairly regular TBP, in spite of the distortions that might have been expected from the Jahn-Teller effect on a low spin d$^7$ complex.

The complex Ni[(C$_6$H$_5$)$_2$PH]$_3$I$_2$ has recently been shown to exhibit only the normal amount of temperature independent paramagnetism, in contrast to the paramagnetism (1.48 B.M.) that was reported initially. The identity of the supposed paramagnetic impurity in the original sample still remains a mystery, but it is much easier to explain the diamagnetism of Ni[(C$_6$H$_5$)$_2$PH]$_3$I$_2$ rather than its paramagnetism, on the basis of a comparison with similar complexes.

Steric factors probably dominated when trimorpholinophosphine failed to form pentacoordinate NiL$_3$X$_2$. Only pseudo-tetrahedral NiL$_2$X$_2$ complexes were isolated.

Five-coordinate, usually TF, complexes are formed by the addition of a fifth ligand to the square planar ML$_2$$^{n+}$, where L is a bidentate ligand: if L is uncharged, $^{n=2}$; if L is uninegative, $^{n=0}$. A number of complexes have been formed with 1,2-dithiolenes and related ligands, the metals involved exhibiting various oxidation states. These compounds have been reviewed extensively. Related
bidentates of the type \((\text{C}_6\text{H}_5)_2\text{PS}_2^-\), \((\text{C}_2\text{H}_5)_2\text{PS}_2^-,\) \((\text{C}_6\text{H}_5\text{CH}_2\text{OCS}_2^-)\) or \((\text{C}_2\text{H}_5)_2\text{NCS}_2^-,\) form the square planar \(\text{ML}_2\) complexes, \((\text{M}=\text{Ni(II)},\) \(\text{Pd(II)},\) or \(\text{Pt(II)}\)) and the corresponding pentacoordinate TP adducts with monodentate amines and phosphines. The structure of the adduct of quinoline with \(\text{Ni}[\text{S}_2\text{P(\text{C}_2\text{H}_5)_2}]\) is a distorted TP\(^{32}\). Whereas most of the adducts of \(\text{ML}_2\) and bidentate amines are hexacoordinate, the 2,9-dimethyl-1,10-phenanthroline adduct of \(\text{Ni}[\text{S}_2\text{P(\text{OCH}_3)_2}]\) has a distorted TP\(^{33}\) structure with both nitrogen atoms coordinated and one sulfur atom uncoordinated.

The complexes of several bidentate ligands containing two nitrogen donors or one nitrogen donor and another different donor have been investigated.\(^{34-41}\) 8-Dimethylarsinoquinoline\(^{34}\) forms four-, five-, and six-coordinate \(\text{PdLX}_2\), \((\text{PdL}_2\text{X})\text{ClO}_4\), and \(\text{PdL}_2\text{X}_2\) complexes, respectively. The corresponding \(\text{CoL}_2\text{X}_2\) complexes\(^{35}\) are too insoluble for solution studies, and their stereochemistry has not been assigned unambiguously. Only the four-coordinate \(\text{PdLX}_2\) complexes\(^{36}\) were isolated with the bidentate ligand \((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{N(\text{C}_2\text{H}_5)_2}\), perhaps indicating differences in donor strengths of As versus P and tertiary amine nitrogen versus pyridyl nitrogen. The isolation of only pseudo-tetrahedral \(\text{ML}_2\) \((\text{M}=\text{Co(II)}\) and \(\text{Ni(II)},\) \(\text{X=halogen})\), was attributed to the steric restrictions of \(\text{L},\) 2-methyl-8-methylthioquinoline. With 8-methylthioquinoline,\(^{38}\) only the octahedral \(\text{ML}_2\text{X}_2\) complexes were isolated. The ligand 2-methyl-6-amino methylpyridine,\(^{39}\) however,
forms the four-, five-, and six-coordinate complexes, $[\text{CoL}_2](\text{ClO}_4)_2$ (CoL$_2$X)ClO$_4$, and CoL$_2$X$_2$, respectively, demonstrating that electronic and steric effects can indeed be quite subtle. Similar subtle effects are found in the NiL$_2$X$_2$ complexes ($L$ is 2-diphenylphosphinomethylpyridine) which are octahedral when $X=\text{Cl}^-$ or CNS$^-$, square planar when $X=\text{ClO}_4^-$, and pentacoordinate when $X=\text{Br}^-$ or I$^-$. Similar CoL$_2$X$_2$ complexes are octahedral when $X=\text{Cl}^-$, Br$^-$, or CNS$^-$, and pentacoordinate when $X=\text{ClO}_4^-$ or I$^-$. The corresponding complexes of 2-diethylphosphinomethylpyridine presumably behave in an analogous fashion.$^{41}$

The complexes of bidentate phosphorous ligands$^{42-55}$ and metal salts have been studied extensively and are often unique. For instance, pi-methallyl(bis-1,2-diphenylphosphinoethane)nickel(II) bromide$^{42}$ is made readily and is air stable for indefinite periods. A recent X-ray structural determination has established its geometry as TP$^{42}$ (Figure 3). The same ligand has been used to isolate the nickel hydrides (NiLiH)$_2$$^{43}$ and (INiH)$_2$, and to give the Ni$_{1.5}$(CN)$_4$ complex.

Figure 3. Inner coordination sphere of pi-methallyl[bis-1,2-(diphenylphosphino)ethane]-nickel bromide.
A number of ligands of the general formula \((C_6H_5)_2P(CH_2)_nP(C_6H_5)_2\) have been used as complexing agents for nickel(II). The ligand \((C_6H_5)_2P(CH_2)_nP(C_6H_5)_2\) \((n=1)\) behaves as a monodentate with nickel(II) halides, but it can also function as a bidentate\(^\text{48}\) whenever the anion does not coordinate readily; thus, the four-coordinate complexes \([\text{NiL}_2]Y_2\), where \(Y=\text{NO}_3^-, \text{ClO}_4^-,\) or \(\text{BF}_4^-\) have been characterized. Addition of halide to these complexes causes the ligand to revert to its monodentate status.

Although \((C_6H_5)_2P(CH_2)_2P(C_6H_5)_2\) \((n=2)\) readily forms \(\text{NiLX}_2\), bischelated five-coordinate species have never been satisfactorily identified\(^\text{47, 48}\). The nonexistence of \([\text{NiL}_2X]^+\) has been attributed to steric effects of the ethylene linkage and the ortho phenyl hydrogens\(^\text{48}\). When \(X=\text{CN}^-\), however, the TBP, binuclear \(\text{NiL}_{1.5}(\text{CN})_2\) complex is obtained\(^\text{49}\). The ligands cis-1,2-bis(diphenylphosphino)ethylene\(^\text{48}\), \(\text{RHPCH}_2\text{CH}_2\text{PR}(\text{R}=C_6H_5 \text{ or } C_2H_5)\)\(^\text{50}\), and \((C_2H_5)_2P(CH_2)_2P(C_2H_5)_2\)\(^\text{51}\) which are free of the steric constraints mentioned above, readily form penta-coordinate, TP, \([\text{NiL}_2X]^+\) complexes. The mixed phosphorous-sulfur bidentate, \((C_2H_5)_2P(CH_2)\text{CH}_2\text{SC}_2H_5\)\(^\text{52}\) behaves similarly. The four-coordinate \(\text{NiLX}_2\)\(^\text{53}\) where \(I=2,2'\)-biphenylenebisdiethylphosphine, in solution are tetrahedral for \(X=I^-\), square planar for \(X=\text{CNS}^-\), and exhibit a square planar-tetrahedral equilibrium for \(X=\text{Cl}^-\) and \(\text{Br}^-\). No pentacoordinate \([\text{NiL}_2X]^+\) complexes were isolated. Only tetrahedral \((X=\text{halogen})\) or square planar \((X=\text{CNS}^-)\) \(\text{NiLX}_2\) complexes were isolated
with \( L = \left( C_6H_5 \right)_2P(CH_2)_nP(C_6H_5)_2 \), \( n=4,5 \). The Co(II) and Ni(II) cyanide complexes with these ligands are TBP binuclear,\(^{49,55}\) the same formulation as the NiL\(_{1.5}\)(CN)\(_2\) complex with \( L = \left( C_6H_5 \right)_2PCH_2CH_2P(C_6H_5)_2 \).

A large number of tridentate Schiff base ligands (Figure 4) have been synthesized recently.\(^{56,57}\) In general, the Co(II) and Ni(II) complexes with these ligands are high spin and possess a pentacoordinate structure that is usually described as being intermediate between a TP and a TBP. Low spin complexes have been obtained with ligands that contain softer donors.\(^{58}\) One ligand of this latter type has been reported to give only octahedral Ni(II) and exclusively Co(III) instead
of the expected Co(II) complexes. The intermediate geometry is illustrated in the five-coordinate complex, dibromo-[1-(o-methoxyphenyl)-2,6-diazaocetane]-nickel(II).

The tridentate amine ligand $R'N(CH_2)$ forms high spin five- and six-coordinate complexes with Ni(II), depending on the nature of $R$ and $R'$. The structure of dibromo-[6,6'-dimethyldi-(2-pyridylmethyl)amine-NNN]-nickel(II) is intermediate between a TBP and a TP. The related ligands $HN(CH_2CH_2-\text{amine})_2$ and $S(CH_2CH_2-\text{amine})_2$ are reported to form pentacoordinate high spin complexes with Co(II) and Ni(II). Of the tridentate amine ligands, $CH_2N[CH_2CH_2N(CH_3)_2]$ forms only pentacoordinate high spin NiLX$_2$ complexes, whereas the parent non-methylated amine, $NH(CH_2CH_2NH_2)_2$, forms only octahedral $[NiL_2]^{2+}$. The ligand $HN(CH_2CH_2N(C_5H_5)_2)_2$ forms pentacoordinate high spin CoLX$_2$, and it was suggested that the gross five-coordinate geometry of these complexes does not greatly affect the electronic structural properties. This fact has been demonstrated by the structural determination of CoLCl$_2$ and Co$\{CH_3N[CH_2CH_2N(CH_3)_2]_2\}Cl_2$. The structure of the former complex is distorted from a TBP more than the latter (i.e., is more nearly a TP), but the gross electronic spectral properties of both complexes has been interpreted in terms of an idealized $D_{3h}$ model.

The ligands $RN[CH_2CH_2P(C_6H_5)_2]_2$, $R=H$, CH$_3$, and cyclo-C$_6$H$_{11}$, form MLX$_2$ with Co(II) and Ni(II) halides. As the R group becomes more
bulky, the nickel(II) complexes vary from low spin, five-coordinate to square planar; the cobalt(II) complexes vary from low spin, five-coordinate to tetrahedral. The structure of Ni[HNCH₂CH₂P(C₆H₅)₂]₂Br₂ is a distorted TP. The related ligands 2,6-bis(2-diphenylphosphinoethyl)pyridine and E[CH₂CH₂As(C₆H₅)₂]₂, E=HN and S, also form NiLₓ₂, presumably with the same stereochemistry. The complexes Ni[HNCH₂CH₂P(C₆H₅)₂]₂Br₂ and dichloro-[2,6-bis(2-diphenylphosphinoethyl)pyridine]nickel(II) contain nickel(II) in both singlet and triplet ground states. The iodide complex of HNCH₂CH₂P(C₆H₅)₂ and the bromide and iodide complex of 2,6-bis(2-diphenylphosphinoethyl)-pyridine are diamagnetic. If one of these types of tridentate ligands contain two soft terminal donor atoms (e.g., P, As) and a hard central donor atom (oxygen), then only the two terminal donors are coordinated to the metal (nickel), and the complexes are pseudo-tetrahedral.

The X-ray structural determination of Ni[C₆H₅P(o-C₆H₄SCH₃)]₂I₂ shows the nickel atom to reside in an almost perfect TP geometry (Figure 5). The authors had originally suggested a TBP structure for this complex on the basis of its visible electronic spectrum.

Cobalt(II) complexes with the tridentate phosphorous ligand, CH₃C[CH₂P(C₆H₅)₂]₃, have been reported recently to be tetrahedral, whereas the corresponding nickel(II) complexes are pentacoordinate.
Figure 5. The inner coordination sphere of \([\text{Ni}(\text{DSP})I_2]\), DSP is bis(o-methylthiophenyl)phenylphosphine. Reproduced from reference 75. Note that the most significant distortions from TP geometry are the angles \(S_1-Ni-P\) and \(S_1-Ni-I_2\), a result of the short \(S-P\) chelate bite.

in the solid state, undergoing a slow isomerization to a square planar species in solution. The \(\text{Ni}LX_2\) complexes are presumed to contain TP coordinated nickel in which one phosphorous donor is bound weakly to the apical position.

The macrocyclic tetradeinate Schiff base ligand formed from 3,3'-diaminodipropylamine and 2,6-diacetylpypyridine (CR, Figure 6) forms the low spin pentacoordinate \(\text{Co}(\text{CR})X_2\). The geometry is assumed to be distorted TBP about cobalt, deduced from the electronic spectra. The corresponding nickel complexes are paramagnetic with the exception of
Ni(CR)Br₂·H₂O which is diamagnetic and possesses a distorted TP structure. The water molecule is hydrogen bonded to the bromine atom that is coordinated to the nickel atom, apparently reducing its donor strength sufficiently to give the low spin complex. Katovic’ and coworkers recently used the coordination template effect to prepare a low spin five-coordinate nickel(II) complex, in which the ligand is a polycyclic pentadentate. At least one low spin pentacoordinate nickel(II) complex is known with a tetradeinate sulfur macrocycle. These two low spin pentacoordinate complexes of the tetradeinate macrocycles are unusual, since high spin complexes are usually formed with predominately nitrogen and sulfur donors.
DuBois and Meek\textsuperscript{81} have reported the \([\text{MLX}]^+\) complexes with the open-chain tetrادentate 1,3-bis(diphenylphosphinopropylthio)propane. The nickel complexes are TBP, whereas the palladium, platinum, and cobalt complexes are TP. The different geometries within the nickel triad most probably are related to the increase in the CFSE upon descending the triad, whereas the geometry of the cobalt complexes may result from the Jahn-Teller effect. Only four-coordinate Pd(II) complexes were reported with a similar linear tetradenate.\textsuperscript{82}

The advent of the tetrادentate 'tripod-like' ligands provided well characterized examples of pentacoordinate TBP metal complexes, and since the description of complexes with P[o-C\textsubscript{6}H\textsubscript{4}P(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}]\textsubscript{3} \textsuperscript{83} and As[o-C\textsubscript{6}H\textsubscript{4}As(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}]\textsubscript{3} \textsuperscript{84} a number of other similar ligands that contain different donors and chelate lengths have been synthesized. 'Tripod-like' tetrادentate ligands that contain N, O, and S donors where the apical donor remains N and the peripheral donors are varied, form high spin pentacoordinate complexes with Co(II) and Ni(II).\textsuperscript{85}

The presence of a tetrادentate 'tripod-like' ligand does not necessarily enforce pentacoordination; for example the ligands N(CH\textsubscript{2}CH\textsubscript{2}OH)\textsubscript{3} \textsuperscript{86} P(CH\textsubscript{2}CH\textsubscript{2}CN)\textsubscript{3} \textsuperscript{87} P[o-C\textsubscript{6}H\textsubscript{4}N(CH\textsubscript{3})\textsubscript{2}]\textsubscript{3} \textsuperscript{88} and P(\begin{figure}\textsubscript{H} N \end{figure})\textsubscript{3} \textsuperscript{89} form complexes with Co(II) and Ni(II) that are not five-coordinate.

Varying the donors of the tripod ligands not only leads to different spin states but sometimes to unexpected variations in the
geometry of the complex. The structure of Ni\{(CH$_3$OCH$_2$CH$_2$)N[CH$_2$CH$_2$P(C$_6$H$_5$)$_2$]$_2$\}I$^{90}$ is a distorted TP with the oxygen atom in the apical position, providing 'a small but significant perturbation' of that site. The complex Co[N(CH$_2$CH$_2$P(C$_6$H$_5$)$_2$)$_3$Cl]PF$_6$$^{91}$ also possesses a weakly bound fifth donor, but in this case that donor is the apical nitrogen, giving a capped tetrahedral structure. The concept of average environment is demonstrated in the structure of Co(CH$_2$SCH$_2$CH$_2$)-N[CH$_2$CH$_2$N(C$_6$H$_5$)$_2$]$_2$(CNS)$_2$$^{92}$ which is a distorted TBP with five nitrogen donors, the sulfur atom remaining uncoordinated. The crystal structures of Ni[N(CH$_2$CH$_2$P(C$_6$H$_5$)$_2$)$_3$I]$^{93}$ and Ni[P(o-C$_6$H$_4$SCH$_3$)$_3$Cl]ClO$_4$ $^{94}$ (Figure 7) demonstrate quite regular TBP geometries.

Figure 7. A perspective drawing of [Ni(TSP)Cl]$^+$; TSP= tris(o-methylthiophenyl)phosphine. Reproduced from reference $^{94}$. Note that the distortions from TBP geometry are in the same direction as those for Ni$_3$(CN)$_2$ (see Figure 2).
The Ni(II) complexes of $\mathrm{N}[\mathrm{CH}_2\mathrm{CH}_2\mathrm{As}(\mathrm{C}_6\mathrm{H}_5)_2]_3$, (NAS$_3$)$_2$, and Co(II) and Ni(II) complexes of $\mathrm{N}[\mathrm{CH}_2\mathrm{CH}_2\mathrm{P}(\mathrm{C}_6\mathrm{H}_5)_2]_3$, (NP$_3$)$_2$, have been reported. Whereas the [NiLX]$^+$ complexes of NAS$_3$ and NP$_3$ are low spin, the [Co(NP$_3$)X]$^+$ cases are all high spin, except [Co(NP$_3$I)]I which is high spin when $\mathrm{Y} = \mathrm{B}(\mathrm{C}_6\mathrm{H}_5)_4$ and low spin when $\mathrm{Y} = \mathrm{I}^-$. Replacing one of the peripheral arsenic or phosphorous donors with nitrogen (donor set $\mathrm{N}_2\mathrm{P}_2$ and $\mathrm{N}_2\mathrm{As}_2$) again causes a change in the spin state. All of the Co(II) complexes are high spin, whereas the Ni(II) complexes are high spin with the donor set $\mathrm{N}_2\mathrm{P}_2\mathrm{X}$ and are low spin with the donor set NP$_3\mathrm{X}$ (X=halogen).

The potentially tetradentate ligand C[CH$_2$P(\mathrm{C}_6\mathrm{H}_5)_2]_4 forms only binuclear four-coordinate complexes with Ni(II), whereas Co(II) forms the pentacoordinate CoL$_2\mathrm{X}_2$ (X=halogen) with one phosphorous atom uncoordinated.

Two similar ligands $\mathrm{O}_2\mathrm{CCH}_2\mathrm{N}[\mathrm{(CH}_2\mathrm{)}_3]_2\mathrm{CH}_2\mathrm{CO}_2$ and H$_2\mathrm{NCH}_2\mathrm{CH}_2\mathrm{N}[\mathrm{(CH}_2\mathrm{)}_3]_2\mathrm{NCH}_2\mathrm{CH}_2\mathrm{NH}_2$ give high spin TP complexes with Ni(II), presumably because of blockage of the sixth position by the amine ring linkage.

The pentadentate amine ligand, $(\mathrm{CH}_2\mathrm{CH}_2)_2\mathrm{NCH}_2\mathrm{CH}_2\mathrm{N}(\mathrm{H})\mathrm{CH}_2\mathrm{CH}_2\mathrm{N}$, gives a high spin distorted TP with Ni(II). Recently, a low spin pentacoordinate structure has been suggested for a Ni(II) complex with a ligand containing the donor set O$_2\mathrm{N}_2\mathrm{S}$.
Examination of the preceding examples demonstrates that in order for pentacoordination to be achieved, one must choose the correct donors in a favorable topological array. Variations of these two main criteria may lead to isomerism in spin states and pentacoordinate geometries, or to quite different coordination patterns.

If we examine only low spin complexes, pentacoordinate Ni(II) may assume either TBP\textsuperscript{94} or TP\textsuperscript{75} geometries. Until recently, the only method of differentiating between TBP and TP geometries was to compare the visible electronic spectra with complexes of known structures;

\[ E \quad d^8 \]

\[ a_1 \quad (d_{z^2}) \]

\[ e \quad (d_{x^2-y^2}, d_{xy}) \]

\[ e \quad (d_{xz}, d_{yz}) \]

\[ D_{3h} \text{ or } C_{3v} \text{ symmetry} \]

Figure 8. Correlation diagram for \( d^8 \) in field of \( D_{3h} \) or \( C_{3v} \) symmetry.
however, two new spectral techniques have been helpful recently. Ferraro\textsuperscript{103} has shown that the $1_A \rightarrow 1_E$ transition of Ni(II) TBP complexes (Figure 8) is substantially more sensitive to pressure than the corresponding absorption of TP and square planar complexes (Figure 9). He finds that the ratio $\Delta v/\Delta P$ (where $\Delta v$ is the change in energy

![Figure 9. The behavior of $v$ under increasing pressure. Note that the plot for the TBP exhibits a steeper slope than the plots for the TP and square plane.](image)
of the band under ΔP, the change in pressure) is 33-50 cm⁻¹/kbar for TBP, 6-18 cm⁻¹/kbar for TP, and <15 cm⁻¹/kbar for square planar structures. Dawson and coworkers¹⁰⁴ have studied the spectra of several TBP Ni(II) complexes at 77⁰K in rigid glasses. Highly distorted TBP complexes (e.g., see ref. 21 and 22) exhibit two bands in the visible region at room temperature (from the splitting of the ³E level in D₃h symmetry), which are replaced by a more intense, symmetrical band at 77⁰K, equidistant between the two room temperature bands (Figure 10). Less

Figure 10. The effect of low temperature on the spectra of [Ni[C₆H₅P(OC₂H₅)₂]₃(CN)₂]. Reproduced from reference 104.
distorted TBP's (e.g., see ref. 92) exhibit only asymmetry in the $^1A \rightarrow ^3E$ transition and at 77$^\circ$K this band becomes more symmetrical and more intense.

Since $\Delta$ for TBP's is less than $\Delta$ for TP's (Figure 11), the geometry of complexes containing similar donors may be deduced from the energy of the absorption in the visible region. However, one must have

\[
\begin{align*}
\Delta_{TBP} & \approx \frac{1}{2} d_{xy}^2 - d_{x^2-y^2} \\
\Delta_{TP} & \approx d_{z^2} - d_{x^2-y^2}
\end{align*}
\]

Figure 11. Correlation diagrams for the $3d^8$ electronic configuration in fields of $D_3h$ or $C_3v$ (TBP) and $C_{4v}$ (TP) symmetries, illustrating that $\Delta_{TBP} < \Delta_{TP}$. 
available the spectra of complexes containing similar donors. Furthermore, using the one electron scheme, similar spectral contours are expected for structures distorted from the idealized TBP and TP.

**STATEMENT OF PROBLEM**

In order to elucidate further the factors which affect formation of pentacoordinate Co(II) and Ni(II) complexes and which five-coordinate stereochemistry is formed, the aliphatic, flexible ligands C₆H₅P[CH₂CH₂P(C₆H₅)₂]₂, DPP, and (CH₃)₂PCH₂CH₂CH₂P(CH₃)₂, dmp, were synthesized and their complexes investigated.

Complexes of DPP with Ni(II) should be enlightening, since the related bidentate, (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂, does not form pentacoordinate nickel complexes. Several bidentate phosphorous ligands have been used to form bis-chelated Co(II) and Ni(II) pentacoordinate complexes. However, most of these ligands have a short chelate bite or are excellent pi-bonders, factors which favor TP complexes. The ligand dmp possesses no phenyl rings to enhance pi-bonding and the trimethylene linkage should place no specific steric restrictions on the resulting complexes.
EXPERIMENTAL

A. Reagents

Reagent grade 1,4-dioxane was distilled (b.p. 101°) under a nitrogen atmosphere from the blue solution of equimolar amounts of sodium metal and benzophenone. Reagent grade tetrahydrofuran was refluxed for 6 hr over excess lithium aluminum hydride and then distilled (b.p. 65°) under a nitrogen atmosphere. Reagent grade 1,2-dichloroethane was refluxed over neutral alumina for 2 hr, and then distilled (b.p. 83.5°). Spectroquality acetonitrile was stirred over calcium hydride for 4 hr, distilled a nitrogen atmosphere from phosphorous pentoxide twice, and finally distilled (b.p. 81°) from calcium chloride. Alternatively, acetonitrile (and nitromethane) was vigorously stirred over molecular seives (4%) for 15 hr and filtered through a medium sintered glass frit. The salt Ni(H₂O)₆(BF₄)₂ was prepared from one equivalent of NiCO₃ and two equivalents (plus a 5% excess) of HBF₄ in water. The light green solid was crystallized from a concentrated
ethanol solution. The salt Ni(H₂O)₆I₂ was prepared similarly from NiCO₃ and HI. Stock solutions of lithium tetrachloropalladate were prepared by dissolving one equivalent of PdCl₂ and two equivalents of LiCl in ethanol at room temperature, filtering the solution, and diluting to an appropriate volume. Chlorodiphenylphosphine was fractionally distilled (121.0/0.65 torr). Technical grade flowers of sulfur was recrystallized from warm benzene. Phenylphosphine was prepared according to literature methods. Other solvents and metal salts were of the best grade obtainable and were used without further purification.

B. Analyses

Analyses for carbon, hydrogen, nitrogen, sulfur, and halogen were performed by either Galbraith Laboratories, Inc., Knoxville, Tennessee, or M-H-W Laboratories, Inc., Garden City, Michigan. Phosphorous analyses were performed by the author using the "heteromolybdenum blue" colorimetric method.

C. Infrared Spectra

Routine infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer as either Nujol or perchlorobutadiene mulls between polished KBr plates, or as KBr disks. These spectra were calibrated with polystyrene. Integrated absorption intensity measurements were determined using a Beckman IR-9 spectrophotometer, which was
calibrated frequently with water vapor. Samples of known concentration were run in matched, sealed KBr cells (path length = 0.1, 0.5, or 1.0mm). These spectra were compared frequently with the optical readout dial of the instrument.

D. Conductivity

Resistance measurements were made on approximately $10^{-3}$ molar solutions in a Fisher Scientific Products Co. cell (cell constant = \(-0.1\)) at 1000cps (electrolytes) or 60cps (non-electrolytes) with the aid of an International Instruments, Inc., Model RC-16E2 conductivity bridge. The electronic spectra of samples in these solutions were compared with those taken in dichloromethane solution and as Nujol mulls.

E. Electronic Absorption Spectra

Electronic absorption spectra were obtained with a Cary Model 14 recording spectrophotometer using matched quartz cells (path length = 0.1, 1.0, and 5.0cm). The solid state spectra were obtained as Nujol mulls suspended on filter paper\(^{108}\). Spectra obtained at 77°K were made on these same Nujol mulls by suspending them in a quartz dewar filled with liquid nitrogen. The spectra were replotted with the molar extinction coefficients as the vertical axis and energy (kilokaisers) as horizontal lower and wavelength (millimicrons) as horizontal upper axis, with the aid of a computer program written by C. Robert Sperati.
F. **Magnetic Measurements**

Magnetic susceptibility measurements were obtained on a Faraday balance constructed in this laboratory incorporating a Sargent Model-SR millivolt pen recorder, a Cahn #2000 RG electrobalance, and a Varian V-4004 four-inch electromagnetic system (V-2300A power supply; V-2301 current regulator).

To insure maximum efficiency and utilization of time while operating the electrobalance, the following precautionary notes should be duly heeded:

1. Always leave electrobalance ON.
2. Use the stopcocks to evacuate and fill the system SLOWLY.
3. Handle all weights and quartz boat with monel tweezers—never with fingers.
4. Do not drop weights or sample into the quartz boat while it is suspended on the fiber.
5. If the fiber sticks to the side of the hangdown tube, it may be detached by gently tapping the side of the tube with a fingernail.
6. Do not touch any of the dials on the electrobalance with which you are unfamiliar.
7. If you are confused about any part of the procedure, seek assistance.

**Calibration Procedure**

1. With the recorder range at position z, set the recorder pen at zero. This zero should be checked periodically during a working day.
2. Place the 10mg calibrating weight in the quartz boat and suspend the boat on the quartz fiber.
(3) With the recorder range in position z evacuate the system (5-10 min. pump-down time) and bleed in helium slowly to the preset mark on the manometer (approximately 40 cm).

(4) Set the mass dial to 0.00 and the recorder range to 0.1. Adjust the pen recorder to zero (extreme right-hand side of the recorder paper) using the set 0/10 dial. Check the setting by returning the recorder range to position z, positioning the recorder pen at zero, and repeating the set 0/10 procedure. Lock the set 0/10 dial.

(5) Return the recorder range to position z, and open the air stopcock.

(6) Place the 5 mg calibrating weight (now 15 mg total) in the quartz boat and evacuate the system. Bleed in helium to the preset mark (~40 cm).

(7) Set the recorder range to position 0.1, and the mass dial to 5.00. Adjust the pen recorder to zero using the set 5 dial.

(8) Set the recorder range to position 1 and the mass dial to 4.00. Adjust the pen recorder to 100% (extreme left-hand side of the recorder paper) using the calibrate recorder dial. Repeat steps (7) and (8) until little variation is noticed. Lock the set 5 and calibrate recorder dials.

(9) Since the set 0/10 and set 5 dials are interdependent, steps (3)-(8) should be repeated to assure the constancy of the settings.

(10) Return the recorder range to position z and open the air stopcock. Return the calibrating weights to their containers. Proceed with the sample determination.

Procedure for the Determination of Magnetic Susceptibilities

In general, 15-18 mg of sample are needed for diamagnetic and weakly paramagnetic samples; 12-15 mg will suffice for strongly paramagnetic samples.

(1) Turn on the cooling water (15-20 lb/in²) and the electromagnetic and power source.

(2) Place the desired amount of sample in the quartz boat and suspend the boat on the quartz fiber. With the recorder range at position z, evacuate the system. Bleed in helium to the preset mark (~40 cm).
With the recorder range at position 0.1, turn the mass dial slowly until the recorder pen is positioned within the limits of the chart paper. It will always be possible to set the mass dial to the nearest 0.05mg with the pen positioned between 0.020mg and 0.080mg on the chart paper (this procedure allows for minimum error in reading the mass dial and in the position of the pen recorder). The sum of the mass dial and the pen recorder readings and 10.000mg is the weight of the sample out of the field.

Select an appropriate field strength and position the magnet so that the sample is in the field. Find the weight as in step (3). Repeat the weighings in and out of the field five times or until reasonable constancy is obtained.

Determine the weight change in and out of the field at least two field strengths. This precaution will indicate the presence (or absence) of ferro- and antiferromagnetic impurities.

When the weighings are complete, return the recorder range to position z, turn off the magnet and cooling water, clean and replace the quartz boat on the fiber, and leave the system evacuated.

A large number of samples can be determined during the course of a working day. For extended periods of operation, the calibration should be checked periodically. The calculations are described in the following paragraphs.

\[ \chi_g = \frac{[\Delta w - (-K_1)]K_0}{w_0} \]  

where \( \chi_g \) = the gram susceptibility  
\( w = w_1 - w_0 \); \( w_1 \) is the actual sample weight in the field, \( w_0 \) is sample weight out of the field  
\( K_1 \) is the diamagnetic contribution of the particular quartz boat used; and \( K_0 \) is the constant required for converting the change in weight of the sample in and out of the field to cgs units as determined from a paramagnetic standard.

These constants were found by the following procedures.
**K_1:** Sufficient weight (tare weights and nichrome wire) are placed in the pan hanging from loop C of the Cahn Electrobalance to counterbalance the weight of the quartz fiber and boat. Approximately 5mg of weight (nichrome wire) is placed on the hook attached just below loop A. The system is evacuated and helium bled into the preset mark (~40cm). The constant K_1, is the weight change in and out of the field at a given field strength (2.0, 2.5, 3.0, 3.5, and 3.9 amps). Several weighings should be made at each field strength to assure an accurate value of K_1.

**K_2:** The 5mg of nichrome wire hanging below loop A is removed, a 10mg tare weight is added to the pan suspended from loop C, and the calibration procedure is performed. Approximately 12-15mg of Ni(en)_3S_2O_3 (en is ethylenediamine) or Hg[Co(NCS)_4] is placed in the quartz boat and the boat is suspended on the quartz fiber (it was found that the use of Hg[Co(NCS)_4] is best at low field strengths and the use of Ni(en)_3S_2O_3 is best at high field strengths, because of the tendency of the boat to swing to the side of the hangdown tube). The change in weight in and out of the field at each field strength is then determined (as above for K_1), carefully noting the temperature. The constant K_2, is calculated from (1) after rearrangement:

\[
K_2 = \frac{(x_0)(m_0)}{[\Delta W - (-K_1)]}
\]
where for \( \text{Ni(en)}_3\text{S}_2\text{O}_3 \):

\[
\chi_g^{20} = 11.04 \times 10^{-6} \text{cgs} \quad \text{and} \quad \frac{d\chi_g}{dT} = -0.04 \times 10^{-6} \text{cgs}
\]

and for \( \text{Hg[Co(NCS)]}_4 \):

\[
\chi_g^{20} = 16.44 \times 10^{-6} \text{cgs} \quad \text{and} \quad \frac{d\chi_g}{dT} = -0.05 \times 10^{-6} \text{cgs}
\]

The effective magnetic moment in Bohr magnetons, \( \mu_{\text{eff}} \), is found from

\[
\mu_{\text{eff}} = 2.84[T(\text{K}) \chi_M^{\text{corr}} x 10^{-6}]^{\frac{1}{2}}
\]

All effective magnetic moments reported are corrected for the diamagnetism of the ligands.

G. Nuclear Magnetic Resonance Spectra

Proton nmr spectra were obtained on a Varian Associates Model A-60 spectrophotometer. Except where indicated, spectra were obtained on the neat liquid. For solid samples, deuterated solvents were used where the resonance of the undeuterated solvent was less than 100cps from the sample resonance. Tetramethylsilane was used as an internal standard.

H. Obtaining an Inert Atmosphere for Reaction Glassware Systems

Prior to any reactions involving compounds that are sensitive to oxygen and/or moisture, the following procedure was used. The glassware was assembled and evacuated. It was warmed briefly with a heat gun and dry nitrogen was admitted to the system. This procedure was repeated and then the solvents and reagents were added as needed. Any
solvents not described in section A and water were deaerated by bubbling dry nitrogen through them for one hr immediately before use. Benzene and diethyl ether were dried over sodium wire when these solvents were required to be anhydrous. Transfers of sensitive materials were made either under a stream of dry nitrogen, or in a glove bag.

I. Preparation of 2-Chloroethyldiphenylphosphine

\[
(C_6H_5)_2PCl + 2K \rightarrow (C_6H_5)_2PK + KCl \quad (1)
\]

\[
(C_6H_5)_2PK + (\text{excess})ClCH_2CH_2Cl \rightarrow (C_6H_5)_2PCH_2CH_2Cl + KCl \quad (2)
\]

**CAUTION**: 2-Chloroethyldiphenylphosphine is a mustard-type compound. Its toxic activities have been described\(^{112}\). Precautions should therefore be taken to avoid contact with the skin or inhalation of the vapors. Potassium diphenylphosphide is a pyrophoric, red solid\(^{113}\)

(See experimental H before continuing)

Potassium (9.36g, 0.24 mole) and p-dioxane (300ml) were placed in a 500ml, round bottom, three-neck flask, fitted with reflux condenser, dropping funnel, and mechanical stirrer. The p-dioxane was heated to reflux (heating mantle) and the molten potassium was beaten into fine beads by the action of the stirrer. The addition of a p-dioxane solution (75ml) of chlorodiphenylphosphine (26.5g, 0.12 mole) was slowly commenced (if no potassium diphenylphosphide has formed after 10-20% of the chlorodiphenylphosphine solution has been added, the addition
should be halted, and the reaction mixture refluxed until the blood red color of the anion \((C_6H_5)_2PF^-\) is evident; a large excess of chlorodiphenylphosphine may start reacting with uncontrollable suddeness). After all of the chlorodiphenylphosphine solution had been added, the reaction mixture was refluxed for one hr and allowed to cool to room temperature to give red crystals of \((C_6H_5)_2PK\cdot2p\text{-dioxane}\) in a red solution. The p-dioxane was removed \textit{in vacuo}, and the red residue was dissolved in freshly distilled tetrahydrofuran (300ml). This solution was transferred through a short glass bend (into which had been inserted a glass wool plug to remove any unreacted potassium) to an addition funnel that was attached to the central joint of a one liter, three-neck, round bottom flask. The flask was also fitted with a nitrogen inlet tube and calcium chloride drying tube, and contained 1,2-dichloroethane (5 moles) and a football-shaped teflon stirrer. The potassium diphenylphosphide solution was added dropwise to the vigorously stirred, cooled (ice-bath) 1,2-dichloroethane. Complete addition required three hrs, and resulted in a cloudy, white suspension. The excess 1,2-dichloroethane was evaporated at 25° \textit{in vacuo}, and the white residue was treated successively with equivalent amounts (100ml) of chloroform and water. The two layers were separated, the water layer washed with two 50ml portions of chloroform, and the combined organic layers were dried over anhydrous sodium sulphate in a closed filter flask (Figure 12). The chloroform solution was filtered, and
Figure 12. Closed filtering flask.
then removed \textit{in vacuo}, to leave a water clear liquid which, when
shaken, solidified spontaneously to a white powder. This white powder
was dissolved in a minimal amount of dichloromethane and the solution
was filtered. Ethanol (75ml) was added and the dichloromethane was
evaporated under a gentle stream of nitrogen. No solid was obtained
from the ethanol solution; consequently, the ethanol was removed \textit{in}
\textit{vacuo}, and the white powder (as before) was used without further
purification. The yield was 24g (80\% based on chlorodiphenylphosphine).

\textbf{J. Preparation of 2-Chloroethyldiphenylphosphine Sulfide}

\[
(C_6H_5)_2PCH_2CH_2Cl + S \rightarrow (C_6H_5)_2P(S)CH_2CH_2Cl
\]

Sulfur (0.256g, 8mmole) and 2-chloroethyldiphenylphosphine (2.00g,
8mmole) were transferred under dry nitrogen to a flask containing 50ml
of dry benzene. The solution was warmed gradually over a period of
0.5 hr with stirring, and it was refluxed for an additional 0.5 hr.
The solvent was evaporated \textit{in vacuo} and the white residue was dissolved
in dichloromethane (20ml) and the solution was filtered. Ethanol was
added (20ml) and slow evaporation of the dichloromethane yielded the
sulphide as a white microcrystalline solid, which was collected on a
filter, washed with ethanol and ether, and dried \textit{in vacuo} (1.90g, 90\%).
m.p. 75°(uncorr).

\textbf{Anal.} Calcd for C_{14}H_{14}ClPS:
P, 11.05.

\text{Found:} \quad P, 10.8.
The proton nmr spectrum determined on a CDCl₃ solution showed three multiplets centered at 6.07ₜ and 6.97ₜ (methylene protons, relative intensity 1:1), and at 2.28ₜ (phenyl protons, relative intensity 5). The infrared P=S stretching frequency is split and occurs at 595, 607, and 620 cm⁻¹.

K. Preparation of Phenylphosphine

\[ \text{C₆H₅PCl₂} + \text{LiAlH₄} \rightarrow \text{C₆H₅PH₂} \]

CAUTION: Phenylphosphine fumes upon contact with air, and will inflame spontaneously upon contact with organic materials such as paper and cotton. Extreme care should be exercised in handling this compound. With the proper precautions, it may be transferred via a syringe.

(See experimental H before continuing)

A one liter, three-neck, round bottom flask was equipped with an addition funnel, nitrogen inlet tube, and calcium chloride drying tube. Previously dried diethyl ether (300ml) and lithium aluminumhydride (~2g) were added to the flask and this mixture was stirred via a football-shaped magnetic stirrer for two hr. Sufficient LiAlH₄ was then added to bring the total to ~10g (approximately a two-fold molar excess). This mixture was cooled to 0°C (ice-bath) and dichlorophenyl-phosphine (53.7g, 0.3 mole in 100ml of ether) was slowly added to the vigorously stirred mixture. As soon as a drop of the dichlorophenyl-phosphine solution made contact with the ether slurry, a white gas,
presumably HCl, was noticed. Consequently, the remaining addition was performed at -78° (Dry Ice-acetone bath). After complete addition, the reaction mixture was allowed to warm slowly to room temperature. Sufficient (~350ml) 1N HCl solution was added slowly to dissolve all of the precipitated aluminum salts. The two layers were separated, the water layer washed with ether (100ml), and the combined organic layers were dried in a closed filter flask (Figure 12) over anhydrous sodium sulphate. The solution was filtered and the ether was distilled at atmospheric pressure. The product was first distilled at atmospheric pressure through a short Vigreux column (the distillation was erratic and no accurate distilling temperature could be obtained), and then redistilled at 11 ± 2 torr and 48° (23g, 70%). The pure phosphine is a water-clear, evil-smelling liquid.

L. Preparation of 1-Diphenylphosphino-2-phenylphosphinoethane

\[ \text{C}_6\text{H}_5\text{PH}_2 + \text{Na} \rightarrow \text{C}_6\text{H}_5\text{PHNa} + \frac{1}{2}\text{H}_2 \]  \quad (1)

\[ \text{C}_6\text{H}_5\text{PHNa} + \text{ClCH}_2\text{CH}_2\text{P(C}_6\text{H}_5)_2 \rightarrow \text{C}_6\text{H}_5\text{(H)PCH}_2\text{CH}_2\text{P(C}_6\text{H}_5)_2 \]  \quad (2)

(See experimental H before continuing)

Dry, freshly distilled tetrahydrofuran (75ml) and liquid ammonia (250ml) were added to a 500ml, three-neck, round bottom flask fitted with a dropping funnel, mechanical stirrer, and Dry Ice-acetone condenser. The flask was placed in a -78° bath (Dry Ice-acetone) and
sodium chips (2.3g, 0.1 mole) were added with stirring. To this blue solution, phenylphosphine (11.5g, 0.105 mole; 5% excess) was added slowly via a syringe until the blue solution became golden yellow. 2-Chloroethyldiphenylphosphine (24.8g, 0.1 mole) in tetrahydrofuran (100ml) was added dropwise to this yellow solution. After complete addition, the reaction mixture was stirred for two hrs at -78°, and then the ammonia was evaporated slowly into a well-ventilated hood. Ethanol (10ml) was added to the ammonia-free solution to destroy any excess phosphide, and the remaining solvent was removed in vacuo. The residue was dissolved in equal volumes (200ml) of ether and water. The water layer was separated and washed with two 50ml portions of ether, and the combined organic layers were dried over anhydrous sodium sulphate in a closed filter flask (Figure 12). After this solution was filtered and the solvent evaporated in vacuo, the resulting water-white, viscous liquid was warmed briefly in vacuo to remove any phenylphosphine. Attempts to distill the compound were unsuccessful. The liquid solidifies at -10°, but remelts on warming to room temperature. An infrared spectrum of this liquid exhibited a strong absorption at 2275 cm⁻¹, attributable to the P-H stretching mode. No absorptions which could be attributed to possible impurities (P=O, POH) were detected. The yield was essentially quantitative based on the 2-chloroethyldiphenylphosphine. The liquid was used without further purification in the subsequent reactions.
M. Attempted Preparation of Derivatives of 1-Diphenylphosphino-2-phenoxyphosphinoethane

1. The title bis-phosphine (1.0g, 3.1 mmole) in benzene (50ml) and a slight excess of hydrogen peroxide were vigorously stirred with moderate warming for 0.5 hr. The two layers were separated, the water layer was washed with benzene (20ml) and the combined organic layers were dried. Removal of the solvent left an intractable oil.

2. The title bis-phosphine (1.3g, 4 mmole) and ethylene bromide (0.75g, 4 mmole) were combined in ether (50ml) and refluxed for 0.5 hr. Ethanol was added and the ether was removed under a fast stream of nitrogen. A solid separated from the ethanol solution only when the solution was cooled to -78°C. Upon warming the solution to room temperature, the white solid slowly turned to a gummy material and redissolved in the ethanol. Evaporation of the solvent *in vacuo* left an intractable oil.

3. The title bis-phosphine (1.3g, 4 mmole) was dissolved in dry ether (50ml). Butyl lithium (2.5ml of a 1.6M hexane solution, 4 mmole) was added *via* a syringe to give a yellow solid. An excess of methyl iodide was added slowly *via* a syringe, to discharge the yellow solid and give a clear solution. This solution was refluxed for 1 hr, and
ethanol (20ml) was added. While the ether was being removed under a stream of nitrogen, a white solid separated. This solid was collected on a frit and briefly air dried. Further drying, either at atmospheric pressure or in vacuo, caused the white solid to darken considerably.

4. Sulfur (0.36g, 11.1 mmole) and the title bis-phosphine (1.2g, 3.7 mmole) were combined in warm benzene (30ml). The solution was refluxed for 0.5 hr and allowed to cool. The solvent was removed in vacuo, leaving a white solid. This solid smelled of hydrogen sulfide throughout a recrystallization from ethanol. The solid that was collected also smelled of hydrogen sulfide and soon became intractable.

5. Excess methyl iodide (30ml) was added to the title bis-phosphine (0.90g, 2.5 mmole). White stirring this solution at room temperature, a white solid separated. Ethanol (20ml) was added and the excess methyl iodide was evaporated slowly. After stirring this ethanol solution briefly at room temperature, the solution became red, and an orange solid separated which darkened further after it was collected on a frit and briefly air dried.
N. Preparation of Bis(2-diphenylphosphinoethyl)phenylphosphine

\[
\text{C}_6\text{H}_5(\text{H})\text{PCH}_2\text{CH}_2\text{P(C}_6\text{H}_5)_2 \; + \; \text{BuLi} \rightarrow (\text{C}_6\text{H}_5(\text{Li})\text{PCH}_2\text{CH}_2\text{P(C}_6\text{H}_5)_2 \; \text{ (1)}
\]

\[
\text{C}_6\text{H}_5(\text{Li})\text{PCH}_2\text{CH}_2\text{P(C}_6\text{H}_5)_2 \; + \; \text{ClCH}_2\text{CH}_2\text{P(C}_6\text{H}_5)_2 \; \rightarrow \; [\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2]\text{P(C}_6\text{H}_5)_2 \; \text{ (2)}
\]

This reaction was conducted using a nitrogen purged (see experimental H) bottom Schlenck tube and a Schlenck addition and filtering funnel.

To a dry tetrahydrofuran solution (50ml) containing 1-diphenylphosphino-2-phenylphosphinoethane (3.00g, 9.3 mmole) was slowly added by syringe 5.8ml of a 1.6M hexane solution of butyl lithium (9.3 mmole). A red color developed immediately and the solution was allowed to stir while it was warmed gently for 0.5 hr; then a dry tetrahydrofuran solution (50ml) of 2-chloroethyldiphenylphosphine (2.31g, 9.3 mmole) was added dropwise. After complete addition, the reaction solution was refluxed for 0.5 hr, and then a small volume (10ml) of ethanol was added to destroy any excess phosphide. The solvent was removed in vacuo, and the white residue was treated with equal volumes (50ml) of benzene and water. The two layers were separated, the water layer was washed with two 20ml portions of benzene, and the combined organic layers were dried over anhydrous sodium sulphate in a closed filtering flask (Figure 12). The benzene solution was filtered and the solvent was removed in vacuo to leave a white solid. An infrared spectrum of this solid exhibited a weak absorption at 2275 cm\(^{-1}\), attributable to the
P-H stretching mode. Consequently, ether was added to the white solid and the slurry was filtered. An infrared spectrum of the resulting solid showed no evidence of the absorption at 2275 cm\(^{-1}\). This compound was used in all subsequent steps without further purification (4.0 g, 80\%).

O. Preparation of Bis(2-diphenylphosphinoethyl)phenylphosphine Trisulfide

\[
\left[\left(\text{CsH}_{5}\right)_{2}\text{PCH}_{2}\text{CH}_{2}\right]_{2}\text{PC}_{6}\text{H}_{5} + 3\text{S} \rightarrow \left[\left(\text{CsH}_{5}\right)_{2}\text{P(S)}\text{CH}_{2}\text{CH}_{2}\right]_{2}\text{P(S)}\text{CsH}_{5}
\]

Bis(2-diphenylphosphinoethyl)phenylphosphine (0.80 g, 1.5 mmole) and sulfur (0.14 g, 4.5 mmole) were combined in 50 ml of warm benzene. The solution was refluxed for 0.5 hr and then the solvent was removed in vacuo. The white residue was washed with 75 ml of hot ethanol, collected on a filter, and dried in vacuo (0.80 g, 90\%), m.p. 226-228\(^{\circ}\) (uncorr). The P=S stretching frequency occurs at 600, 607, and 620 cm\(^{-1}\) in the infrared spectrum.

Anal. Calcd for C\(_{34}\)H\(_{32}\)P\(_3\)S\(_3\):

- C, 64.74; H, 5.27; S, 15.25.
- Found: C, 64.67; H, 5.30; S, 15.51.

P. Preparation of Coordination Compounds of DPP

All manipulative operations were carried out under dry nitrogen and all solvents were deoxygenated by bubbling nitrogen through them for one hr prior to use to protect against oxidation of the ligand. In general, the appropriate M(II) salt was added to a well-stirred
solution of DPP in ethanol or chloroform. In most instances, the complex was extremely soluble in ethanol; consequently the solvent was removed in vacuo, the residue was dissolved in dichloromethane and this solution was filtered. The complex was obtained by adding an appropriate counter solvent (e.g., t-butylchloride) to the solution and allowing the dichloromethane to evaporate slowly. The crystalline complexes were then collected on a filter, washed briefly, air dried, and finally dried in vacuo over calcium chloride at room temperature for one hr.

1. [Ni(DPP)Cl₂]

An ethanol solution (20ml) of Ni(H₂O)₆Cl₂ (0.262g, 1.10 mmole) was added rapidly to a chloroform solution (20ml) of DPP (0.587g, 1.10 mmole). The deep red solution was stirred as the chloroform was removed under a gentle stream of nitrogen. No solid had separated from this ethanol solution after it had been kept at -10°C for two days. Consequently, the ethanol was evaporated in vacuo, the red residue was dissolved in dichloromethane (30ml), and this solution was filtered and combined with t-butylchloride (20ml). As the dichloromethane evaporated slowly at room temperature, dark red microcrystals were deposited. These were collected on a frit and dried (0.420g, 60%).

Anal. Calcd for C₃₄H₃₃Cl₂NiP₃:

C, 61.48; H, 5.01; Cl, 10.68.

Found: C, 61.41; H, 5.12; Cl, 10.90.
2. \([\text{Ni(DPP)Br}_2]\)

Anhydrous nickel(II) bromide (0.214g, 0.980 mmole) in ethanol (10ml) was quickly added to DPP (0.522g, 0.980 mmole) in chloroform (25ml). This deep red solution was warmed under a slow stream of nitrogen until all of the chloroform had evaporated. Cooling this ethanol solution at \(-10^\circ\) for two days yielded dark red crystal, which were recrystallized from a minimum volume of ethanol (5ml) at \(-10^\circ\) (0.50g, 67\%).

Anal. Calcd for \(C_{34}H_{33}Br_2NiP_3\):

- C, 54.23; H, 4.43; Br, 21.22.
- Found: C, 54.05; H, 4.37; Br, 21.45.

3. \([\text{Ni(DPP)I}_2\cdot 1/2\text{CH}_2\text{Cl}_2]\)

To a warm rapidly stirring ethanol solution (25ml) of DPP (0.450g, 0.840 mmole) was added \(\text{Ni(H}_2\text{O)}_6\text{I}_2\) (0.355g, 0.840 mmole) in ethanol (25ml). This deep purple solution was stirred and warmed under nitrogen until the volume of the solution was approximately 30 ml. Upon Cooling, deep purple crystals began to separate. The flask was stoppered and set aside at room temperature for 24 hr. The crystals were collected and recrystallized from dichloromethane/ethanol (0.60g, 85\%).
Anal. Calcd for $C_{34.543}H_{34}Cl_2NiP_3$:

C, 46.52; H, 3.85; Cl, 3.99; I, 28.53.

Found: C, 46.42; H, 3.75; Cl, 3.70; I, 28.32.

4. $[\text{Ni}(\text{DPP})(\text{NCS})_2]$  
An ethanol solution containing $\text{Ni}($NCS$)_2$ (0.294 g, 1.68 mmole) was added to a rapidly stirring chloroform solution (20 ml) of DPP (0.895 g, 1.68 mmole). The volume of the solution was reduced with heating under a gentle stream of nitrogen until deep red crystals began to separate. After cooling this solution to room temperature, these crystals were collected and recrystallized from warm ethanol (0.75 g, 70%).

Anal. Calcd for $C_{36.833}N_2NiP_3S_2$:

C, 60.92; H, 4.69; N, 3.95; S, 9.04.

Found: C, 60.72; H, 4.54; N, 3.80; S, 9.10.

5. $[\text{Ni}(\text{DPP})(\text{CN})_2]$  
The $[\text{Ni}(\text{DPP})I_2]$ complex was prepared in situ in ethanol (50 ml) from $\text{NiI}_2$ (0.175 g, 0.560 mmole) and DPP (0.300 g, 0.560 mmole). This solution was warmed and stirred rapidly as a methanol solution (20 ml) of KCN (0.073 g, 1.12 mmole) was added all at once. The color of the solution changed immediately from deep purple to pastel red. After warming the solution for 0.5 hr, the solvent was evaporated in vacuo. The red residue was dissolved in dichloromethane (30 ml) and this solution was filtered to remove the KI. At this point, several solvents (ethanol,
n-butanol, isopropylalcohol, benzene) and solvent systems (dichloromethane/t-butylchloride, ethanol/ether, dichloromethane/hexane) were employed in an attempt to obtain a solid, crystalline product. However, in those instances where a solid could be obtained, only red powders of varying composition were isolated. A crystalline product was finally isolated by dissolving the red residue in DMF (10ml) and slowly reducing the volume using a water aspirator until approximately one ml of solution remained. At this point, a substantial quantity of red needles crystallized spontaneously. These were rapidly collected on a filter and dried (0.18g, 50%).

**Anal.** Calcd for C$_{36}$H$_{33}$N$_2$NiP$_3$:

C, 67.01; H, 5.15; N, 4.34.

Found: C, 67.02; H, 4.91; N, 4.29.

6. $[\text{Ni(DPP)Cl}]_2B(C_6H_5)_4$

To an ethanol solution (40ml) of $[\text{Ni(DPP)Cl}_2]$, prepared from Ni(H$_2$O)$_6$Cl$_2$ (0.457g, 1.90 mmole) and DPP (1.02g, 1.90 mmole), was added all at once an ethanol solution (20ml) of NaB(C$_6$H$_5$)$_4$ (0.657g, 1.90 mmole). The color of the solution changed immediately from red to orange and orange crystals separated from the solution as the volume was reduced under a stream of nitrogen. These crystals were collected and dissolved in dichloromethane. This solution was filtered
and t-butylchloride was added. Slow evaporation of the dichloromethane yielded the product as orange platelets (1.50g, 80%).

*Anal.* Calcd for C$_5$H$_5$ClNiP$_3$:
C, 73.49; H, 5.64; Cl, 3.74.

Found: C, 73.31; H, 5.49; Cl, 4.01.

7. [Ni(DPP)Br]B(C$_6$H$_5$)$_4$

An ethanol solution (20ml) of NaB(C$_6$H$_5$)$_4$(0.151g, 0.440 mmole) was added rapidly to a warm ethanol solution (20ml) of [Ni(DPP)Br$_2$] (0.332g, 0.440 mmole). The red color of the solution changed to orange, and orange crystals were deposited within two hrs. These were collected and dissolved in dichloromethane. This solution was filtered and ethanol was added. The orange platelets that separated as the dichloromethane evaporated slowly were collected and dried (0.33g, 67%).

*Anal.* Calcd for C$_5$H$_5$BrNiP$_3$:
C, 70.20; H, 5.38; Br, 8.05.

Found: C, 70.21; H, 5.38; Br, 8.31.

8. [Ni(DPT)I]B(C$_6$H$_5$)$_4$

To an ethanol solution (40ml) containing [Ni(DPT)I$_2$](0.694g, 0.770 mmole) was rapidly added an ethanol solution (20ml) of NaB(C$_6$H$_5$)$_4$(0.265g, 0.770 mmole). The original purple color changed to red, and red needles crystallized while the solution was being heated under a stream of
nitrogen. These crystals were collected and recrystallized from warm ethanol (0.64g, 80%).

**Anal. Calcd for C_{56}H_{53}BNiP_3:**

C, 67.02; H, 5.14; I, 12.21.

**Found:** C, 66.88; H, 5.00; I, 12.22.

9. [Ni(DPP)NCS]B(C_{6}H_{5})_{4}

Ethanol solutions (50ml) of [Ni(DPP)(NCS)]_{2}(0.662g, 0.930 mmole) and NaB(C_{6}H_{5})_{4}(0.319g, 0.930 mmole) were combined rapidly. As the ethanol from this solution was evaporated by warming under a stream of nitrogen, orange platelets separated. These were collected on a frit and dissolved in dichloromethane (10ml). t-Butylchloride (30ml) was added to the filtered dichloromethane solution, and large, blocky orange crystals were deposited as the dichloromethane slowly evaporated at room temperature (0.61g, 75%).

**Anal. Calcd for C_{56}H_{53}BNNiP_3S:**

C, 73.01; H, 5.50; P, 9.57; S, 3.30.

**Found:** C, 73.09; H, 5.54; P, 9.53; S, 3.56.

10. Attempted Preparation of [Ni(DPP)CN]B(C_{6}H_{5})_{4}; Isolation of [Ni_{2}(DPP)_{2}(CN)_{3}]B(C_{6}H_{5})_{4}

A methanol solution of KCN (0.110g, 1.68 mmole) was added to an ethanol solution (30ml) of DPP (0.450g, 0.840 mmole) and Ni(H_{2}O)_{6}(NO_{3})_{2}
To this pastel red solution was added NaB(C₆H₅)₄ (0.288g, 0.840 mmole) in ethanol (20ml) and the resulting solution was stirred with warming for 0.5 hr. The solvent was removed in vacuo and the residue was dissolved in dichloromethane (30ml). This solution was filtered to remove the separated inorganic salts and ethanol was added (30ml). Warming this solution under a stream of nitrogen caused the deposition of feathery red crystals, which were collected and dried (0.60g, 75%).

Anal. Calcd for C₅₉H₃₉BNNiP₃:

C, 75.51; H, 5.69; P, 9.90; N, 1.49.

Calcd for C₅₉H₈₆BN₃Ni₂P₆:

C, 72.04; H, 5.47; P, 11.73; N, 2.65.

Found: C, 71.01; H, 5.37; P, 11.40; N, 2.55.

11. [Pd(DPP)I]I

Palladous chloride (0.99g, 0.560 mmole) and LiCl (0.0476g, 1.12 mmole) were dissolved in vigorously stirring ethanol (30ml) at room temperature. To this solution was added NaI (0.42g, 2.8 mmole) in ethanol (20ml). This deeply colored solution was stirred briefly and DPP (0.300g, 0.560 mmole) in chloroform (20ml) was added all at once. Concentration of the resulting yellow solution by warming under a stream of nitrogen followed by cooling (~10°C) did not give a precipitate. Consequently, the solvent was removed in vacuo and the residue was
dissolved in dichloromethane (20ml). Ethanol (20ml) was added to this filtered solution, and the volume was reduced to 10ml. The flask was stoppered and kept at -10° for two days. The orange needles that separated were collected and recrystallized from 5ml of cold (-10°) ethanol (0.25g, 50%).

**Anal.** Calcd for C$_{34}$H$_{33}$I$_{2}$P$_{3}$Pd:

C, 45.64; H, 3.72; I, 28.36.

Found: C, 45.75; H, 3.51; I, 28.33.

Q. Attempted Preparation of Some additional Coordination Compounds of DPP

Several attempts were made to isolate nickel(II)-DPP complexes with other anions, and to oxidize the Ni(II) complex to Ni(III). Palladium(II) complexes with other halides were extremely soluble in the solvents used, and although crystalline solids could be obtained, they gave inconsistent elemental analyses.

1. Attempted Preparation of [Ni(DPP)Br$_{2}$]Br

The reaction was conducted in a nitrogen purged Schlenck tube. The solvents were dried and deaerated immediately prior to use.

A chloroform solution (30ml) of bromine (0.092g, 0.58 mmole) was added dropwise to a vigorously stirred chloroform solution (30ml) of [Ni(DPP)Br$_{2}$] (0.866g, 1.15 mmole). No significant color change of the
solution was noticed. The solution was warmed and stirred for one hr, and the solvent was removed in vacuo to give a light red powder.

**Anal.** Calcd for C_{34}H_{33}Br_3NiP_3:

C, 49.02; H, 3.99; Br, 28.78.

Found: C, 51.24; H, 4.17; Br, 22.21.

The compound lost weight rapidly on the Faraday balance, and exhibited a loss of weight in the magnetic field. These data indicate that the compound is [Ni(DPP)Br_2] contaminated with a small amount of bromine. Similar results were obtained when benzene was used instead of chloroform as the solvent.

2. **Attempted Preparation of [Ni(DPP)(NO_3)_2]**

An ethanol solution (40ml) of Ni(H_2O)_6(NO_3)_2 (0.291g, 1.00 mmole) was combined with a chloroform solution (20ml) of DPP (0.534g, 1.00 mmole). The light yellow solution was stirred on a hotplate under a stream of nitrogen for one hr. This ethanol solution gave a light yellow powder when it was cooled. Attempts to recrystallize this powder led to decomposition of the compound, as indicated by the fading yellow color and failure to recover the original yellow solid.

3. **Attempted Preparation of [Ni(DPP)(ClO_4)_2]**

Ethanol solutions (30ml) of Ni(H_2O)_6(ClO_4)_2 (0.344g, 0.940 mmole) and DPP (0.502g, 0.940 mmole) were combined rapidly with stirring under dry nitrogen at room temperature. A deep red color developed.
immediately, and became yellow within 0.5 hr. A partially crystalline, yellow compound, which exhibited symmetrical perchlorate absorptions in the infrared at ~1200 cm\(^{-1}\) and ~640 cm\(^{-1}\), was obtained from cold (-10\(^{\circ}\)) ethanol (25ml). The visible electronic spectrum of this yellow compound was essentially identical with that of a sample of \([\text{Ni(DPP)Cl}]\text{B}(\text{C}_6\text{H}_5)\)_4. The yellow compound was diamagnetic, and is therefore most likely \([\text{Ni(DPP)Cl]}(\text{ClO}_4)\). No comment is given here concerning the mechanism involved in the formation of this compound, but because of the potential hazard involved, the reaction was not re-examined.

4. Attempted Preparation of \([\text{Ni(DPP)NO}]\text{B}(\text{C}_6\text{H}_5)\)_4

To \(\text{Ni(H}_2\text{O)}_6\text{Cl}_2\) (0.336g, 1.41 mmole) and DPP (0.752g, 1.41 mmole) in ethanol (50ml) was added an ethanol solution (20ml) of \(\text{NaNO}_2\) (0.195g, 2.82 mmole). After refluxing this yellow solution for two hr under dry nitrogen, \(\text{NaB}(\text{C}_6\text{H}_5)\)_4 (0.482g, 1.21 mmole) in ethanol (20ml) was added dropwise. This yellow solution containing a small amount of white solid, was refluxed for one hr. after which the solvent was removed in vacuo. The cream colored residue was dissolved in dichloromethane (30ml) and this solution was filtered. Ethanol (20ml) was added and as the dichloromethane evaporated slowly at room temperature, small light yellow crystals separated. These were collected on a frit and dried.
Anal. Calcd for C$_{58}$H$_{53}$BNMOP$_3$:

C, 72.68; H, 5.57; N, 1.46.

Found: C, 75.65; H, 5.94; N, none.

No evidence was found for NO or NO$_2$ in the infrared spectrum.

The C and H analyses do not satisfactorily fit those expected for the other possible products in this reaction mixture (e.g., [Ni(DPP)Cl]B(C$_6$H$_5$)$_4$).

5. Attempted Preparation of [Pd(DPP)Cl$_2$]

An ethanol solution (50ml) of Li$_2$PdCl$_4$ was prepared by dissolving PdCl$_2$ (0.177g, 1.00 mmole) and LiCl (0.085g, 2.00 mmole) in vigorously stirring ethanol at room temperature. To this solution was added DPP (0.534g, 1.00 mmole) in chloroform (20ml). The yellow solution was stirred on a hotplate under a stream of dry nitrogen until the volume had been reduced to 20 ml. The remaining solvent was removed in vacuo, and the residue was dissolved in dichloromethane (30ml). This solution was filtered to remove the LiCl, and ethanol (10ml) was added. The dichloromethane was removed under a gentle stream of nitrogen and the flask was stoppered and set at -10° for two days. The pale yellow, almost white crystals that separated were collected and recrystallized from cold (-10°) ethanol (0.42g, 60%).

Anal. Calcd for C$_{34}$H$_{33}$Cl$_2$P$_3$Pd:

C, 57.37; H, 4.67; Cl, 9.96.

Found: C, 55.65; H, 4.35; Cl, 12.48.
Recrystallizing the complex did not substantially improve the analytical results.

R. Preparation of Tetramethylbiphosphine

$\text{(CH}_3\text{)}_2P\text{-P(}	ext{CH}_3\text{)}_2 + 2(n\text{-C}_4\text{H}_9)_3P \longrightarrow \text{(CH}_3\text{)}_2\text{P}=\text{P(}	ext{CH}_3\text{)}_2 + 2(n\text{-C}_4\text{H}_9)_3P=S$

(See experimental H before continuing)

CAUTION: Tetramethylbiphosphine inflames spontaneously on contact with air, and extreme care should be exercised in handling this compound (see page 57).

The reactants, (CH$_3$)$_4$P$_2$S$_2$ (46.5g, 0.25 mole) and (n-C$_4$H$_9$)$_3$P (11g, 0.55 mole; 10% excess) were added to a 250ml, three-neck, round bottom flask fitted with a nitrogen inlet tube and a compact distilling head. The nitrogen exited from the distilling head and was bubbled through a 10% HNO$_3$ solution. The reaction flask was heated (oil bath) gradually to 130°, at which point the (CH$_3$)$_4$P$_2$S$_2$ dissolved in the tributylphosphine. At 135°, the desulfurization commenced, as indicated by a gentle frothing of the solution. The frothing subsided substantially after 0.5 hr, and the oil bath was maintained at 150° for an additional hr. An attempt was made to distill the (CH$_3$)$_4$P$_2$ at atmospheric pressure, but only a few drops of distillate were collected at a pot temperature of 220°. Consequently heating was discontinued,
and a vacuum system was attached to the distillation apparatus. The product was distilled at 12±2 torr and 55-60° (22.4g, 73%).

The biphosphine was used without further purification in the next step. The following procedure was used to transfer the (CH₃)₄P₂.

A hollow glass stopper fitted with a septum cap, into which had been inserted a short syringe needle, was attached to a source of dry nitrogen. The nitrogen source was connected between two bubblers such that a stream of nitrogen passes through the syringe at all times. The flask containing the (CH₃)₄P₂ (attached to the vacuum system under dry nitrogen) was cooled to -78° (at this temperature, the phosphine is a solid). The flask was detached and the glass cap was quickly attached. The (CH₃)₄P₂ was warmed to room temperature, the syringe needle was removed, and the flask was weighed. The weight of the biphosphine was later found by difference. To transfer the biphosphine preparatory to the next step, the syringe needle was replaced and the flask was cooled again to -78°. The cap was removed and the flask was connected quickly to a short, bent piece of glass tubing connected to a nitrogen purged addition funnel.

S. Preparation of 1,3-Bis(dimethylphosphino)propane

\[
(CH₃)₂PP(CH₃)₂ + 2Na \rightarrow 2(CH₃)₂PNa
\]

(1)

\[
2(CH₃)₂PNa + ClCH₂CH₂CH₂Cl \rightarrow (CH₂)₂PCH₂CH₂CH₂P(CH₃)₂
\]

(2)

(See experimental H before continuing)
CAUTION: 1,3-Bis(dimethylphosphino)propane is a pyrophoric liquid possessing the typical phosphine odor. Although its toxic activities are unknown, one should take precautions to avoid contact with skin or inhalation of vapors.

A 500ml, three-neck, round bottom flask fitted with a mechanical stirrer, Dry Ice-acetone reflux condenser, and addition funnel containing (CH$_3$)$_4$P$_2$ (22.4g, 0.18 mole) was charged with liquid ammonia (300ml) and sodium chips (8.4g, 0.36 mole). The flask was maintained at -78° (Dry Ice-acetone bath) throughout all additions, and the nitrogen effluent gas was bubbled through a 10N HNO$_3$ solution. The (CH$_3$)$_4$P$_2$ was added dropwise to the blue liquid ammonia solution to give a deep green colored solution. The addition funnel was rinsed with a small volume of dry, deaerated ether, and then was charged with an ether solution (50ml) of 1,3-dichloropropane (20.7g, 0.18 mole). As the dropwise addition of this solution proceeded, the color of the liquid ammonia solution changed from green to brilliant red, and finally became colorless. At this point, the addition of the 1,3-dichloropropane solution was stopped (approximately 5ml remaining), since an excess of the dichloropropane would react with the product to form phosphonium salts. The ammonia was allowed to evaporate slowly into a well-ventilated hood, and ether (100ml) was added to the residue. This ether slurry (NaCl) was transferred to a closed filtering flask (Figure 12) containing anhydrous sodium sulphate. The ether was
filtered into a micro-distillation setup and was removed at 20 torr. The product was distilled at 62-70/4 torr (24.3g, 80%).

T. Preparation of 1,3-Bis(dimethylphosphino)propane Disulfide

\[(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P(}\text{CH}_3)_2 + 2\text{S} \rightarrow \text{(CH}_3)_2\text{P(S)CH}_2\text{CH}_2\text{CH}_2\text{P(S)(CH}_3)_2\]

The bis-phosphine (0.60g, 3.6 mmole) was added to dry deaerated benzene (30ml). Sulfur (0.23g, 7.2 mmole) was added to the rapidly stirring solution. The reaction was exothermic as the sulfur dissolved and a white solid separated. This solid was collected on a frit and dissolved in dichloromethane (75ml). Evaporation of the solvent at room temperature resulted in the deposition of long, colorless needles. These were collected on a frit and dried in vacuo (0.1g, 58%). An additional crop of crystals was obtained by concentrating the mother liquor; m.p. 226-7.5°C (uncorr).

Anal. Calcd for C\(_7\)H\(_{18}\)P\(_2\)S\(_2\):

C, 36.83; H, 7.95; S, 28.09.

Found: C, 36.25; H, 8.01; S, 28.74.

U. Preparation of Coordination Compounds of dmp

In general, the appropriate molar amounts of metal salts and ligand were mixed in a deaerated n-butanol/ethanol solvent mixture. If the complex did not crystallize from this solvent mixture, the volume of the solution was reduced under nitrogen until crystallization began. The solids were then collected on a filter frit, washed with butanol
and ether, and dried in vacuo at room temperature for one hr. Recrystallization generally was unsuccessful unless it could be accomplished within one hr. Solutions of the complexes decompose upon prolonged (24 hr) standing.

1. \([\text{Ni}(\text{dmp})_2\text{I}]\text{BF}_4\)

An ethanol solution of '*\(\text{Ni(H}_2\text{O)}_6\text{I(BF}_4)\)' was prepared by mixing ethanol solutions (15ml) of \(\text{NiI}_2\) (0.213g, 0.680 mmole) and \(\text{Ni(H}_2\text{O)}_6\text{-(BF}_4\text{)}_2\) (0.232g, 0.680 mmole). This solution was added dropwise to a well-stirred, warm n-butanol solution (20ml) of dmp (0.446g, 2.73 mmole). A deeply colored precipitate formed slowly as the nickel(II) solution was added. After complete addition, the precipitate and the deeply colored solution were warmed under a moderate stream of dry nitrogen until the solvent remaining was only n-butanol. The solution was cooled to room temperature, filtered rapidly, and the purple, microcrystalline solid was washed with n-butanol and ether and dried (0.674g, 82%).

**Anal. Calcd for \(\text{C}_{14}\text{H}_{36}\text{BF}_4\text{INiP}_3\):**

\[ \text{C}, 27.99; \text{H}, 6.02; \text{I}, 21.12.\]

**Found:** \[ \text{C}, 27.19; \text{H}, 6.01; \text{I}, 21.37.\]

2. \([\text{Ni}(\text{dmp})_2\text{Br}]\text{BF}_4\)

A solution of \(\text{Ni(H}_2\text{O)}_6\text{(BF}_4\text{)}_2\) (0.225g, 0.660 mmole) in 20ml ethanol and \(\text{NiBr}_2\) (0.145g, 0.660 mmole) in 10ml ethanol were combined and added
dropwise to a warm n-butanol solution (20ml) of dmp (0.432g, 2.64 mmole). A red color formed immediately and persisted until all of the nickel(II) solution had been added. The solution was concentrated to a volume of 20ml on a hotplate under a moderate stream of nitrogen. The solution was set aside to cool and large red platelets separated in about 10 min. These were collected, washed with n-butanol, and dried (0.50g, 70\%).

**Anal.** Calcd for C\textsubscript{14}H\textsubscript{28}EBBrF\textsubscript{4}NiP\textsubscript{4}:

- C, 30.36; H, 6.55; Br, 14.43.
- Found: C, 29.53; H, 6.30; Br, 16.15.

These analyses indicated that an excess of bromide ion was present. The crystals were recrystallized from warm deaerated n-butanol.

**Anal.** Found: C, 30.42; H, 6.71, Br, 14.48.

3. \(\text{[Ni(dmp)\textsubscript{2}Cl]}\text{B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}}\)

An ethanol solution (30ml) of Ni(H\textsubscript{2}O)\textsubscript{6}Cl\textsubscript{2} (0.314g, 1.32 mmole) was added dropwise to a warm n-butanol solution of dmp (0.434g, 2.64 mmole). After complete addition of the Ni(II) salts, the solution was deep red in color. An ethanol solution (20ml) of NaB(C\textsubscript{6}H\textsubscript{5})\textsubscript{4} (0.451g, 1.32 mmole) was added dropwise to this solution to give an immediate dark colored precipitate. The volume of the solution was reduced to 30ml by stirring on a hotplate under nitrogen. The solution was allowed to cool and the resulting precipitate was collected on a filter, dissolved in dichloromethane (30ml), the solution filtered to remove NaCl, and finally
combined with ethanol (30ml). The resulting purple crystals were collected on a frit and recrystallized from dichloromethane/ethanol. Approximately 30 min after isolation and briefly air drying, these crystals changed color, in the solid state, from deep purple to deep green. The green needles dissolve in dichloromethane to give a purple solution. The color change is repeatable (0.48g, 50%).

**Anal.** Calcd for C₃₈H₅₆BClNiP₄:

- C, 61.53; H, 7.61; Cl, 4.78.
- Found: C, 61.49; H, 7.87; Cl, 5.03.

4. [Ni(dmp)₂NCS]PF₆

An ethanol solution (10ml) of NaPF₆ (0.240g, 1.43 mmole) was combined with Ni(NCS)₂ (0.250g, 1.43 mmole) in 20ml ethanol. This solution was added dropwise to a warm n-butanol solution (20ml) of dmp (0.470g, 2.86 mmole), giving a green precipitate immediately. The mixture was stirred briefly on a hotplate under nitrogen, and then the green solid was collected on a filter, washed with warm ethanol, and dried (0.729g, 87%).

**Anal.** Calcd for C₁₅H₃₆F₁₀NNi₅S:

- C, 30.54; H, 6.15; N, 2.37.
- Found: C, 30.83; H, 6.25; N, 2.31.
5. $[\text{Ni}_2(\text{dmp})_3(\text{NCS})_2](\text{BF}_4)_2$

An ethanol solution of $\text{Ni}(\text{NCS})_2 (0.111g, 0.630 \text{ mmole})$ was combined with an ethanol solution (20ml) of $\text{Ni}((\text{H}_2\text{O})_6)(\text{BF}_4)_2 (0.217g, 0.630 \text{ mmole})$. This solution was added slowly to a warm n-butanol solution of dmp (0.417g, 2.54 mmole), to produce an immediate deep red colored solution and precipitate. After complete addition, the mixture was warmed on a hotplate under nitrogen until the solvent was n-butanol only. The solution was allowed to cool and the resulting red precipitate was collected on a filter frit (0.53g, 80%).

Anal. Calcd for $\text{C}_{15}\text{H}_{36}\text{BF}_4\text{NNiP}_4\text{S}$:

$\text{C}, 33.87; \text{H}, 6.82; \text{S}, 6.03$.

Found: $\text{C}, 32.03; \text{H}, 6.56; \text{S}, 5.38$.

The above sample was dissolved in dichloromethane, the solution was filtered, an equal volume of ethanol was added, and the dichloromethane was evaporated on a hotplate under nitrogen. The rhombohedral, red crystals that separated were collected and dried (0.27g, 30%). The analytical results now agreed with a binuclear formulation, instead of the simple $[\text{Ni}(\text{dmp})_2\text{NCS}]\text{BF}_4$.

Anal. Calcd for $\text{C}_{23}\text{H}_{54}\text{B}_2\text{F}_9\text{N}_2\text{Ni}_2\text{P}_6\text{S}_2$:

$\text{C}, 30.71; \text{H}, 6.05; \text{N}, 3.11$.

Found: $\text{C}, 30.25; \text{H}, 5.76; \text{N}, 2.96$. 
6. \([\text{Ni(dmp)}_2](\text{ClO}_4)_2\)

An ethanol solution (30ml) of \(\text{Ni(H}_2\text{O)}_6(\text{ClO}_4)_2\) (0.516g, 2.82 mmole) was added dropwise to a cold n-butanol solution of dmp (0.465g, 2.82 mmole). A yellow solid separated immediately on mixing of the reagents. After complete addition, the solution was stirred briefly at room temperature. The precipitate was then collected on a frit, washed with ethanol and ether, and dried in vacuo (0.82g, 100%).

**Anal.** Calcd for \(\text{C}_{14}\text{H}_{33}\text{Cl}_2\text{NiO}_8\text{P}_4\):

C, 28.71; H, 6.19; Cl, 12.10.

Found: C, 28.00; H, 6.06; Cl, 11.94.

7. \([\text{Ni(dmp)}_n(\text{CN})_2]\), \(n=1, 1.5\)

Anhydrous nickel(II) cyanide (0.299g, 2.69 mmole) was added in portions to a warm and stirred n-butanol solution (40ml) of dmp (0.441g, 2.69 mmole). All the Ni(CN)_2 dissolved and the solution became red, immediately. The n-butanol solution was refluxed for one hr; then the solvent was removed in vacuo. The red residue was dissolved in dichloromethane (30ml) and this solution was filtered. Petroleum ether (b.p. 55-110\(^\circ\); 20 ml) was added to the filtrate and the volume of the solution was gradually reduced with warming under a stream of dry nitrogen. Blocky, yellow crystals separated from the red solution and these were collected on a frit and dried (0.14g, 19%).
Further reduction of the volume of the dichloromethane/petroleum ether solution resulted in the deposition of a red oil. Consequently, the solvent was evaporated in vacuo and the residue was dissolved in dichloromethane (50ml). This solution was filtered and di-isopropyl ether (15ml) was added. Slow evaporation of the dichloromethane gave initially a small amount of the yellow crystals and some red needles. This mixture was collected on a frit and discarded, and the mother liquor was concentrated further. When red needles began to form, the flask was stoppered, and either shaking or cooling the flask resulted in copious quantities of red needles. These were collected, washed with a 2/1 (v/v) solution of di-isopropyl ether/dichloromethane, and dried in vacuo (0.256g, 30%).

Anal. Calcd for C_{12}H_{18}N_{2}NiP_{3}:
C, 42.04; H, 7.62; N, 7.85.
Found: C, 41.35; H, 7.77; N, 7.67.

8. [Ni(dmp)(NCS)₂]

Anhydrous nickel(II) thiocyanate (0.320g, 1.83 mmole) in 26ml of ethanol was added dropwise to a rapidly stirring, warm n-butanol solution (20ml) of dmp (0.300g, 1.83 mmole). The deep, red-brown color that was formed during the first half of the addition was gradually replaced by
a yellow precipitate as the remainder of the solution was added. The solution volume was reduced to 20ml on a hotplate under a stream of nitrogen. The solution was allowed to cool and the microcrystalline yellow solid was collected on a frit, washed with ethanol, and dried in vacuo (0.54g, 90%).

**Anal.** Calcd for C$_{9}$H$_{18}$N$_{2}$NiP$_{2}$S$_{2}$:

- C, 31.89; H, 5.35; N, 8.27.
- Found: C, 31.81; H, 5.37; N, 8.16.

9. [Ni(dmp)I$_{2}$]

An ethanol solution (30ml) of Ni(H$_{2}$O)$_{6}$I$_{2}$ (0.707g, 1.68 mmole) was added dropwise to a warm n-butanol solution of dmp (0.275g, 1.68 mmole). The deep purple solution that formed immediately soon faded somewhat as the addition proceeded. After all of the Ni(II) solution had been added, dark crystals were present in a deep blue solution. The solution was stirred briefly, and then the crystals were collected, washed with ethanol and dried (0.703g, 88%).

**Anal.** Calcd for C$_{7}$H$_{18}$I$_{2}$NiP$_{2}$:

- C, 17.64; H, 3.81; I, 53.24.
- Found: C, 17.70; H, 3.69; I, 53.44.
10. $[\text{Ni(dmp)Cl}_2]$ 

To a warm n-butanol solution (20ml) of dmp (0.444g, 2.71 mmole) was added slowly with stirring an ethanol solution (30ml) of Ni(H$_2$O)$_6$Cl$_2$ (0.645g, 2.71 mmole). As the addition of the Ni(II) solution progressed, the solutions original deep purple color changed to yellow. Golden yellow needles began to precipitate as the solution was concentrated on a hotplate under nitrogen. When the volume had reached 30ml, the yellow needles were collected (0.71g, 90%).

Anal. Calcd for C$_7$H$_{12}$Cl$_2$NiP$_2$: 


Found: C, 28.55; H, 6.18; Cl, 24.38.

11. $[\text{Ni(dmp)Br}_2]$ 

To a warm n-butanol solution (20ml) of dmp (0.560g, 3.41 mmole) was slowly added an ethanol solution of NiBr$_2$(0.747g, 3.41 mmole). A deep red solution was present during the addition of the first half of the nickel(II) solution; while the remaining solution was added, light red crystals separated. The solution was concentrated under nitrogen until the volume had reached 25ml. The red crystals were then collected on a frit and dried (0.156g, 90%).

Anal. Calcd for C$_7$H$_{15}$Br$_2$NiP$_2$: 

C, 21.97; H, 4.74; Br, 41.76.

Found: C, 21.86; H, 4.69; Br, 41.80.
solid, anhydrous cobalt(II) chloride (0.147 g, 1.13 mmole) was added to a hot n-butanol solution (30 ml) of dmp (0.373 g, 2.27 mmole). The CoCl₂ dissolved rapidly and the solution developed a deep green color. This solution was stirred for 10 min, and then an ethanol solution (30 ml) of NaB(C₆H₅)₄ (0.388 g, 1.13 mmole) was added dropwise. A deep green powder separated immediately. The mixture was stirred briefly, and then the precipitate was collected on a frit. The precipitate was dissolved in dichloromethane (70 ml) and the resulting solution was filtered. Ethanol was added, and the dichloromethane was evaporated slowly under a gentle stream of nitrogen. The deep green, flakey crystals that separated were collected and dried (0.652 g, 74%).

**Anal.** Calcd for C₃₈H₂₆BCIC₄O₄:

C, 61.51; H, 7.61; Cl, 4.78.

Found: C, 61.44; H, 7.66; Cl, 5.04.

13. \([\text{Co(dmp)}₂\text{Br}]\text{B(C₆H₅)}₄\)

To a hot n-butanol solution (30 ml) of dmp (0.444 g, 2.71 mmole) was added solid CoBr₂ (0.296 g, 1.35 mmole). The CoBr₂ dissolved almost immediately to produce a deep green solution. The solution was stirred briefly, and an ethanol solution (30 ml) of NaB(C₆H₅)₄ (0.465 g, 1.35 mmole) was added dropwise, giving a green, powdery
precipitate. After stirring this mixture briefly, the green precipitate was collected on a frit. The green solid was dissolved in 70ml dichloromethane, and this solution was filtered. Ethanol (30ml) was added to the deep green solution, and the dichloromethane was evaporated slowly under a gentle stream of nitrogen. The deep green, flaky crystals that separated were collected and dried (0.836g, 83%).

**Anal.** Calcd for $C_{36}H_{56}EBrCoP_4$

- C, 58.04; H, 7.18; Br, 10.16.
- Found: C, 58.17; H, 7.23; Br, 10.41.

14. [Co(dmp)$_2$I]I

A stock solution of 'Co(H$_2$O)$_6$I$_2$' was prepared in the following manner and used immediately. Ethanol solutions (20ml) of Co(H$_2$O)$_6$(NO$_3$)$_2$ (2.91g, 10 mmole) and NaI (3.00g, 20 mmole) were combined rapidly. The solid that separated initially was removed by filtration (1.49g), and the volume of the solution was reduced to 15ml. The flask was stoppered and placed in the refrigerator at -10° for 24 hrs. After collecting the precipitated solid on a filter, the solution was diluted to 100ml to contain 0.1 mmole/ml 'Co(H$_2$O)$_6$I$_2$'.

The dmp (0.532g, 3.24 mmole) was dissolved in hot n-butanol (30ml) and 16.2ml of the 'Co(H$_2$O)$_6$I$_2$' solution was added dropwise. Deep green crystals began to separate from this solution within five min. Stirring and heating under a stream of dry nitrogen were continued.
until a substantial quantity of the green crystals had separated.
The crystals were then collected on a filter and dried (0.945g, 90%).

**Anal. Calcd for C_{14}H_{38}CoI_{2}P_{4}**:  

**Found:**  
C, 26.20; H, 5.72; I, 39.37.

### 15. [Co(dmp)_{2}Cl]SnCl_{3}

To a hot n-butanol solution (20ml) of dmp (0.517g, 3.15 mmole) was added dropwise an ethanol solution (20ml) of Co(H_{2}O)_{6}Cl_{2} (0.374g, 1.57 mmole). The deep green solution was stirred briefly with warming; then SnCl_{2} (0.297g, 1.57 mmole) in ethanol (20ml) was added dropwise. The green crystals that soon separated were stirred briefly under nitrogen, collected, and dried (0.844g, 84%).

**Anal. Calcd for C_{14}H_{38}Cl_{4}CoP_{4}Sn:**  
C, 25.97; H, 5.60; Cl, 21.89.

**Found:**  
C, 25.81; H, 5.53; Cl, 21.81.

### 16. [Co(dmp)_{2}Cl_{2}]ClO_{4}

The dmp (0.594g, 3.62 mmole) was dissolved in warm n-butanol (30ml). To this solution were added, successively, ethanol solutions (30ml) of Co(H_{2}O)_{6}Cl_{2} (0.431g, 1.81 mmole) and NaClO_{4} (0.221g, 1.81 mmole). This solution was stirred vigorously while one drop of concentrated HCl (37%) was added. With continuous stirring, air was bubbled through the solution for six hr. Additional solvent was added periodically to keep
the volume between 50 and 70 ml. A light green precipitate formed throughout the oxidation; finally the volume of the solution was reduced to 20ml and the precipitate was collected on a frit. The solid was dissolved in a minimal amount of DMF (20ml), and this solution was filtered. Ethanol (50ml) was added and the solution was set at -10° for two days. The resulting green platelets were collected and dried (0.435g, 43%).

**Anal.** Calcd for C_{14}H_{36}Cl_{3}CoO_{4}P_{4}:

- C, 30.16; H, 6.51; Cl, 19.08.
- Found: C, 30.08; H, 6.57; Cl, 18.88.

17. [Co(dmp)_{2}Br_{2}]ClO_{4}

To a n-butanol solution (30ml) of dmp (0.676g, 4.12 mmole) were added ethanol solutions (30ml) of Co(H_{2}O)_{6}Br_{2} (0.674g, 2.06 mmole) and NaClO_{4} (0.251g, 2.06 mmole). This green solution was stirred vigorously as one drop of an aqueous solution of HBr (50%) was added; finally, air was bubbled through the solution for six hrs. When the volume of the solution had reached 20ml, the light green solid that had separated was collected on a frit and dried briefly with air. The solid was dissolved in warm DMF (25ml) and this solution was filtered. Ethanol (70ml) was added and the solution was placed in the refrigerator (-10°) for two days. The light green platelets that separated were collected and dried (0.681g, 52%).
Anal. Calcd for $\text{C}_{14}\text{H}_{36}\text{Br}_{2}\text{ClCoO}_{4}\text{P}_{4}$:

C, 26.02; H, 5.61.

Found: C, 26.15; H, 5.87.

18. $[\text{Co(dmp)}_{2}\text{I}_{2}]\text{ClO}_{4}$

An ethanol solution (40ml) of NaClO$_4$ (0.226g, 1.85 mmole) and 18.5ml of the stock $'\text{Co(H}_2\text{O)}_{3}\text{I}_{2}'$ solution (1.85 mmole; see #14) were added to a warm n-butanol solution (30ml) of dmp (0.607g, 3.70 mmole). One drop of an aqueous HI (50%) solution was added, and air was bubbled through the vigorously stirred solution until the original green color and precipitate had been replaced completely by a red precipitate (4hr). The volume of the solution was concentrated to 20ml and the red precipitate was collected on a filter. The red solid was dissolved in a minimal amount of warm DMF (20ml), and this solution was filtered. Ethanol (70ml) was added to this solution and it was placed in the refrigerator (-10°) for two days. The resulting red platelets were collected and dried (0.801g, 60%).

Anal. Calcd for $\text{C}_{14}\text{H}_{36}\text{ClCoI}_{2}\text{O}_{4}\text{P}_{4}$:

C, 22.71; H, 4.90.

Found: C, 22.45; H, 5.12.
V. Attempted Preparation of Some Additional Coordination Compounds of dmp

In general, in the preceding examples the complex must be isolated from the initial reaction solution; attempts to recrystallize most Ni(II) and Co(II) complexes led to decomposition. The following examples are complexes which were not obtained in sufficient purity to warrant further study, or decomposed during recrystallization.

1. Attempted Preparation of [Co(dmp)gBr]SnBr₃

An ethanol solution (20ml) of Co(H₂O)₆Br₂ (0.553g, 1.69 mmole) was added dropwise to a hot n-butanol solution (20ml) of dmp (0.555g, 3.38 mmole). The initial deep green solution was stirred briefly and an ethanol solution (20ml) of SnBr₂ (0.472g, 1.69 mmole) was added slowly. A pale green, leafy precipitate separated almost immediately; concentrating the volume of the solution under nitrogen resulted in the precipitation of more green crystals. This precipitate was filtered from the warm solution (0.567g, 43%), and the mother liquor was placed in a stoppered flask and kept at -10⁰ for 24 hr. Large green crystals separated and were collected (0.224g, 18%); yet another crop was obtained after further concentration of the solution (0.217g, 17%). The initial green precipitate was recrystallized from n-butanol to give similar green crystals. The crystals lost some of their brilliant luster after they were briefly air dried on a frit. The complex was
diamagnetic (Faraday balance), and the elemental analyses indicate that \([\text{Co(dmp)}_2\text{Br}_2]\)Br had been formed.

**Anal.** Calcd for \(\text{C}_{14}\text{H}_{36}\text{Br}_3\text{CoP}_4\):

- C, 26.82; H, 5.79; Br, 38.22.

  Found: C, 26.77; H, 5.83; Br, 39.92.

Calcd for \(\text{C}_{14}\text{H}_{36}\text{Br}_4\text{CoP}_4\text{Sn}\):

- C, 20.37; H, 4.39; Br, 38.70.

2. **Attempted Preparation of \([\text{Ni(dmp)}_2\text{I}]\)I**

An ethanol solution (30ml) of \(\text{Ni(H}_2\text{O)}_6\text{I}_2\) (0.552g, 1.21 mmole) was added dropwise to a warm ethanol solution (30ml) of dmp (0.430g, 2.62 mmole). The deep purple solution was concentrated under nitrogen to 20ml. The flask was stoppered and set at -10° for 15 hr. No solid had separated, and on further standing, the compound decomposed, as indicated by the fading color.

3. **Attempted Preparation of \([\text{Ni(dmp)}_2]\text{[B(C}_6\text{H}_5\text{)_4]}_2\)**

A solution of \{"Ni(H}_2\text{O)}_6[B(C}_6\text{H}_5\text{)_4}\}_2\" was prepared by combining an ethanol solution of \(\text{Ni(H}_2\text{O)}_6\text{Cl}_2\) (0.428g, 1.80 mmole) and an acetone solution of \(\text{NaB(C}_6\text{H}_5\text{)}_4\) (1.24g, 3.61 mmole). The precipitated NaCl was removed by filtration and the solution was added dropwise to dmp (0.593g, 3.61 mmole) in ethanol. The dark, almost black, solution was warmed gently under a stream of nitrogen. As the acetone evaporated, a light red precipitate was deposited. Complete removal of the acetone
yielded a large amount of red precipitate and a clear solution. The precipitate was collected on a frit, and examination with a microscope (30X) showed that the sample consisted of blocky red crystals and a substantial amount of white solid. The complex was subsequently dissolved in acetone and allowed to set at room temperature overnight. This resulted in complete fading of the original deep purple color and the deposition of an intractable beige solid.

4. Attempted Preparation of $[\text{Ni}(\text{dmp})_2](\text{BF}_4)_2$

An acetone solution (30ml) containing $\text{Ni(H}_2\text{O)}_6(\text{BF}_4)_2$ (0.196g, 1.19 mmole) was added slowly to a hot ethanol solution (30ml) of dmp (0.390g, 2.38 mmole). The deep red solution was concentrated by heating under a stream of nitrogen, and as the acetone evaporated, red crystals separated. The precipitate was collected on a frit and briefly air dried. Examination with a microscope (30X) showed that the red precipitate consisted of well-formed red crystals and a nondescript white solid. An attempt to recrystallize the red solid from acetone/ethanol was unsuccessful; the original deep red solution faded (6 hr) to light green, indicating the presence of the octahedral Ni(II).

5. Attempted Preparation of $[\text{Ni}(\text{dmp})_2\text{Cl}](\text{BF}_4)_2$

Equimolar amounts of $\text{Ni(H}_2\text{O)}_6\text{Cl}_2$ (0.124g, 0.540 mmole) and $\text{Ni(H}_2\text{O)}_6(\text{BF}_4)_2$ (0.177g) in ethanol (40ml) were added to a warm n-butanol
solution (20 ml) of dmp (0.358 g, 2.18 mmole). The resulting deep red solution was concentrated under nitrogen until the volume was 25 ml. Red crystals separated when the solution was cooled to room temperature. These were collected on a frit and briefly air dried. Microscopic examination (30X) showed that the red crystals were interspersed with a quantity of black material. In attempting to recrystallize the red compound from ethanol, a green powder was isolated. Further attempts led to complete decomposition, as indicated by the fading of the red color to light green.

6. Attempted Preparation of [Ni(dmp)Br$_2$]

The reaction was conducted using a small Schlenck bottom and filter tube. The benzene solvent was distilled from CaH$_2$ under dry nitrogen immediately prior to use.

Benzene (10 ml) and [Ni(dmp)Br$_2$] (0.404 g, 1.06 mmole) were added to the bottom Schlenck tube. To this vigorously stirring solution was added dropwise a benzene solution containing bromine (0.0844 g, 0.530 mmole). The originally red benzene solution became dark brown immediately and a dark brown precipitate was deposited. This precipitate was warmed and stirred briefly and then the solution and precipitate were transferred to the filter tube. The solid was isolated on the frit, washed with two 3 ml portions of benzene, and dried in vacuo for two hr at room temperature. In the process of determining the magnetic susceptibility of the compound, some of the
solid was exposed to the atmosphere and it fumed briefly. A sample exposed to the atmosphere lost its dark brown color after a period of two weeks. The solid is then red, and is presumably Ni(dmp)Br₂. Determined at two field strengths (3.0 and 3.5 amps), the magnetic moment was 1.24±0.02 B.M. No further characterizations were attempted.

7. Attempted Preparation of [Co(dmp)₂(NCS)₁(CNS)]

Solid anhydrous cobalt(II) thiocyanate (0.183g, 1.05 mmole) was added to a warm n-butanol solution (40ml) of dmp (0.344g, 2.10 mmole). The Co(NCS)₂ dissolved immediately to give a deep blue-green solution. The solution was stirred briefly and then the solvent was removed in vacuo. The residue was dissolved in dichloromethane (50ml) and this solution was filtered. The flask was stoppered and set aside at room temperature. After two days, the deep color had faded, and an intractable, light-colored solid had separated.

8. Attempted Preparation of [Co(dmp)NO₃]B(C₆H₅)₄

To a warm n-butanol solution (30ml) containing dmp (0.490g, 2.99 mmole) was added an ethanol solution (30ml) of Co(H₂O)₆(NO₃)₂ (0.434g, 1.49 mmole). The deep green solution was stirred briefly and an ethanol solution of NaB(C₆H₅)₄ (0.510g, 1.49 mmole) was added dropwise. The deep green solid that separated was stirred with warming briefly, and then collected on a frit. The green solid was dissolved in dichloromethane (40ml) and this solution was filtered to remove
the NaNO₃. n-Butanol was added (40ml), and the dichloromethane was evaporated under a stream of nitrogen. The n-butanol solution was set aside at -10°C for four hrs. After this time, the deep green color had faded completely, and a large amount of intractable white solid had separated.

9. Attempted Preparation of \([\text{Ni(dmp)}₂\text{CN}⁺]Y; Y = \text{B}(\text{C₆H₅})₄\) or BF₄⁻

Reaction of \([\text{Ni(dmp)}₂\text{X}]\text{BF}_4 \) (X = I, Cl) in ethanol with methanol solutions of KCN led to deeply colored powders which exhibited a CN stretch, vide infrared, but which could not be recrystallized without decomposition. Combining ethanol solutions of NaB(C₆H₅)₄ and \(\text{''Ni(dmp)}₂(\text{CN})₂''\) resulted in the precipitation of a white solid (the presence of the phenyl moiety and no CN, was indicated, vide infrared), and a red solution from which no solid was isolated. However, the following procedure did lead to a crystalline, tractable product.

To an ethanol solution (40ml) containing Ni(H₂O)₆Cl₂ (0.381g, 1.60 mmole) and dmp (0.526g, 3.20 mmole) was added NaB(C₆H₅)₄ (0.547g, 1.60 mmole) in ethanol (20ml). The solution was stirred under nitrogen, allowing the deeply colored precipitate of \([\text{Ni(dmp)}₂\text{Cl}]\text{B}(\text{C₆H₅})₄\) to form. While this slurry was stirred vigorously, KCN (0.104g, 1.60 mmole) in methanol (20ml) was added slowly. The original dark color seemed to lighten slightly as the solution was stirred and warmed for
one hr. The solution was cooled and filtered to yield a red filtrate and a peppery solid. This solid was dissolved in dichloromethane (40ml) and this solution was filtered. Ethanol (40ml) was added slowly, causing deep red platelets to precipitate. These crystals were collected and recrystallized from the same solvent mixture. Although the crystals are distinctly different in color and shape from those of \([\text{Ni(dmp)}_2\text{Cl}]_2\text{B(C}_6\text{H}_5)_4\), the elemental analyses indicate the presence of Cl as well as CN.

Anal. Calcd for \(\text{C}_{38}\text{H}_56\text{BCl}_A\text{CN}_B\text{NiP}_4\):

A = \(\frac{1}{2}\), B = \(\frac{1}{2}\) C, 62.74; H, 7.66; Cl, 2.41; N, 0.95.
A = \(\frac{3}{4}\), B = \(\frac{1}{4}\) C, 62.13; H, 7.63; Cl, 3.60; N, 0.47.
A = \(\frac{4}{5}\), B = \(\frac{1}{5}\) C, 62.01; H, 7.63; Cl, 3.83; N, 0.38.

Found: C, 62.64; H, 7.66; Cl, 4.24; N, 0.52.

62.51 7.70 3.94 0.46

The experimental atom ratios (Cl/N) are 3.2-3.4; the limits of the Cl and N analyses are ±0.3%.

10. Attempted Preparation of \([\text{Pd(dmp)}\text{Cl}_2]\)

An ethanol stock solution of \(\text{Li}_2\text{PdCl}_4\) (0.1 mmole/ml, 21.8ml) was added slowly to a n-butanol solution (30ml) of dmp (0.358g, 2.18 mmole). A colorless solution and white precipitate remained after complete addition of the Pd(II) solution. The volume of the solution was reduced to 20ml with warming under nitrogen. The solid was collected
on a frit and found to weigh approximately 0.5 g. Since this amount was considerably more than the total amount of recoverable LiCl (4.36 mmole, 0.18 g), some palladium-phosphine complex must have been present also. The solid was dissolved in warm DMF (20 ml) and the solution was filtered. Ethanol (30 ml) was added and upon standing at room temperature white crystals were deposited; these were collected and dried.

**Anal.** Calcd for C$_7$H$_8$Cl$_2$P$_2$Pd:


  Found: P, 7.23.

Recrystallization of the sample did not improve the analysis.

Reversing the order of addition of Pd(II) and dmp led to similar results.

11. **Attempted Preparation of [Pd(dmp)(CNS)$_2$]**

Sodium thiocyanate (0.305 g, 3.77 mmole) in ethanol (20 ml) was added to 37.7 ml of a stock solution of Li$_2$PsCl$_4$ (0.1 mmole/ml in ethanol. The solution was stirred briefly, filtered, and added drop-wise to a n-butanol solution (30 ml) of dmp (0.618 g, 3.77 mmole). After complete addition, there resulted a pale yellow solution and much white solid. The mixture was stirred and warmed briefly, and then the solid was collected on a frit. This solid weighed 2.14 g; the total inorganic salts must weigh 1.46 g. The solid was dissolved in cold DMF (20 ml) and this solution was filtered (0.63 g white solid remained on the frit).
Ethanol (50ml) was added to this solution and after setting at -10°C for six hr, white crystals had separated; these were collected (1.10g, 70%).

**Anal.** Calcd for C₉H₁₈N₂P₂PdS₂:
- C, 27.95; H, 4.69; N, 7.25; S, 16.58.
- Found: C, 27.37; H, 4.59; N, 5.45.

The complex was subsequently dissolved in DMF (10ml) and this solution was set at -10°C for one day to yield a flakey white precipitate (0.55g). Ethanol was added to the mother liquor, and upon cooling, white platelets were deposited (0.40g).

- from DMF; Found: C, 27.57; H, 4.73; N, 6.04; S, 14.47.
- from DMF/ethanol; Found: C, 26.97; H, 4.73; N, 5.50; S, 13.80.

12. **Attempted Preparation of [Pd(dmp)₂Cl]BF₄**

To dmp (0.472g, 2.88 mmole) in n-butanol (30ml) was added dropwise 14.4ml of a stock Li₂PdCl₄ ethanol solution (0.1 mmole/ml). A pale yellow solution was present after complete addition. This solution was stirred briefly, and an ethanol solution (25ml) of HBF₄ (0.127g, 1.44 mmole; 50% aqueous solution) was added dropwise. A white precipitate separated from the yellow solution within five min. This was collected and briefly air dried. Elemental analysis (P) indicated that practically no phosphorous was present (< 3%). No tractable solid could be isolated from the remaining yellow solution.
RESULTS AND DISCUSSION

A. The Ligands

1. Bis(2-diphenylphosphinoethyl)phenylphosphine, DPP

This tridentate phosphorous ligand was first prepared by Hewerton and Watson\textsuperscript{114} in low yield (16\%) from the reaction of $C_6H_5P(CH_2CH_2Br)_2$ and two moles of $(C_6H_5)_2PNa$. The low yield was most probably a result of the partial self-quaternization of the reactive intermediate, $C_6H_5P(CH_2CH_2Br)_2$. More recently\textsuperscript{115}, the reaction between $C_6H_5P(CH=CH_2)_2$ and $(C_6H_5)_2PH$ in boiling benzene and with catalytic amount of phenyl lithium or potassium t-butoxide has yielded DPP in substantially greater yields (~80\%).

The synthetic route illustrated in Scheme 1 was developed independently and concurrently by the author with the recent procedure\textsuperscript{115} and results in a high yield of DPP. The key to the synthesis of DPP is the preparation and availability of $(C_6H_5)_2PCH_2CH_2Cl$. Although tertiary
**Scheme 1**

Phosphines will react with alkyl halides to produce phosphonium salts, the rate of this reaction is reduced when aryl phosphines and alkyl chlorides are the reacting species (as compared with, for example, the reaction of alkyl phosphines and alkyl iodides). The original preparation of 2-chloroethylidiphenylphosphine was essentially the same as that described in Experimental I, but these authors vacuum distilled the crude product. Although the vacuum distillation is a reflection of the stability of the \((C_6H_5)_2PCH_2CH_2Cl\) towards quaternization, only a 2% yield was obtained. In the present study the phosphine was isolated directly from the reaction mixture in sufficient purity to obviate the need for distillation or recrystallization. The reaction of potassium diphenylphosphide with a large excess of 1,2-dichloroethane (\(~1:40\) molar ratio) readily produces \((C_6H_5)_2PCH_2CH_2Cl\). Removal of the excess 1,2-dichloroethane at 25°C in vacuo followed by extraction of the residue with, successively, chloroform and water, and evaporation of the dried chloroform solution in vacuo yields the

\[
\begin{align*}
C_6H_5PH_2 + Na & \xrightarrow{\text{liquid NH}_3} C_6H_5PHNa + \frac{1}{2}H_2 \quad (1) \\
C_6H_5PHNa + ClCH_2CH_2P(C_6H_5)_2 & \xrightarrow{\text{liquid NH}_3} C_6H_5(H)PCH_2CH_2P(C_6H_5)_2 \quad (2) \\
C_6H_5(H)PCH_2CH_2P(C_6H_5)_2 & \xrightarrow{1. \text{n-C}_4H_9Li/hexane} \xrightarrow{2. \text{ClCH}_2CH_2P(C_6H_5)_2/THF} C_6H_5P(CH_2CH_2P(C_6H_5)_2)_2 \quad (3)
\end{align*}
\]
phosphine. The compound initially is a water-clear liquid which solidifies to a white powder upon standing or cooling. The absence of hydrolysis products of the anion \((\text{C}_6\text{H}_5)_2\text{P}^-\) (e.g., \((\text{C}_6\text{H}_5)_2\text{PH}\) or \((\text{C}_6\text{H}_5)_2\text{P(OH)}\)) was determined by the absence of their characteristic absorptions in the infrared spectrum. A possible by-product whose presence is not indicated by the infrared spectrum is the bis-phosphine, \((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P(}H)\text{C}_6\text{H}_5\))\(_2\). However, its formation can be minimized by rapid stirring of the large excess of 1,2-dichloroethane and by the slow addition of the potassium diphenylphosphide solution.

The secondary-tertiary bis-phosphine, \((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P(}H)\text{C}_6\text{H}_5\))\(_2\), was isolated as a viscous liquid which solidified to a glassy solid just below room temperature. Attempts to distill or crystallize this material were unsuccessful. A slight excess of \(\text{C}_6\text{H}_5\text{PHNa}\) in equation 2 of Scheme 1 assured its isolation in relatively pure form. After this reaction was completed, the addition of ethanol readily converted the excess \(\text{C}_6\text{H}_5\text{PHNa}\) to \(\text{C}_6\text{H}_5\text{PH}_2\). Since phenylphosphine boils at \(~25^\circ\) and 1 torr, this compound was easily removed from the reaction mixture.

The infrared spectrum of \((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P(}H)\text{C}_6\text{H}_5\))\(_2\) exhibited a P-H stretching frequency at 2275 cm\(^{-1}\). No moderate to strong absorptions were present which could not be attributed to this bis-phosphine, (e.g., P=O, POH). The proton nmr spectrum exhibited multiplets centered at 2.75\(\tau\) (phenyl protons) and 8.00\(\tau\) (methylene protons), and
Figure 13. $^1$H nmr Spectrum of $(C_6H_5)_2PCH_2CH_2P(H)C_6H_5$. 
Table I

$^1$H nmr Resonances of Some Selected Bis-phosphines

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>Resonance $^b$</th>
<th>P-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(H)C$_6$H$_5$</td>
<td>2.75m 8.00m</td>
<td>5.81t($J_{P-H} = 208$cps)</td>
</tr>
<tr>
<td>(C$_6$H$_5$)(H)P(CH$_2$)$_3$P(H)C$_6$H$_5$</td>
<td>2.87m 8.37m</td>
<td>5.98t($J_{P-H} = 206$cps)</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$</td>
<td>2.43m 7.84t</td>
<td>--------------</td>
</tr>
<tr>
<td>(CH$_3$)$_2$P(CH$_2$)$_2$P(CH$_3$)$_2$</td>
<td>---- 8.57m</td>
<td>--------------</td>
</tr>
</tbody>
</table>

$^a$ The figures are given in $\tau$ units; m=multiplet, d=doublet, t=triplet.

$^b$ All of the compounds were synthesized in this laboratory by the author.

two triplets centered at 5.81t ($J_{P-H} = 208$cps) arising from the coupling of the $\alpha$-methylene protons with P-H (Figure 13). The resonance positions are consistent with those of other similar compounds (Table I).

The author was unsuccessful in isolating a sulfide derivative of (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(H)C$_6$H$_5$. This may be related to the tendency of the $R_2P(S)SH$ moiety to form a thioanhydride, ($R_2P(S)SH$)$_2$. Although a white solid was isolated initially (Experimental M), it smelled of hydrogen sulfide and rapidly turned into a gummy material upon standing. White solids also were obtained initially in attempts to isolate phosphonium halide derivatives (Experimental M); however, during attempts to recrystallize these solids from ethanol, the solutions darkened rapidly.
and gave orange colored solids. The solids also darkened spontaneously even in a desicator. The phosphonium salts were probably formed initially, but were unstable with respect to the formation of the tertiary phosphine (or the phosphine oxide) and HX or RX.

The crude product from equation (3) in Scheme 1 usually contained an impurity, presumably unreacted \((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P(\text{H})C}_6\text{H}_5)\), which was detected by a weak absorption in the infrared spectrum at 2275 cm\(^{-1}\). A quick ether wash of the crude product followed by filtration, removed the "\(\text{P-H}\)" impurity and left the pure DPP, as indicated by the disappearance of the absorption at 2275 cm\(^{-1}\).

2. 1,3-Bis(dimethylphosphino)propane, dmp

Although the preparation of dmp is outlined in Scheme 2 is not particularly difficult, the ready availability of the air-sensitive anion, \((\text{CH}_3)_2\text{P}^-\) by equations (1) and (2) greatly facilitated the preparation. The desulfurization, equation (1), is nearly quantitative,

\[
(\text{CH}_3)_4\text{P}_2\text{S}_2 + 2(n-\text{C}_4\text{H}_9)_3\text{P} \rightarrow (\text{CH}_3)_4\text{P}_2 + 2(n-\text{C}_4\text{H}_9)_3\text{P}=\text{S} \quad (1)
\]

\[
(\text{CH}_3)_4\text{P}_2 + 2\text{Na} \xrightarrow{\text{liquid NH}_3} 2(\text{CH}_3)_2\text{PNa} \quad (2)
\]

\[
2(\text{CH}_3)_2\text{PNa} + \text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{liquid NH}_3, (\text{C}_2\text{H}_5)_2\text{O}} (\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{CH}_3)_2 \quad (3)
\]

\text{SCHEME 2}
but the solubility of the tetramethylbiphosphine in tributylphosphine sulfide results in tetramethyldiphosphine being isolated in ~70% yields\textsuperscript{118}. Addition of excess 1,3-dichloropropane in equation (3) would react with dmp to form phosphonium salts; this situation is easily avoided since the reaction between (CH\textsubscript{3})\textsubscript{2}P\textsuperscript{−} and 1,3-dichloropropane is rapid and may be followed visually by the dissappearance of the anion's characteristic deep red color in liquid ammonia.

**B. Nickel(II) Complexes of DPP**

The reaction of equimolar amounts of NiX\textsubscript{2} (X= halogen, NCS, and CN) and DPP in ethanol produces deeply colored solutions from which [Ni(DPP)X\textsubscript{2}] can be isolated. These complexes are extremely soluble in ethanol. Whereas the iodide and thiocyanate complexes crystallized from 10\textsuperscript{−2} molar solutions at 25\textdegree, the bromide complex was isolated only from ~1 molar solutions at -10\textdegree. The chloride complex did not crystallize using the same conditions as for the bromide, but it was isolated from a solvent mixture of dichloromethane and t-butylchloride. The cyanide complex was isolated as crystals from very concentrated DMF solutions. Addition of solvents such as diethyl ether, n-hexane, or benzene to dichloromethane solutions of the cyanide complex yielded red powders which were always impure as indicated by their elemental analyses and/or magnetic susceptibilities.
Addition of one equivalent of sodium tetraphenylborate to ethanol solutions of \([\text{Ni}(\text{DPP})X_2]\) (except for \(X=\text{CN}\)) produces the \([\text{Ni}(\text{DPP})X^+\text{B}(\text{C}_6\text{H}_5)_4]\) complexes. These complexes crystallized readily from ethanol. They also formed large, well-formed crystals from the slow evaporation of dichloromethane from solutions of these complexes in dichloromethane/t-butylchloride.

The complexes of both formulations, \([\text{Ni}(\text{DPP})X]\text{B}(\text{C}_6\text{H}_5)_4\) and \([\text{Ni}(\text{DPP})X_2]\), were diamagnetic, exhibiting only the 'normal amount' of temperature independent paramagnetism; i.e., less than 0.6 B.M. Approximately \(10^{-3}\) molar acetonitrile solutions of these complexes exhibited conductance values appropriate for uni-univalent electrolytes (Table II; the range for uni-univalent electrolytes in acetonitrile\(^{117}\) is 140-160 cm\(^2\)/ohm mole). The conductance values for \([\text{Ni}(\text{DPP})X]\text{X}\) are reduced \(\sim 20\%\) from those of simple electrolytes because of the relative immobility of the large cation, \([\text{Ni}(\text{DPP})X]^+\). The conductance values of \([\text{Ni}(\text{DPP})X]\text{B}(\text{C}_6\text{H}_5)_4\) are reduced by \(\sim 40\%\) because of the presence of two relatively immobile ions, \([\text{Ni}(\text{DPP})X]^+\) and \(\text{B}(\text{C}_6\text{H}_5)_4^-\).

The conductivity data for \([\text{Ni}(\text{DPP})X]\text{X}\) and \([\text{Ni}(\text{DPP})X]\text{B}(\text{C}_6\text{H}_5)_4\) in acetonitrile and the electronic spectra of these complexes in the same solvent (Table III), are consistent with the four-coordinate, square planar species \([\text{Ni}(\text{DPP})X]^+\). The single, intense electronic transition
### Table II
Four- and Five-Coordinate $d^8$ Complexes of DPP$^a$

<table>
<thead>
<tr>
<th>Complex $^{b}$</th>
<th>Color</th>
<th>$\Lambda_M^{c}$ cm$^2$/ohm mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(DPP)I]II·0.5CH$_2$Cl$_2$</td>
<td>Deep purple</td>
<td>119</td>
</tr>
<tr>
<td>[Ni(DPP)Br$_2$]Br</td>
<td>Red</td>
<td>126</td>
</tr>
<tr>
<td>[Ni(DPP)Cl]Cl</td>
<td>Red</td>
<td>120</td>
</tr>
<tr>
<td>[Ni(DPP)NCS]CNS</td>
<td>Red</td>
<td>123</td>
</tr>
<tr>
<td>[Ni(DPP)(CN)$_2$]</td>
<td>Red</td>
<td>1.90</td>
</tr>
<tr>
<td>[Ni(DPP)I]B(C$_6$H$_5$)$_4$</td>
<td>Orange-red</td>
<td>111</td>
</tr>
<tr>
<td>[Ni(DPP)Br]B(C$_6$H$_5$)$_4$</td>
<td>Orange</td>
<td>97.0</td>
</tr>
<tr>
<td>[Ni(DPP)Cl]B(C$_6$H$_5$)$_4$</td>
<td>Orange</td>
<td>94.2</td>
</tr>
<tr>
<td>[Ni(DPP)NCS]B(C$_6$H$_5$)$_4$</td>
<td>Orange</td>
<td>91.6</td>
</tr>
<tr>
<td>[Ni$_2$(DPP)$_2$(CN)$_3$]B(C$_6$H$_5$)$_4$</td>
<td>Red</td>
<td>93.0</td>
</tr>
<tr>
<td>[Pd(DPP)I]I</td>
<td>Orange</td>
<td>130</td>
</tr>
</tbody>
</table>

---

a. DPP is the triphosphine $C_6H_5P(CH_2CH_2P(C_6H_5)_{2})_2$.  
b. All of these complexes are diamagnetic.  
c. These are molar conductance values on freshly prepared $\sim 10^{-3}$ M solutions in acetonitrile.
### Table III

Solution Electronic Spectra of Nickel-DPP Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Acetonitrile cm$^{-1}$ (ε$_{\text{max}}$)</th>
<th>1,2-Dichloromethane cm$^{-1}$ (ε$_{\text{max}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(DPP)$_2$·0.5CH$_2$Cl$_2$</td>
<td>22,350 (1860)$^a$ 35,690 (22,020) 40,820 (34,860)</td>
<td>15,700 (288) 21,300 (1840) 28,600 (7660) 34,500 (27,930)</td>
</tr>
<tr>
<td>Ni(DPP)Br$_2$</td>
<td>23,530 (2970) 35,090 (21,030)</td>
<td>16,700$^b$ (183) 23,150 (3070) 35,100 (18,810)</td>
</tr>
<tr>
<td>Ni(DPP)Cl$_2$</td>
<td>24,100 (3450)</td>
<td>16,700 (100) 23,800 (3410) 34,850 (17,400)</td>
</tr>
<tr>
<td>Ni(DPP)(CNS)$_2$</td>
<td>24,550 (4220) 35,700 (24,270)</td>
<td>18,200$^b$ (325) 23,800 (3950) 35,700 (19,740)</td>
</tr>
<tr>
<td>Ni(DPP)(CN)$_2$</td>
<td>24,400 (1850) 32,300 (7600) 40,000 (23,600)</td>
<td>24,400 (1830) 32,300 (7000) 40,000 (23,000)</td>
</tr>
<tr>
<td>[Ni$_2$(DPP)$_2$(CN)$_2$]B(C$_6$H$_5$)$_4$</td>
<td>25,600 (4120) 37,740 (43,790)</td>
<td>23,550 (4600) 31,250 (10,700) 37,050 (40,640)</td>
</tr>
<tr>
<td>[Ni(DPP)]B(C$_6$H$_5$)$_4$</td>
<td>23,530 (2430) 34,780 (22,770)</td>
<td></td>
</tr>
<tr>
<td>[Ni(DPP)Br]B(C$_6$H$_5$)$_4$</td>
<td>23,700 (3200) 35,090 (20,880)</td>
<td></td>
</tr>
<tr>
<td>[Ni(DPP)Cl]$B$(C$_6$H$_5$)$_4$</td>
<td>24,100 (3550)</td>
<td></td>
</tr>
<tr>
<td>[Ni(DPP)(CNS)]B(C$_6$H$_5$)$_4$</td>
<td>24,690 (4020) 36,040 (23,040)</td>
<td></td>
</tr>
<tr>
<td>Pd(DPP)$_2$</td>
<td>25,650$^b$ (2800) 28,600 (3600) 35,350 (23,00)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ calculated on the basis of the solvent free species.  
$^b$ S= shoulder
observed for [Ni(DPP)X]⁺ can then be assigned to the transition of
d-orbital character \( d_{xy} \rightarrow d_{x^2-y^2} \), as in Figure 14 (\( ^1A_{1g}(D) \rightarrow ^1A_{2g}(G) \)
in \( D_{4h} \) symmetry).

In solvents that are less polar than acetonitrile, such as
dichloromethane or 1,2-dichloroethane, the intense visible band of
the [Ni(DPP)X₂] complexes (except for \( X = CN \)) observed in acetonitrile
solutions shifts to lower energies; a much less intense shoulder
appeared around 16,000 cm⁻¹ (Table III). These spectral features of
the bromide complexes are compared in Figure 15.

The solid state spectra at room temperature exhibit a low energy
shoulder (15,000-19,000 cm⁻¹) in addition to maxima at higher energy
(20,000-24,000 cm⁻¹), but the mull spectra at 77°K exhibit two well-
defined maxima (Table IV, Figure 16). These spectral features
resemble those of pentacordinate Ni(II) complexes with similar sets
of donors\(^{25}e^{26}e^{27}\); thus, the [Ni(DPP)X₂] complexes are assigned as
pentacordinate in the solid state.

In contrast to the other [Ni(DPP)X₂] complexes, the [Ni(DPP)(CN)₂]
complex is a non-conductor in acetonitrile (Table II). The visible
electronic spectra in acetonitrile and dichloromethane are identical
and exhibit a broad, asymmetrical absorption at \( \sim 24,000 \) cm⁻¹ (Figure
17); the solid state spectra at both room temperature and 77°K also
exhibit this broad band. This complex, therefore, remains penta-
coordinate in the solid state and in solution.
Figure 14. d-Orbital splitting diagram for the 3d\textsuperscript{8} electronic configuration in square planar and tetragonal pyramidal environments.
Figure 15. Solution electronic spectra of [Ni(DPP)Br₂] in CH₂Cl₂ (---) and CH₃CN (-----); [Ni(DPP)Br]B(C₆H₅)₄ in CH₃CN (----). The absorbance scale is molar absorptivity x10².
<table>
<thead>
<tr>
<th>Complex</th>
<th>Room Temperature</th>
<th>77°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(DPP)I₂]·0.5CH₂Cl₂</td>
<td>15,380S</td>
<td>15,200</td>
</tr>
<tr>
<td></td>
<td>20,200</td>
<td>20,650</td>
</tr>
<tr>
<td></td>
<td>27,800</td>
<td>28,200</td>
</tr>
<tr>
<td>[Ni(DPP)Br₂]</td>
<td>17,200S</td>
<td>18,500</td>
</tr>
<tr>
<td></td>
<td>22,900</td>
<td>23,100</td>
</tr>
<tr>
<td></td>
<td>28,600</td>
<td>27,800</td>
</tr>
<tr>
<td>[Ni(DPP)Cl₂]</td>
<td>18,180S</td>
<td>18,700</td>
</tr>
<tr>
<td></td>
<td>23,530</td>
<td>23,800</td>
</tr>
<tr>
<td></td>
<td>27,780</td>
<td>27,800</td>
</tr>
<tr>
<td>[Ni(DPP)(NCS)₂]</td>
<td>22,450B</td>
<td>19,200S</td>
</tr>
<tr>
<td></td>
<td>29,400</td>
<td>22,750</td>
</tr>
<tr>
<td></td>
<td></td>
<td>29,600</td>
</tr>
<tr>
<td>[Ni(DPP)(CN)₂]</td>
<td>22,600B</td>
<td>22,750</td>
</tr>
<tr>
<td></td>
<td>30,800</td>
<td>29,600</td>
</tr>
<tr>
<td>[Ni₂(DPP)₂(CN)₃]B(C₆H₅)₄</td>
<td>22,800B</td>
<td>23,100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31,800</td>
</tr>
</tbody>
</table>

*S= shoulder, B=broad
Figure 16. Solid state electronic spectra of \([\text{Ni(DPP)}X_2]\) as Nujol mulls at 77°C; X=I (-----); X=Br (-----), X=Cl (-----), X=NCS (-----). The absorbance scale is arbitrary.
Figure 17. Solution and solid state electronic spectra of \( \text{[Ni(DPP)CN]}_2 \). Nujol mull at room temperature (-----); Nujol mull at 77\(^\circ\)K (-----); CH\(_3\)CN solution (----). The solid state absorbance scale is arbitrary; in solution the absorbance scale is molar absorptivity \( \times 10^2 \).
Although the \([\text{Ni(DPP)}X_2]\) complexes have been formulated as penta-coordinate, nothing has yet been said about the particular penta-coordinate geometry; i.e., do the complexes possess a trigonal bipyramidal (TBP), a tetragonal pyramidal (TP), or an intermediate geometry.

The structures of pentacoordinate Ni(II) complexes, in lieu of X-ray structural data, have usually been assigned by comparing electronic spectra of the new complexes with those of previously assigned complexes. Since \(\Delta\) for TBP is less than \(\Delta\) for TP (Figure 11), the geometry can often be assigned confidently, if only a single absorption is present as is expected if the structures are not distorted significantly (e.g., see \([\text{Ni(TSP)}\text{Cl}]^+\) reference 94 and \([\text{Ni(DSP)}\text{I}_2]\) reference 75). Figure 18 illustrates the result that is expected in the ordering of the d levels upon distortion of the two regular pentacoordinate structures. The distortion that produces the ordering of d levels is illustrated in Figure 19. For the TBP, the degeneracy of the e levels is removed, since the symmetry of the trigonal plane is destroyed, with the \(\Delta E\) value between the \(d_{x^2-y^2}\) and \(d_{xy}\) levels being larger than the \(\Delta E\) value between the \(d_{xz}\) and \(d_{yz}\) levels; the energy of \(d_{x^2-y^2}\) is slightly lower. For the TP, the degeneracy of \(d_{yz}\) and \(d_{xz}\) is removed; \(d_{xy}\) is lowered and \(d_{z^2}\) is raised in energy; and \(d_{x^2-y^2}\) is lowered in energy. Thus, the intermediate structure can be described, in the one-electron limit, as arising from the distortion of a TBP or
Figure 18. The effect on the splitting of the d-orbitals when the symmetry is lowered to $C_s$ from either $D_{3h}$ (or $C_{3v}$) or $C_{4v}$.
Figure 19. The vibrational mode associated with the interconversion of the trigonal bipyramid (D$_{3h}$ or C$_{3v}$) to the tetragonal pyramid (C$_{4v}$).
a TP. Although the orbital designations are not the same, the relative ordering of the d levels must be quite similar. Consequently, for distorted structures, at least two d-d transitions would be expected, and depending upon the degree of distortion, one cannot say, a priori, to which ideal pentacoordinate structure, the distorted structure, is most closely related. For example, \([\text{Ni}[\text{C}_6\text{H}_5\text{P(OC}_2\text{H}_5)_2\text{]}_3(\text{CN})_2]^{22}\) and \([\text{Ni}[\text{C}_6\text{H}_5\text{PH}]_3\text{I}_2]^{26}\) both exhibit two absorptions in their visible electronic spectra, but the structure of the former complex is a distorted TBP, whereas the latter complex possesses a distorted TP structure.

The electronic spectra of the \([\text{Ni}(\text{DPP})X_2]\) complexes can, however, be explained more consistently using the d level diagram for tetragonal pyramidal \((C_4v)\) symmetry (Figure 14). The transition observed in the square planar \([\text{Ni}(\text{DPP})X]^+\) complexes has the d-orbital character \(d_{xy} \rightarrow d_{x^2-y^2}\). In the pentacoordinate complexes, a second X moiety is added at the apical position, and the energy of the \(d_{2z}\) orbital should be raised above the energy of the \(d_{xy}\) orbital, which should be relatively unaffected. The position of the high energy maxima in the solid state spectra of \([\text{Ni}(\text{DPP})X_2]\) is not significantly different from the position of \(\nu_1\) in \([\text{Ni}(\text{DPP})X]^+\). Therefore this absorption is assigned to the transition, \(d_{xy} \rightarrow d_{x^2-y^2}\). Pentacoordination is observed spectro-photometrically by the appearance of the maxima at lower energy, which is assigned to the transition, \(d_{z^2} \rightarrow d_{x^2-y^2}\). Interpreting these
spectra in terms of a distorted TBP is not satisfactory, since the high energy maxima ($v_2$ in Figure 14) of $[\text{Ni(DPP)X}_2]$ would be expected to occur at substantially lower energies from the position of $[\text{Ni(DPP)X}]^+$ than is observed. Finally, the sensitivity of the absorptions of $[\text{Ni(DPP)I}_2].1/2\text{CH}_2\text{Cl}_2$ to pressure indicates that this complex possesses a TP structure.

The order for anions in promoting pentacoordination, CN $>$ I $>$ Br $>$ Cl $>$ NCS, observed previously by Alyea and Meek, is also found in the $[\text{Ni(DPP)X}_2]$ series. The cyanide complex remains pentacoordinate in acetonitrile solution and is a reflection of its stability. The two sharp absorptions in the CN stretching region of the infrared spectrum (Nujol mull; 2100 cm$^{-1}$ and 2110 cm$^{-1}$) are not an accurate indication of the distortion of the structure, since cyanides in the apical position and one basal position of a tetragonal pyramid would be expected to give rise to two such absorptions (in dichloromethane solution, these absorptions occur at 2120 cm$^{-1}$ and 2113 cm$^{-1}$ (Figure 20). The two absorptions overlap so that $v_2$ cannot be obtained accurately for each maxima, but for the envelope, the integrated absorption intensity, $A = 3.3 \times 10^{-4} \text{M}^{-1}\text{cm}^{-1}$). However, the asymmetric absorption in the visible electronic spectrum indicates that the cyanide is less distorted than the other complexes, where two distinct maxima are present.
Figure 20. Infrared spectrum in dichloromethane solution of Ni(DHP)(CN)$_2$. 
Since $v_1$ of $[\text{Ni(DPP)}X]\,^+$ and $v_2$ of $[\text{Ni(DPP)}X_2]$ arise from orbitals of the same character ($d_{xy} \rightarrow d_{x^2-y^2}$), the difference $v_1-v_2$ should be an indication of the degree of pentacoordination (see Figure 14).

From Table IV, $v_1-v_2$ increases in the order I $<$ Br $<$ Cl. The $[\text{Ni(DPP)}(\text{NCS})_2]$ complex is assessed as having the least amount of pentacoordinate character, since its solid state electronic spectrum at 77°K exhibits only a shoulder on the low energy side of the high energy maximum. This fact cannot be interpreted in the same sense as the cyanide complex, since the Nujol mull infrared spectrum exhibits two absorptions attributable to the CN stretch at 2100 cm$^{-1}$ and 2070 cm$^{-1}$. The latter absorption is indicative of ionic thiocyanate. In acetonitrile solution the positions and integrated absorption intensities are 2062 cm$^{-1}$ ($A = 1.99 \times 10^{-4} M^{-1} cm^{-1}$) and 2086 cm$^{-1}$ ($A = 7.22 \times 10^{-4} M^{-1} cm^{-1}$), indicative of ionic and N-bonded thiocyanate, respectively. The second thiocyanate (the one at the apical position), then, must perturb the $d_{z^2}$ orbital only enough to raise it slightly above $d_{xy}$, and as a result, $v_1$ and $v_2$ lie very close together.

When an excess of $\text{C}_6\text{H}_5\text{P(CH}_3\text{)}_2$ is added to dichloromethane solutions of $[\text{Ni(DPP)}X_2]$ ($X =$ halogen), the yellow solutions become deep purple. The spectral changes are recorded in Table V, and in Figure 21 for the iodide case. The new absorption cannot be attributed to either $[\text{Ni(DPP)}X_2]$ or $[\text{Ni}[\text{C}_6\text{H}_5\text{P(CH}_3\text{)}_2]_2X_2]$; thus, it is attributed to the new pentacoordinate species, $[\text{Ni(DPP)}[\text{C}_6\text{H}_5\text{P(CH}_3\text{)}_2]X]^+$. The new species
Table V

Solution Electronic Spectra and Conductance Values of Solutions of Ni(DPP)X₂ and excess C₆H₅P(CH₃)₂ in Dichloromethane.

<table>
<thead>
<tr>
<th>X</th>
<th>Ni(DPP)X₂</th>
<th>Ni(DPP)X₂+C₆H₅P(CH₃)₂</th>
<th>Ni[C₆H₅P(CH₃)₂]₃X₂</th>
<th>( \Lambda_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>23,800 (3410)</td>
<td>19,500 (1000)</td>
<td>15,050 (482)</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>22,750</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>23,150 (3070)</td>
<td>19,200 (1250)</td>
<td>15,150 (950)</td>
<td>164</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20,700 (554)</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>21,300 (1840)</td>
<td>18,700 (1650)</td>
<td>15,400 (1085)</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>22,200</td>
<td></td>
</tr>
</tbody>
</table>

a. The ratio C₆H₅P(CH₃)₂/Ni(DPP)X₂ is ~100 for the iodide and bromide, and ~10 for the chloride.

b. Taken from reference 20.

c. These are molar conductance values on freshly prepared ~10⁻³ M acetonitrile solutions. The same spectral features are observed in this solvent.
Figure 21. Solution (CH₂Cl₂) electronic spectra of [Ni(DPP)I₂] (-----) and [Ni(DPP)I₂] plus C₆H₅P(CH₃)₂ (-----); ~100 fold molar excess of C₆H₅P(CH₃)₂. The absorbance scale is molar absorptivity x10².
perhaps could be four-coordinate with one of the phosphorous donors of the tridentate dangling; however, this possibility is discounted, since this species would have an electronic absorption at least as high in energy as \([\text{Ni(DPP)}X]^{+}\). Furthermore, these solutions exhibit conductance values in acetonitrile typical of uni-univalent electrolytes (Table V). Since the electronic absorption of the new species lies below that of \([\text{Ni(DPP)}X_2]\) (\(v_2\) in Figure 14), it must possess a TBP structure. This conclusion is obvious from the fact that \(\Delta \text{TBP} < \Delta \text{TP}\) (Figure 11). If the new species possessed a TP structure, the absorption would be expected to lie at higher energies than \([\text{Ni(DPP)}X_2]\), since the ligand field strength of the donor set \(P_4X\) is more than that of the donor set \(P_3X_2\). Also, this result is additional evidence for the TP structure of the \([\text{Ni(DPP)}X_2]\) complexes. These results also indicate that the structure of DPP does not enforce any particular geometry on these Ni(II) complexes, but that the TP geometry of \([\text{Ni(DPP)}X_2]\) and the TBP geometry of \([\text{Ni(DPP)[C_6H_5P(CH_3)_2]}X]\) is a result of the electronic requirements of the respective donor sets \(P_3X_2\) and \(P_4X\).

The stability of \([\text{Ni(DPP)}(CN)_2]\) is further illustrated by the author's failure to isolate \([\text{Ni(DPP)}(CN)]B(C_6H_5)_4\) from the reaction of \([\text{Ni(DPP)}(CN)_2]\) and sodium tetraphenylborate in ethanol. The elemental analyses indicated the formulation \([\text{Ni}_2(\text{DPP})_2(CN)_3]B(C_6H_5)_4\) for the red crystals that were isolated (see Experimental P). This complex is diamagnetic, and its conductance in acetonitrile is consistent with a
uni-univalent electrolyte (Table II). The cyanide stretching region of the infrared spectrum (Nujol mull) exhibits a weak absorption at 2100 cm$^{-1}$ which has sharp shoulders at both higher and lower energies (in dichloromethane solution, Figure 22, this absorption occurs at 2121 cm$^{-1}$; the integrated absorption intensity, $A = 3.1 \times 10^{-4} M^{-1} cm^{-1}$ calculated on the basis of the dimer; although no values of the integrated absorption intensities for cyanides could be found in the literature, on the basis of the present study, see pages 102, 113, and 144, A per cyanide is approximately $1 \times 10^{-4} M^{-1} cm^{-1}$; hence, the presence of three cyanides is indicated in this complex). The visible electronic spectra in both solid state and solution are similar to the corresponding spectra of $[Ni(DPP)(CN)]_2^+$ (Figure 23). The complex may possess a binuclear pentacoordinate structure, utilizing one bridging cyanide. The formation of $[Ni_2(DPP)_2(CN)_3]B(C_6H_5)_4$ can be viewed as arising from the transitory formation of $[Ni(DPP)CN]^+$, which immediately combines with another $[Ni(DPP)(CN)]_2^+$. Several attempts were made to prepare Pd(II) complexes, but only the Pd(DPP)I$_2$ complex exhibited satisfactory elemental analyses. The chloride and thiocyanate complexes are extremely soluble in ethanol, and although crystalline solids could be obtained at -10$^0$, they did not exhibit reproducible analyses. The iodide complex is diamagnetic and is a uni-univalent electrolyte in acetonitrile (Table III), and is typical of a four-coordinate, square planar complex of palladium(II).
Figure 22. Infrared spectrum in dichloromethane solution of $[\text{Ni}_2(\text{DPP})_2(\text{CN})_3]B(\text{C}_6\text{H}_4)_4$. 
Figure 23. Solution and solid state electronic spectra of \([\text{Ni(DPP)(CN)}_2\](-) Nujol mull at 77°K \([\text{Ni}_2(\text{DPP})_2(\text{CN})_3]B(\text{C}_8\text{H}_8)_4\) (——) Nujol mull at 77°K, and \([\text{Ni}_2(\text{DPP})_2-(\text{CN})_3]B(\text{C}_8\text{H}_8)_4\) (----) 1,2-dichloroethane solution. The solid state absorbance scale is arbitrary; in solution, the absorbance scale is molar absorptivity \(\times 10^2\).
C. Coordination Compounds of \( (\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P(\text{CH}_3)}_2, \text{dmp} \)

1. Four-coordinate Nickel(II) Complexes

The reaction of equimolar amounts of \( \text{NiX}_2 \) (\( X = \text{halogen, NCS} \)) and \text{dmp} in alcoholic solutions readily produces the crystalline, four-coordinate \( [\text{Ni(dmp)}X_2] \) complexes. The \( [\text{Ni(dmp)}(\text{CN})_2] \) complex was isolated from the reaction of equimolar amounts of \( \text{Ni(CN)}_2 \) and \text{dmp} in warm \( n \)-butanol, but these reaction conditions also produced a substantial amount of \([\text{Ni(dmp)}_{1.5}(\text{CN})_2] \) (discussed on page 141). The colors and magnetic susceptibility and conductivity data are given in Table VI. The deep purple color of solutions (dichloromethane, acetonitrile) rapidly faded to green and finally red, with the concomitant deposition of a white solid. This behavior prohibited any study of the complex in solution. Freshly prepared \( \sim 10^{-3} \) molar acetonitrile solutions of the bromide complex exhibited initial conductance values of \( \sim 50 \text{cm}^2/\text{ohm mole} \), and increased within 30 min to \( \sim 150 \text{cm}^2/\text{ohm mole} \). Similar solutions of the chloride complex require two hr to attain conductances of \( \sim 150 \text{cm}^2/\text{ohm mole} \). The thiocyanate and cyanide complexes were stable indefinitely under similar conditions. The Nujol mull infrared spectra of the thiocyanate and cyanide complexes exhibited a broad, incipiently split band centered at 2090 cm\(^{-1}\) and 2115 cm\(^{-1}\), respectively, in the CN stretching region. In acetonitrile solution, the thiocyanate complex has two sharp absorptions at 2092 cm\(^{-1}\) and 2111 cm\(^{-1}\) and the integrated absorption intensity values are
Table VI

Four-Coordinate Nickel(II) Complexes of \((\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{CH}_3)_2\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Color</th>
<th>(10^5\chi_M)</th>
<th>(\Lambda_M^{b}) cm²/ohm mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(dmp)Cl₂</td>
<td>Yellow</td>
<td>95</td>
<td>0.028 (in 1,2-dichloroethane)²</td>
</tr>
<tr>
<td>Ni(dmp)Br₂</td>
<td>Red</td>
<td>108</td>
<td>0.225 (in 1,2-dichloroethane)</td>
</tr>
<tr>
<td>Ni(dmp)I₂</td>
<td>Purple</td>
<td>490</td>
<td>----d</td>
</tr>
<tr>
<td>Ni(dmp)(NCS)₂</td>
<td>Yellow</td>
<td>137</td>
<td>2.51 (in acetonitrile)</td>
</tr>
<tr>
<td>Ni(dmp)(CN)₂</td>
<td>Yellow</td>
<td>81</td>
<td>1.00 (in acetonitrile)</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BClO%7D_4">\text{Ni(dmp)}_2</a>_2)</td>
<td>Yellow</td>
<td>600</td>
<td>195 (in nitromethane)³</td>
</tr>
</tbody>
</table>

a. The magnetic susceptibility was the same for each sample within experimental error at two different field strengths.

b. Molar conductance values obtained on freshly prepared \(\sim 10^3\) molar solutions.

c. The value for a \(10^{-3}\) molar solution of \((n-\text{C}_4\text{H}_9)_4\text{NI}\) in 1,2-dichloroethane is 20.7.

d. Freshly prepared solutions decompose too rapidly to obtain conductance values.

e. Di-univalent electrolytes exhibit conductance values in the range 180-200 (see reference 117).
11.0 \times 10^{-4} \text{M} \text{cm}^{-1} \text{cm}^{-1} \text{and} 9.08 \times 10^{-4} \text{M} \text{cm}^{-1} \text{cm}^{-1}, \text{respectively}, \text{both indicative of} \text{N-bonded thiocyanate. In dichloromethane solution (Figure 24), two bands are present in the spectrum of the cyanide complex at } 2112 \text{ cm}^{-1} (A = 0.62 \times 10^{-4} \text{M} \text{cm}^{-1}) \text{and} 2124 \text{ cm}^{-1} (A = 1.4 \times 10^{-4} \text{M} \text{cm}^{-1}). \text{These infrared spectral data are consistent with a cis square planar structure for the complexes. The visible electronic spectra in solution and Nujol mulls at 77^\circ \text{K} \text{are given in Figures 25 and 26, respectively, and in Table VII. The spectra of the chloride, thiocyanate and cyanide complexes exhibited one absorption assignable to the transition of d-orbital character } d_{xy} \rightarrow d_{x^2-y^2} \text{in square planar symmetry}^{118}. \text{The spectrum of the bromide complex in solution (Figure 27) exhibits two bands at } 21,050 \text{ cm}^{-1} \text{and} 27,200 \text{ cm}^{-1} \text{which are assigned to the transitions } d_{xy} \rightarrow d_{x^2-y^2} \text{and } d_{z^2} \rightarrow d_{x^2-y^2} \text{respectively,} (^{1}A_{1g(D)} \rightarrow ^{3}A_{2g(G)} \text{and } ^{1}A_{1g(D)} \rightarrow ^{1}B_{2g(G)}, \text{respectively for } D_{4h} \text{symmetry). The other transitions expected}^{118} \text{in these square planar complexes are presumably masked by the more intense charge transfer bands.}

The [Ni(dmp)I_2] complex does not possess the same structure as the other [Ni(dmp)X_2] complexes, since the corresponding absorption in the visible electronic region is extremely broad and asymmetrical (no other transitions lie below 14,000 cm^{-1}; see Figure 26) and the room temperature magnetic susceptibility is abnormally high. The
Figure 24. Infrared spectrum in dichloromethane solution of Ni(dmp)(CN)$_2$. 
Figure 25. Solution (CH$_2$Cl$_2$) electronic spectra of [Ni(dmp)Br$_2$] (—), [Ni(dmp)Cl$_2$] (——), and [Ni(dmp)(CN$_5$)$_2$] (-----). The absorbance scale is molar absorptivity $\times 10^2$. 

WAVELENGTH [CNM]

400 500 600 700

WAVENUMBERS [KK]

31 29 27 25 23 21 19 17 15

ABSORBANCE

1.5 1.2 0.9 0.6 0.3

0.0
Figure 25. Solid state electronic spectra as Nujol mulls at 77°K of [Ni(dmp)Br₂] (--), [Ni(dmp)Cl₂] (-----), [Ni(dmp)I₂] (----), and [Ni(dmp)₂](ClO₄)₂ (------). The absorbance scale is arbitrary.
Table VII

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solution (dichloromethane) cm(^{-1})((\varepsilon_{\text{max}}))</th>
<th>Solid State</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Room Temperature</td>
<td>77(^\circ)K</td>
</tr>
<tr>
<td>Ni(dmp)Cl(_2)</td>
<td>22,000(705)</td>
<td>34,500(52000)</td>
</tr>
<tr>
<td>Ni(dmp)Br(_2)</td>
<td>21,050(720)</td>
<td>27,200(940)</td>
</tr>
<tr>
<td>Ni(dmp)I(_2)</td>
<td>(-)- (\text{c})</td>
<td>(\text{---d})</td>
</tr>
<tr>
<td>Ni(dmp)(CNS)(_2)(^\text{a})</td>
<td>24,400(14,70)</td>
<td>(\text{---d})</td>
</tr>
<tr>
<td>Ni(dmp)(CN)(_2)</td>
<td>30,1008(649)</td>
<td>(\text{---d})</td>
</tr>
<tr>
<td>([\text{Ni(dmp)}_2]\text{(ClO}_4\text{)}_2)(^\text{b})</td>
<td>22,270(660)</td>
<td>(\text{---d})</td>
</tr>
</tbody>
</table>

S= shoulder

a. in acetonitrile solution
b. in nitromethane solution
c. decomposes
d. not measured
Figure 27. Solution and solid state electronic spectra of \([\text{Ni(dmp)Br}_2]\) CCHCl solution (---); Nujol mull at room temperature (-----) and at 77°K (---------). The solid state absorbance scale is arbitrary, in solution, the absorbance scale is molar absorptivity.
magnetic data are the same within experimental error at two different field strengths, ruling out the possibility of the presence of ferro- or antiferromagnetic impurities. The instability of \([\text{Ni(dmp)}]_2\) in solution precludes obtaining additional information; with such scant data, the structure cannot be assigned unambiguously.

Addition of an ethanol solution of \(\text{Ni(H}_2\text{O)}_6(\text{ClO}_4)_2\) to a n-butanol solution of dmp causes the immediate deposition of the yellow \([\text{Ni(dmp)}]_2^-\)(\text{ClO}_4)_2. This complex is insoluble in most inorganic solvents except nitromethane, and \(\sim 10^{-3}\) molar solutions exhibit conductance values characteristic of di-univalent electrolytes (Table VI). The Nujol mull infrared spectrum exhibits no splitting in the perchlorate absorptions at \(\sim 1100\) cm\(^{-1}\) and \(\sim 625\) cm\(^{-1}\). There are no absorptions present which could be attributed to coordinated water. Although these infrared data indicate that no perchlorate or water is coordinated in this complex, the yellow complex dissolves in nitromethane to give a red solution, and the Nujol mull is red. These observations indicate that the four-coordinate \([\text{Ni(dmp)}]_2^2^+\) has coordinated another donor (e.g., solvent, water, or perchlorate) to become five-coordinate, thereby producing the visibly observed bathochromic shift (Figure 28). This is supported by the fact that the visible maximum (Table VII) for \([\text{Ni(dmp)}]_2(\text{ClO}_4)_2\) occurs close to the maxima for \([\text{Ni(dmp)}X_2]\). Since the ligand field strength of the donor set \(P_4\) is more than that of the donor set \(P_2X_2\), the transition for the square planar \([\text{Ni(dmp)}]_2^2^+\)
Figure 28. Solution and solid state electronic spectra of [Ni(dmp)$_2$](ClO$_4$)$_2$; Nujol mull at 77$^\circ$K (---), CH$_3$NO$_2$ solution (-----). The solid state absorbance scale is arbitrary; in solution, the absorbance scale is molar absorptivity x10$^2$. 
should occur at an appreciably high energy than the transition for
the square planar \([\text{Ni(dmp)}_X]_2\). The nitromethane solutions of
\([\text{Ni(dmp)}_2]\text{(C10}_4)_2\) decompose within one hr (depositing a white, intract-
able solid), and hence, no solvated species could be isolated.

The position of the electronic absorption could also be explained
by the following. The trimethylene linkage between the two phosphorous
donors is slightly too long to accommodate a P-Ni-P angle of 90°,
consequently the true symmetry of the complex is probably distorted
from the ideal D\(_{4h}\) symmetry to coordinate both chelating ligands. As
a consequence of this distortion, the d orbitals would not be
perturbed as much as in the ideal D\(_{4h}\) symmetry; thus, the absorption
would be expected to occur at lower energy. However, in the absence of
further data, no definitive statement can be made concerning the
constitution of this complex.

2. Five-coordinate Ni(II) Complexes of dmp

Mixing ethanol solutions of "\(\text{NiXY}\)" (X = halogen or NCS; Y is
a large non-coordinating anion) to n-butanol solutions of dmp results
in the immediate precipitation of the \([\text{Ni(dmp)}_2X]Y\) complexes. These
complexes are diamagnetic and exhibit conductance values in acetonitrile
indicative of uni-univalent electrolytes (Table VIII).

Two cyanide complexes, \([\text{Ni(dmp)}(\text{CN})_2]\) and \([\text{Ni(dmp)}_{1.5}(\text{CN})_2]\) were
isolated from the reaction of equimolar amounts of anhydrous \(\text{Ni(CN)}_2\)
and dmp in n-butanol. Both complexes were isolated under the same reaction conditions, and the equimolar amounts of the reactants were expected to produce only \([\text{Ni(dmp)}(\text{CN})_2]\). A bridging bidentate phosphine in a nickel(II) cyanide complex has been reported previously\(^{49}\), hence, the isolation of a similar complex with dmp is not surprising. The presence of both the four- and five-coordinate complexes under these reaction conditions is reasonable, since as the anhydrous Ni(CN)_2 dissolves in the dmp solution, an excess of the ligand is present. Hence, the pentacoordinate species is formed initially, and in the greatest amount; as the concentration of dmp is decreased, the four-coordinate complex would be formed.

The original intense colors of solutions of \([\text{Ni(dmp)}_2X]^+\) fade completely upon standing for 24 hr. However, the solutions are sufficiently stable to obtain conductance and spectral data. The conductance values of these solutions remain constant for at least one hr. The decomposition gives, presumably, the four-coordinate \([\text{Ni(dmp)}X_2]\) complex, although the instability of \([\text{Ni(dmp)}X_2]\) in these solutions prevented their isolation. This mode of decomposition has been observed previously in similar \([\text{NiL}_2X]^+\) complexes\(^{48}\). An 'intermediate' complex was isolated (Experimental U) in the attempted preparation of \([\text{Ni(dmp)}_2\text{NCS}]\text{BF}_4\). The elemental analyses of the well-defined red crystals suggests the formulation \([\text{Ni}_2(\text{dmp})_3(\text{NCS})_2](\text{BF}_4)_2\).
The conductance in acetonitrile (Table VIII) suggests that the complex is a uni-divalent electrolyte. Comparisons of the visible electronic spectra of this complex (Table IX; Figure 29) with those of [Ni(dmp)(NCS)₂] (Table VII; Figure 25) and [Ni(dmp)₂NCS]PF₆ (Table IX; Figure 32) indicate that [Ni₂(dmp)₃(NCS)₂](BF₄)₂ possesses a different structure than the other two complexes. The visible electronic spectrum obtained on a Nujol mull at 77°K (Figure 29), exhibits not only the absorption found at ~24,000 cm⁻¹ in solution at room temperature, but also an absorption at ~20,800 cm⁻¹. If it assumed, as is indicated by the elemental analyses, that the complex is binuclear, then the high energy absorption may be assigned to one Ni(II) in a square planar environment, and the low energy absorption may be assigned to the other Ni(II) in a five-coordinate environment. Although the exact structure cannot be deduced without further data, one thiocyanate must bridge in order for the total number of coordination sites to be nine. The infrared spectrum of a Nujol mull of this complex exhibits two bands at 2080 cm⁻¹ and 2115 cm⁻¹ in the CN stretching region, indicating that the two thiocyanates occupy nonequivalent positions. Although the 2115 cm⁻¹ band in the infrared is low for a bridging thiocyanate, the low energy band in the visible electronic spectrum was not observed distinctly except at 77°K in the solid state. Hence, the probable structure (Figure 30) may consist of a bridging dmp and a thiocyanate which "bridges" weakly to the second nickel atom.
Table VIII

Five-Co ordinate Nickel(II) Complexes with dmp

<table>
<thead>
<tr>
<th>Complex</th>
<th>Color</th>
<th>$10^3X_M^a$</th>
<th>$\Lambda_M^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(dmp)$_2$I]BF$_4$</td>
<td>Purple</td>
<td>177</td>
<td>150</td>
</tr>
<tr>
<td>[Ni(dmp)$_2$Br]BF$_4$</td>
<td>Red</td>
<td>130</td>
<td>150</td>
</tr>
<tr>
<td>[Ni(dmp)$_2$Cl]B(C$_6$H$_5$)$_4$</td>
<td>Green</td>
<td>243</td>
<td>106</td>
</tr>
<tr>
<td>[Ni(dmp)$_2$NCS]PF$_6$</td>
<td>Green</td>
<td>302</td>
<td>146</td>
</tr>
<tr>
<td>Ni(dmp)$_{1.5}$(CN)$_2$</td>
<td>Red</td>
<td>65</td>
<td>0.08</td>
</tr>
<tr>
<td>Ni$_2$(dmp)$_3$(NCS)$_2$(BF$_4$)$_2$</td>
<td>Red</td>
<td>158</td>
<td>312</td>
</tr>
</tbody>
</table>

a. The magnetic susceptibilities agreed within experimental error when measured at two different field strengths.

b. These are molar conductance values on freshly prepared $10^{-3}$ molar solutions in acetonitrile.

c. The range for a uni-divalent electrolyte in this solvent is 300-320 (see reference 117).
### Table IX


<table>
<thead>
<tr>
<th>Complex</th>
<th>Solution</th>
<th>Solid State</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(dichloromethane) cm(^{-1}) ((\varepsilon) max)</td>
<td>Room Temperature 77(^{\circ})K cm(^{-1})</td>
</tr>
<tr>
<td>[Ni(dmp)(_2)](\text{BF}_4)</td>
<td>19,800(2510) 29,400(2410) 38,450(22,000)</td>
<td>19,300 30,800(^a) 30,000</td>
</tr>
<tr>
<td>[Ni(dmp)(_2)](\text{Br})(\text{BF}_4)</td>
<td>20,400(1740) 30,800(2650) 39,200(22,200)</td>
<td>19,500 32,300(^\circ) 32,100</td>
</tr>
<tr>
<td>[Ni(dmp)(_2)](\text{Cl})(\text{B}(_6\text{H}_5)_4)</td>
<td>16,700(610) 20,800(1375) 31,400(6150) 34,500(6600)</td>
<td>16,700 30,800 30,300</td>
</tr>
<tr>
<td>&quot;[Ni(dmp)(_2)](\text{CN}\text{B}(_6\text{H}_5)_4)&quot;</td>
<td>16,700(354) 20,800(956) 26,300(513) 31,800(4130)</td>
<td>16,700 30,300 29,900</td>
</tr>
<tr>
<td>[Ni(dmp)(_2)](\text{NCS})(\text{PF}_6)</td>
<td>17,600(647) 22,450(1270) 29,800(3290) 37,750(22,400)</td>
<td>16,800 30,300 29,950</td>
</tr>
<tr>
<td><a href="dmp">Ni(_2)</a>(_3)](\text{NCS})_2)(\text{BF}_4)_2</td>
<td>23,650(2000)(^b) 35,700(23,700)(^b) 38,000(33,900)(^b)</td>
<td>20,000(^a) 24,100 24,700 31,600</td>
</tr>
<tr>
<td>Ni(dmp)(_1)](\text{S})(\text{CN})_2</td>
<td>22,350(949)(^b) 28,200(2250)</td>
<td>------(^c)</td>
</tr>
</tbody>
</table>

\(^a\) S=shoulder, B=broad  \(^b\) \(\varepsilon\) max calculated on basis of the dimer.  \(^c\) not measured
Figure 29. Solution and solid state electronic spectra of [Ni₂(dmp)₃(NCS)₂][BF₄]₂; CH₂Cl₂ solution (--); Nujol mull at room temperature (---) and at 77°K (-----). The solid state absorbance scale is arbitrary; in solution, the absorbance scale is molar absorptivity x10².
Figure 30. A possible structure for the cation, 
\([\text{Ni}_2(\text{dmp})_3(\text{NCS})_2]^{2+}\).
The failure to isolate a discrete [Ni(dmp)$_2$CN]$^+$ complex is not surprising in light of previous studies of complexes of Ni(CN)$_2$ with bidentate phosphines$^{49}$ and considering the remarkable stability$^{20}$ of five-coordinate Ni(II) complexes with the donor set P$_3$(CN)$_2$. In fact, no mononuclear [Ni$_2$CN]$^+$ has been reported (L is a bidentate phosphine$^{49}$). The reaction of KCN with [Ni(dmp)$_2$Cl]B(C$_6$H$_5$)$_4$ did produce a complex which contained a small amount of CN, as indicated by a weak CN stretching absorption in the infrared spectrum and nitrogen analysis (Experimental U), but a substantial amount of chloride ion was also present. Although the crystals of this "[Ni(dmp)$_2$CN]B(C$_6$H$_5$)$_4$" complex are substantially different in appearance and color from the crystals of [Ni(dmp)$_2$Cl]B(C$_6$H$_5$)$_4$, the visible electronic spectra in solution and in the solid state of the 'cyanide' complex are essentially identical to those of the chloride complex (Table IX). With only these data to draw from, the nature of this 'cyanide' complex cannot be assigned unambiguously.

The freshly isolated crystals of [Ni(dmp)$_2$Cl]B(C$_6$H$_5$)$_4$ are deep purple needles, which change color in the solid state within 30 min to deep green. The green needles dissolve in dichloromethane to give a deep purple solution from which purple needles can again be isolated. This 'color change' process is repeatable. No structural change
accompanies this color change, since the visible electronic spectral features are the same for the solid state (green needles) and (purple) solution (Table IX; Figures 33, 36).

The solution electronic spectra (Table IX; Figure 31-33) of \([\text{Ni(dmp)}_{2}X]^{+}\) are similar to the spectra of other pentacoordinate, low-spin Ni(II) complexes\(^{48}\), and coupled with the conductance and magnetic data, these complexes are assigned as pentacoordinate. However, as was the case with the \([\text{Ni(DPP)}_{2}X_{2}]\) complexes, these spectra alone do not present sufficient data to establish the particular pentacoordinate geometry of \([\text{Ni(dmp)}_{2}X]^{+}\). Furthermore, these spectra of the bromide and iodide complexes exhibit only one absorption, whereas the chloride and thiocyanate complexes exhibit two absorptions. This suggests that the pentacoordinate geometry of the bromide and iodide is different than the pentacoordinate geometry of the chloride and thiocyanate.

Comparison of the visible electronic spectra as Nujol mulls at 77°C of \([\text{Ni(DPP)}_{2}Cl_{2}]\) and \([\text{Ni(dmp)}_{2}Cl]^{+}\) (Figure 34) clearly illustrates that the two complexes cannot possess the same structure. The two maxima for the dmp complex occur at, respectively, lower energies than do the maxima for the DPP complex. Both complexes are pentacoordinate, and the DPP complex has been assigned a tetragonal pyramidal geometry; the dmp complex must then possess a distorted trigonal bipyramidal geometry, since the relative position of the maxima can only be explained by assuming that \(\Delta TB < \Delta TP\) (Figure 11). Therefore, by
Figure 31. Solution (CH₂Cl₂) electronic spectra of [Ni(dmp)₂X]⁺; X=I (--), X=Br (----), X=Cl (-----), X=CNS (-------). The absorbance scale is molar absorptivity x 10².
Figure 32. Solution (CH$_2$Cl$_2$) electronic spectra of [Ni(dmp)$_2$X]$^+$; X=I (-----), X=CNS (-----). The absorbance scale is molar absorptivity $\times 10^2$. 
Figure 33. Solution (CH\textsubscript{2}Cl\textsubscript{2}) electronic spectra of [Ni(dmp)\textsubscript{2}X]\textsuperscript{+}; X=I (--), X=Cl (-----).

The absorbance scale is molar absorptivity x 10\textsuperscript{2}.
Figure 34. Solid state electronic spectra as Nujol mulls at 77°C of \([\text{Ni}(\text{dmp})_2\text{Cl}]\text{B}((\text{C}_6\text{H}_5)_4)\) (---) and \([\text{Ni}(\text{DPP})\text{Cl}_2]\) (-----). The absorbance scale is arbitrary.
analogy, the thiocyanate possesses a distorted TBP geometry, and the 
bromide and iodide complexes possess a more regular TBP geometry.
Referring to Figure 35, the single absorption for the regular structures 
may be assigned to the $\nu_1$ transition ($^1A_1 \rightarrow ^1E'$ for $D_{3h}$ symmetry). The 
solid state Nujol mull spectra for the $[Ni(dmp)_2X]^+$ complexes at room 
temperature and 77°C are given in Figures 36 and 37, respectively (see 
also Table IX). These spectra for the iodide complex are compared in 
Figure 38, and the less intense absorption appearing at 24,100 cm$^{-1}$ in 
the spectrum at 77°C is assigned to the formally forbidden (in $D_{3h}$ 
symmetry) $\nu_2$ transition. In the spectrum, of the bromide complex, 
$\nu_2$ is much weaker (Figure 37).

The spectra under these same conditions are illustrated in Figure 
39 for the chloride complex and in Figure 40 for the thiocyanate 
complex (see also Table IX). These spectra may be readily interpreted 
in terms of a distorted TBP ($C_5$ symmetry) geometry (Figure 35). For 
the chloride complex, the absorptions at 17,500 cm$^{-1}$ and 21,750 cm$^{-1}$ 
are assigned to $\nu_1'$ and $\nu_1''$, respectively. The weak absorption, that 
is present in the spectrum at 77°C, at 27,800 cm$^{-1}$ is assigned to $\nu_2$. 
Similar assignments are made for the thiocyanate complex. Finally, 
the sensitivity of the visible band to pressure of the iodide, bromide,
Figure 35. Energy level correlation diagram for the trigonal bipyramidal (C<sub>3v</sub>) and distorted trigonal bipyramidal (C<sub>s</sub>) geometries.
Figure 36. Solid state electronic spectra as Nujol mulls at room temperature of $[\text{Ni(dmp)}_2X]^+$; $X=\text{I}(-----)$, $X=\text{Br}(-.-.-)$, $X=\text{Cl}(----)$, $X=\text{CNS}(----)$. The absorbance scale is arbitrary.
Figure 37. Solid state electronic spectra as Nujol mulls at 77°K of $[^{Ni(dmp)}_2X]^{+}$; $X=I$ (-----), $X=Br$ (----), $X=Cl$ (-----), $X=CNS$ (------). The absorbance scale is arbitrary.
Figure 38. Solid state electronic spectra as Nujol mulls of [Ni(dmp)$_2$I]BF$_4$ at room temperature (---) and 77 K (-----). The absorbance scale is arbitrary.
Figure 39. Solid state electronic spectra as Nujol mulls of \([\text{Ni(dmp)}_2\text{Cl}]\text{B}(\text{C}_6\text{H}_5)_4\) at room temperature (-----) and 77°C (-----). The absorbance scale is arbitrary.
Figure 40. Solid state electronic spectra as Nujol mulls of [Ni(dmp)₂CNS]PF₆ at room temperature (---) and 77°C (-----). The absorbance scale is arbitrary.
and chloride complexes indicates a TBP geometry (the sensitivity to pressure of both bands of the chloride complex was observed)*.

The absorption which lies at \( \sim 30,000 \text{ cm}^{-1} \) for \( \left[ \text{Ni}(\text{dmp})_2X \right]^+ \) (Table IX; Figure 37) is attributed to a nickel to phosphorous charge transfer. A similar assignment has been made in other pentacoordinate Ni(II) complexes containing bidentate phosphorous ligands\(^4\).

The spectra of the chloride and thiocyanate complexes at \( 77^\circ\text{K} \) are compared in Figure 41. The difference between \( \nu_1' \) and \( \nu_1'' \) is greater for the thiocyanate than for the chloride (see also Table IX), indicating that the former complex is more distorted than the latter. This observation is consistent with the order obtained previously for the ability of the anion to promote pentacoordination\(^2\).

The solution electronic spectrum of \( \left[ \text{Ni}(\text{dmp})_{1.5}(\text{CN})_2 \right] \) is given in Figure 42 (see also Table IX). The same spectral features are observed for this complex as were observed for the chloride and thiocyanate complexes. Therefore, the cyanide complex possesses a distorted TBP geometry, and the same assignments of \( \nu_1' \) and \( \nu_1'' \) can be made. The \( \nu_2 \) transition is presumably obscured in the intense charge transfer region. The calculated molecular weight for a binuclear formulation

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*The author is indebted to John R. Ferraro, Chemistry Division, Argonne National Laboratories, Argonne, Illinois, for these measurements on the dmp and DPP complexes.
Figure 41. Solid state electronic spectra as Nujol mulls at 77°K of [Ni(dmp)₂X]⁺; X=Cl (---), X=CNS (-----). The absorbance scale is arbitrary.
Figure 42. Solution (CH₂Cl₂) electronic spectra of [Ni(dmp)(CN)₂] (---) and [Ni(dmp)₁₅(CN)₂] (-----). The absorbance scale is molar absorptivity x 10².
is 714, and the experimental value of 805 in benzene indicates partial association in this solvent. A sharp, intense band at 2090 cm\(^{-1}\) and a weak spike at 2100 cm\(^{-1}\) in the infrared spectrum (Nujol mull) indicate that the cyanides occupy non-equivalent positions in the coordination sphere. These data are remarkably similar to those reported for penta-coordinate nickel(II) cyanide complexes with other bidentate phosphines\(^{49}\), which were assigned a binuclear, bis-phosphine bridged, pentacoordinate geometry. In addition, in dichloromethane solution (Figure 43), the sharp, intense band occurs at 2100 cm\(^{-1}\) (\(A = 5.2 \times 10^{-4} \text{M}^{-1} \text{cm}^{-1}\)) with a weak shoulder at 2115 cm\(^{-1}\).

The distortions from a regular TBP observed for the chloride and thiocyanate complexes are not of the same origin as the distortion in the cyanide complex. The arrangement of donor atoms is considered to be that illustrated in Figure 44a, since the arrangement in Figure 44b would require the bidentate to span two equatorial positions, and molecular models indicate that the equatorial angle would have to be less than 120°.\(^{49}\) The electronic spectral differences observed in, for example, the iodide and chloride complexes also substantiate the arrangement in Figure 44a. If the actual arrangement were that of Figure 44b, then the iodide complex should exhibit two absorptions. The difference in the iodide and chloride geometries can then be interpreted in terms of the relative composition (in terms of either polarizability or optical electronegativity) of the iodide or chloride.
Figure 43. Infrared spectrum in dichloromethane solution of Ni(dmp)$_{1.5}$(CN)$_2$. 
Figure 44. Possible arrangements of the bidentate phosphorous ligand, dmp, in the inner coordination sphere of $[\text{Ni(dmp)}_2X]^+$. 
with the phosphine donors for the nickel orbitals in the equatorial plane. In the cyanide complex, the stability of the donor set \( P_3(CN)_2 \) has been mentioned previously\(^{20} \), and in order to achieve pentacoordination, one dmp must bridge two equatorial positions, and another dmp must bridge two nickel atoms (Figure 45). The distortion in the cyanide complex must then arise from a compression of an equatorial bond angle as a result of the chelation of dmp.

No evidence was found for the formation of pentacoordinate Pd(II) species with dmp. Solutions of PdX\(_2\) containing a two mole ratio of dmp are pale yellow, indicating that the main absorbing species is a square planar palladium(II) complex. A pentacoordinate species, such as \([\text{Pd(dmp)}_2X]^+\), is expected to absorb in the visible electronic region\(^{121} \).

The instability in solution of the Ni(II) four- and five-coordinate complexes may indicate that the corresponding Pd(II) complexes are likewise unstable. This instability is further indicated by the fact that the \([\text{Pd(dmp)}(\text{NCS})_2]^+\) complex demonstrated progressively poorer elemental analyses as the complex was successively recrystallized.

3. **Cobalt(II) Complexes of dmp**

Mixing solid CoBr\(_2\) or CoCl\(_2\) with two equivalents of dmp in n-butanol produces deep green solutions, which precipitate \([\text{Co(dmp)}_2X]^+\)-B(C\(_6\)H\(_5\))\(_4\) when sodium tetraphenylborate is added. These complexes are sufficiently stable in a dichloromethane/ethanol solvent mixture to
Figure 45. Proposed structure for Ni(dmp)$_{1.5}$(CN)$_2$. 
### Table X

**Five-Coordinate Cobalt(II) Complexes with dmp**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Color</th>
<th>$10^3 \chi_M$ a</th>
<th>$u_{eff}$ B. M. b</th>
<th>$\Lambda_M$ c</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(dmp)$_2$Cl]B(C$_6$H$_5$)$_4$</td>
<td>Green</td>
<td>14.75</td>
<td>1.88</td>
<td>110</td>
</tr>
<tr>
<td>[Co(dmp)$_2$Cl]SnCl$_3$</td>
<td>Green</td>
<td>14.90</td>
<td>1.89</td>
<td>130</td>
</tr>
<tr>
<td>[Co(dmp)$_2$Br]B(C$_6$H$_5$)$_4$</td>
<td>Green</td>
<td>15.09</td>
<td>1.91</td>
<td>110</td>
</tr>
<tr>
<td>[Co(dmp)$_2$I]I</td>
<td>Green</td>
<td>16.50</td>
<td>1.98</td>
<td>147</td>
</tr>
</tbody>
</table>

---

a. The magnetic susceptibilities agreed within experimental error when measured at two different field strengths.

b. The deviation is ± 0.01 B. M.

c. These are molar conductance values on freshly prepared ~10$^{-3}$ molar solutions in acetonitrile.

permit their recrystallization. Combining ethanol solutions of Co(H$_2$O)$_6$I$_2$ and dmp produces initially a deep green solution, from which green crystals of [Co(dmp)$_2$I$_2$] are rapidly precipitated. Even in deaerated dichloromethane solutions, the iodide complex is rapidly converted to the red Co(III) complex (discussed on page 160).

Acetonitrile solutions are sufficiently stable for conductance and spectral measurements. If SnCl$_2$ is added to solutions of Co(dmp)$_2$Cl$_2$,
Table XI

Solution and Solid State Electronic Spectra of Five-Coordinate Cobalt(II) Complexes with dmp.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solution (dichloromethane) cm(^{-1}) ((\epsilon_{\text{max}}))</th>
<th>Solid State Room Temperature cm(^{-1})</th>
<th>Solid State 77°K cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(dmp)(_2)Cl](_2)(C(_6)H(_5))(_4)</td>
<td>7530 (69) 14,300S (316) 16,400 (419) 24,800 (1120) 31,800 (7610)</td>
<td>7700 11,900S 16,100B 24,800 31,000</td>
<td>7800 12,700S 16,100 25,000</td>
</tr>
<tr>
<td>[Co(dmp)(_2)Cl]SnCl(_3)</td>
<td>7550 (65) 14,100S (290) 16,450 (425) 24,700 (1150) 31,900 (7700)</td>
<td>7650 12,000S 16,100B 24,700 31,100</td>
<td>---- b</td>
</tr>
<tr>
<td>[Co(dmp)(_2)Br](_2)(C(_6)H(_5))(_4)</td>
<td>7250 (69) 14,100S (312) 16,100 (455) 24,300 (1620) 31,200 (6310)</td>
<td>7600 11,900S 15,000B 23,900 29,850</td>
<td>7700 12,500S 16,600 24,600</td>
</tr>
<tr>
<td>[Co(dmp)(_2)I](_2)</td>
<td>6400 (12) 13,500S (166) 16,800 (330) 23,800 (1020)</td>
<td>6700 13,500 16,400 25,700</td>
<td>6700B 13,400 16,250A 23,850</td>
</tr>
</tbody>
</table>

a. S = shoulder, B = broad, A = asymmetrical

b. not measured
c. in acetonitrile solution
the complex \([\text{Co(dmp)}_2\text{Cl}]\text{SnCl}_3\) is rapidly deposited. The analogous reaction of the bromide with \(\text{SnBr}_2\) yielded the \([\text{Co(dmp)}_2\text{Br}_2]\text{Br}\) complex (see Experimental V).

The conductance and electronic spectral data (Tables X and XI) suggest that the complexes possess low-spin, pentacoordinate \(\text{Co(II)}\). The similarity of these data for the chloride complexes with the two weakly coordinating anions \(\text{B}((\text{C}_6\text{H}_5)_4^-\text{SnCl}_3^-\text{indicates that the identity of the cation remains the same in both complexes.}

The main spectral features of \([\text{Co(dmp)}_2\text{X}]^+\) in solution are given in Table X and are illustrated in Figure 46. These spectra are very similar to the spectrum of \([\text{Co(QP)}\text{Cl}]^+\) which has been assigned a distorted TBP \((C_{2v})\) geometry\(^{14}\). In the solid state as Nujol mulls at 77\(^\circ\)K (Figures 47-50), these spectra exhibit two shoulders on the low energy side of the absorption at \(~16,000\) cm\(^{-1}\), which from their appearance, are relatively weak and narrow. These spectral features can be conveniently explained using the energy level diagram for a d\(^7\) electronic configuration in \(C_{4v}\) symmetry (Figure 51)\(^{122}\). The assignments are given in Table XII for the \([\text{Co(dmp)}_2\text{X}]^+\) complexes. This diagram was constructed for a \(L_{\text{apical}}-\text{Co-L_{basal}}\) angle of 90\(^\circ\). Since the chelate bite of dmp is slightly too large to fit an angle of 90\(^\circ\)\(^{120}\), a distortion from the basic \(C_{4v}\) geometry is expected. Whereas the spectral contours for these complexes are similar to those observed for \([\text{Co(QP)}\text{Cl}]^+\), which has been interpreted (and confirmed by an X-ray
Figure 46. Solution ($CH_2Cl_2$) electronic spectra of [Co(dmp)$_2X$]B($C_6H_5$)$_4$; $X$=Cl (—), $X$=Br (——). The absorbance scale is molar absorptivity x $10^2$. 
Figure 47. Solid state electronic spectra of \([\text{Co(dmp)}_2\text{Cl}]\text{B(C}_6\text{H}_5\text{)}_4\) as Nujol mulls at room temperature (---) and 77°C (-----). The absorbance scale is arbitrary.
Figure 48. Solid state electronic spectra of [Co(dmp)2Br]B(C6H5)4 as Nujol mulls at room temperature (-----) and 77°K (-----). The absorbance scale is arbitrary.
Figure 49. Solid state electronic spectra of [Co(dmp)₂]⁺ as Nujol mulls at room temperature (----) and 77°K (-----). The absorbance scale is arbitrary.
Figure 50. Solid state electronic spectra as Nujol mulls at 77°C of \([\text{Co(dmp)}_2\text{X}]\text{B(C}_6\text{H}_5)_4\), X=Cl (---) and X=Br (--.--); \([\text{Co(dmp)}_2\text{I}]\text{I} (-.-.-). The absorbance scale is arbitrary.
Figure 51. Low-lying energy levels of a d⁷ electronic configuration in a ligand field of C₄ᵥ symmetry. The 2A₁ state is fixed as the zero of energy. All energies are expressed in units of cm⁻¹ x 10⁻³. Adopted from reference 122.
Table XII
Assignments for the Solid State Electronic Spectra at 77°K of the [Co(dmp)$_2$X]$^+$ Complexes.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Cl</th>
<th>Observed $v^a$</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2A_1 \rightarrow ^2B_1$</td>
<td>7800</td>
<td>7700</td>
<td>6700</td>
<td></td>
</tr>
<tr>
<td>$\rightarrow ^4E$</td>
<td>12,700</td>
<td>12,500</td>
<td>13,400</td>
<td></td>
</tr>
<tr>
<td>$\rightarrow ^4A_2$</td>
<td>14,200</td>
<td>14,000</td>
<td>-----$b$</td>
<td></td>
</tr>
<tr>
<td>$\rightarrow ^2E(a)$</td>
<td>16,100</td>
<td>16,000</td>
<td>16,250$^c$</td>
<td></td>
</tr>
<tr>
<td>$\rightarrow ^2A_2$</td>
<td>25,000</td>
<td>24,600</td>
<td>23,850</td>
<td></td>
</tr>
<tr>
<td>$\rightarrow ^2E(b)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. energy in cm$^{-1}$
b. not observed
c. asymmetrical absorption

structural determination$^{14}$) in terms of a distorted C$_{3v}$ (C$_{2v}$) geometry, the appearance of three absorptions in the 16,000 cm$^{-1}$ region cannot be satisfactorily explained in terms of this model. The structure of [Co(QP)Cl]$^+$ may be a result of the Jahn-Teller distortion for this low-spin d$^7$ complex; this effect must be considerable, since the ligand itself possesses an inherent rigid trigonal symmetry. The appearance of similar spectral contours for the C$_{2v}$ and C$_{4v}$ geometries is not
surprising when one examines Figure 18 for the 3d\(^7\) electronic configuration. The only way to differentiate between the two geometries, short of epr or X-ray structural investigations, would be the observance of the two spin forbidden transitions. The low temperature spectra facilitated the observance of these peaks in the present study.

The magnetic moments (Table X) of \([\text{Co(dmp)}_2\text{X}]^+\) are also consistent with the low-spin, pentacoordinate geometry, and are indicative of one unpaired electron with some orbital contribution. The fact that the moment for the iodide complex is some 0.10 B.M. higher than the moments for the bromide and chloride complexes suggests that the second iodide may be interacting slightly with the sixth coordination position of \([\text{Co(dmp)}_2\text{I}]^+\). The more asymmetric nature of the electronic spectral features of the iodide complex also indicates a more distorted structure. Finally, in all likelihood, the geometry of \([\text{Co(dmp)}_2\text{X}]^+\) is not rigorously C\(_4\)v, since both Jahn-Teller distortions and the chelate bite of dmp will act to distort the geometry.

The complexes \([\text{Co(dmp)}_2\text{X}]^+\) with anions other than halogen were not isolated. When Co(II) salts other than the halogens were combined with two molar equivalents of dmp, decomposition soon occurred, as indicated by the fading of the initial intense colors of the solutions and/or the deposition of light-colored, intractable solids.
Table XIII

Solution Electronic Spectra and Conductivities of $\text{trans-}[\text{Co(dmp)}_2X_2]\text{ClO}_4$

<table>
<thead>
<tr>
<th>X</th>
<th>Transitions $\text{cm}^{-1}$ ($\varepsilon_{\text{max}}$)</th>
<th>$\lambda_{\text{B}}^a$</th>
<th>$\Lambda_m^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>16,700 (154) 26,500 (5560)</td>
<td>9800</td>
<td>99.3</td>
</tr>
<tr>
<td>Br</td>
<td>15,900 (128) 24,100 (2910)</td>
<td>8200</td>
<td>97.6</td>
</tr>
<tr>
<td>I</td>
<td>14,800 (100) 17,600 (4565)</td>
<td>2800</td>
<td>90.3</td>
</tr>
</tbody>
</table>

a. Calculated using equations given in reference 123.
b. These are molar conductance values on freshly prepared $\sim10^{-3}$ molar solutions in nitromethane.

4. **Co(III) Complexes of dmp**

Air oxidation of acidic (HX) ethanol solutions of $[\text{Co(dmp)}_2X]\text{ClO}_4$ readily produces the $[\text{Co(dmp)}_2X_2]\text{ClO}_4$ complexes. In fact, dichloromethane solutions of $[\text{Co(dmp)}_2\text{I}]\text{I}$ produce the Co(III) complex without the presence of HI or oxygen within 30 min, as indicated by the color change of the solution from green to red. The complexes exhibit conductance values indicative of uni-univalent electrolytes in nitromethane (Table XIII). The electronic spectra of $[\text{Co(dmp)}_2X_2]^+$ (Table XIII) exhibit two d-d absorptions which are assigned to the $^1\text{A}_{\text{ig}} \rightarrow ^3\text{T}_{\text{ig}}$ and $^1\text{A}_{\text{ig}} \rightarrow ^3\text{T}_{\text{eg}}$ transitions in octahedral symmetry$^{123}$. Comparison
of these spectra with those of other trans-[CoL₂X₂]⁺ complexes, indicate that the [Co(dmp)₂X₂]⁺ complexes also possess a trans structure. The true symmetry of the complexes is, at best, D₄h instead of O₃, and consequently the ¹A₁g → ¹T₂g transition should be split into two bands. No splitting of this absorption was noted for the [Co(dmp)₂X₂]⁺ complexes. The spectra generate the familiar spectrochemical series, I < Br < Cl, and the reduction of B (Table XIII) follows the Nephelauxetic series, with the iodide exhibiting a remarkable reduction from the free ion value.

The 60 mc ¹H nmr spectra for the [Co(dmp)₂X₂]⁺ are given in Table XIV. In general, the resonances for dmp in the complexes are found at lower field than in the free ligand. The extreme splitting of the methyl and methylene resonances prohibits any correlation between these resonance positions and the anion X.

<table>
<thead>
<tr>
<th>X</th>
<th>methyl ¹τ</th>
<th>methylene ¹τ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>8.50 (m)ᵇ</td>
<td>7.91 (m)ᵇ</td>
</tr>
<tr>
<td>Br</td>
<td>8.40 (m)</td>
<td>7.90 (m)</td>
</tr>
<tr>
<td>I</td>
<td>8.33 (m)</td>
<td>7.90 (m)</td>
</tr>
<tr>
<td>dmp</td>
<td>9.03 (d)</td>
<td>8.57 (d)</td>
</tr>
</tbody>
</table>

a. The spectra were obtained on saturated nitromethane solutions.

b. m= multiplet, d= doublet; the figures refer to the center of the multiplet resonances.

c. This spectrum was obtained on the neat liquid.
CONCLUSIONS

Two new flexible multidentate phosphorous ligands have been synthesized and their transition metal complexes have been investigated. Both of these ligands incorporate flexible, aliphatic linkages between the phosphorous donor atoms, and hence, the geometry of the metal complexes should be determined by the electronic requirements of the metal-ligand system, and not by inherent steric requirements of the ligand.

The Ni(II) complexes of DPP, [Ni(DPP)x2] (x= halogen, NCS) containing the donor atom set P3X2, exhibit distinct pentacoordination only in the solid state. In polar solvents (acetonitrile), the complexes are four-coordinate, planar cations, [Ni(DPP)X]+. In non-polar solvents (dichloromethane, 1,2-dichloroethane), there is spectroscopic evidence for a small concentration of the pentacoordinate species. The [Ni(DPP)(CN)2] complex is five-coordinate in both solution
and the solid state. The following spectral correlations support a
tetragonal pyramidal geometry for \([\text{Ni(DPP)}X_2]\): (1) the comparison of
the visible electronic spectra of \([\text{Ni(DPP)}X_2]\) in the solid state with
\([\text{Ni(DPP)}X]^+\) in solution, (2) the sensitivity of the absorptions of
\([\text{Ni(DPP)}I_2]\) to pressure, and (3) the formation of the trigonal bi-
pyramidal \([\text{Ni(DPP)}[\text{C}_6\text{H}_5\text{P(CH}_3)_2]X]^+\) when excess \text{C}_6\text{H}_5\text{P(CH}_3)_2\) is added
to solutions of \([\text{Ni(DPP)}X_2]\).

The ligand dmp forms both the four-coordinate, planar \([\text{Ni(dmp)}X_2]\)
\((X = \text{halogen, NCS, CN})\) and the pentacordinate, trigonal bipyramidal
\([\text{Ni(dmp)}_2X]^+\) \((X = \text{halogen, NCS})\) complexes with \text{Ni(II)} salts. With
\text{Ni(CN)}_2\), the binuclear, pentacordinate \([\text{Ni(dmp)}_\text{i.5(CN)}_2]\) is formed,
utilizing a bridging bidentate phosphorous ligand. The pentacordinate
complexes were assigned a basic trigonal bipyramidal geometry on the
basis of the following spectral correlations: (1) comparison of
the spectra of \([\text{Ni(DPP)}\text{Cl}_2]\) and \([\text{Ni(dmp)}_2\text{Cl}]^+\) shows that \(\Delta\) for the
former complex is larger than for the latter complex, indicating
a difference in geometry between the two complexes, (2) at 77°K in
the solid state, the formally forbidden \(^1A_1 \rightarrow E^\prime\) transition in \text{D}_{3h}
symmetry is observed for \([\text{Ni(dmp)}_2\text{I}]^+\), and (3) the sensitivity of the
absorptions of \([\text{Ni(dmp)}_2X]^+\) to pressure. Furthermore, the chloride
and thiocyanate complexes are more distorted TBP's than the iodide
and bromide complexes, since in the case of the former complexes,
two d-d transitions are observed, whereas in the case of the latter complexes, only one absorption is observed.

These data indicate, that for flexible multidentate phosphine ligands in coordination with Ni(II), the donor set P_3X_2 will generate a TP geometry, whereas the donor set P_4X will generate a TBP geometry.

The corresponding pentacoordinate [Co(dmp)_2X]^+ complexes are assigned a TP structure (C_4v) on the basis of their visible electronic spectra. A pentacoordinate, low-spin 3d^7 complex is expected to experience the Jahn-Teller distortion; since a distorted TBP (C_2v symmetry) and a distorted TP complex of this type are expected to exhibit similar spectral contours on the basis of a one electron approximation, the observance of two absorptions at 770K attributable to spin forbidden transitions in C_4v symmetry facilitated the assignment of this geometry.

The [Co(dmp)_2X_2]^+ complexes are readily obtained from the corresponding [Co(dmp)_2X]^+ complexes. These complexes possess a trans D_4h geometry on the basis of their electronic spectra.
Comparisons of the distortion of an experimentally determined structure with that of the idealized structure are usually made by calculating the mean angular deviation. A pentacoordinate structure is somewhat unique in that there are two closely related idealized geometries. The mean angular deviation in this case could be taken as a measure of the distortion of the experimentally determined structure from the idealized structures. The following procedure is suggested as an alternative to calculating mean angular deviations (for only pentacoordinate structures) and is presented in the hope that it will provide a faster and more readily interpretable analysis of the distortions of a pentacoordinate structure.

**JUSTIFICATION:** The ten angles involved for a regular trigonal
bipyramid are readily calculated. The regular tetragonal pyramid adopted here is the one suggested by Stalick and Ibers (reference 22) as most representative of the idealized geometry. It is assumed for the structure to be examined, that it would be possible to pass from one geometry to the other by the vibrational mode illustrated in Figure 1. This assumption is justified by most structural analyses extant, since for trigonal bipyramidal structures the distortion exhibited most often is a lengthening of one equatorial bond and the opening (increasing from $120^\circ$) of the equatorial angle opposite to this bond. For tetragonal pyramidal structures, the apical bond (corresponding to the lengthening equatorial bond in the trigonal bipyramid) is the long bond; also, there are usually two angles in the range $140^\circ$ - $180^\circ$. The smaller of these two large angles is most often opposite the long apical bond. It should be obvious to the reader, that for a mean angular deviation to have meaning, the same assumptions are made implicitly.

**PROCEDURE:** The experimentally determined structure is oriented so that it corresponds to the illustrations in Figure 1. It is often helpful to orient tetragonal pyramids so that they 'look like' the trigonal bipyramid. The experimental angles are then compared to the numbers in the middle column of Table 1. If the experimental angle is greater than the number in the column it corresponds to, then the
<table>
<thead>
<tr>
<th>Trigonal Bipyramid</th>
<th>Intermediate Structure</th>
<th>Tetragonal Pyramid</th>
</tr>
</thead>
<tbody>
<tr>
<td>120°</td>
<td>+</td>
<td>110°</td>
</tr>
<tr>
<td>120°</td>
<td>+</td>
<td>110°</td>
</tr>
<tr>
<td>120°</td>
<td>-</td>
<td>140°</td>
</tr>
<tr>
<td>180°</td>
<td>+</td>
<td>170°</td>
</tr>
<tr>
<td>90°</td>
<td>-</td>
<td>95°</td>
</tr>
<tr>
<td>90°</td>
<td>-</td>
<td>95°</td>
</tr>
<tr>
<td>90°</td>
<td>+</td>
<td>89°</td>
</tr>
<tr>
<td>90°</td>
<td>+</td>
<td>89°</td>
</tr>
<tr>
<td>90°</td>
<td>+</td>
<td>89°</td>
</tr>
</tbody>
</table>

Figure 1
difference carries the sign to the left of the column; if the experimental angle is less than the number in the column, then the difference carries the sign to the right of the column. The reader should satisfy himself that a 'perfect' trigonal bipyramid would have a total value of $+64^\circ$, whereas a 'perfect' tetragonal pyramid would have a total value of $-64^\circ$. The plus and minus signs do not imply an order of magnitude. Finally, although some pentacoordinate structures are distorted in a fashion not described by Figure 1, the method is still applicable, if the true nature of the distortion is kept in mind (e.g., see reference 91). The method is applied to a number of complexes in Table 2. Although the mean angular deviations will give essentially the same information as compiled in Table 2, the imposition of the imaginary limits of $+64^\circ$ for the TBP and $-64^\circ$ for the TP provides an artificality to which the reader can compare the values as determined by this method.
### Table 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>Atom Position</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>{CoN[CH₂CH₂P(C₆H₅)₂]₃Cl}PF₆</td>
<td>N Cl P₃ P₂ P₁</td>
<td>+49.7</td>
<td>91</td>
</tr>
<tr>
<td>Ni(NNN)Br₂</td>
<td>N₂ N₃ N₁ Br₂ Br₁</td>
<td>+ 4.9</td>
<td>62</td>
</tr>
<tr>
<td>[Ni(ONN)Br₂]²⁻</td>
<td>O N₂ N₁ Br₂ Br₁</td>
<td>- 8.8</td>
<td>60</td>
</tr>
<tr>
<td>{CoCH₂N[CH₂CH₂N(CH₃)₂]Cl₂}²⁻</td>
<td>N₂ Cl₁ Cl₂ N₁ N₃</td>
<td>-20.0, b</td>
<td>69</td>
</tr>
<tr>
<td>(-18.6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co[(C₆H₅)₂PF₇]₃Br₂</td>
<td>P₂ P₁ Br₁ P₃ Br₂</td>
<td>+34.5</td>
<td>125</td>
</tr>
<tr>
<td>Ni[(C₆H₅)₂PF₇]₃I₂</td>
<td>P₂ P₁ I₁ P₃ I₂</td>
<td>+45.0</td>
<td>125</td>
</tr>
<tr>
<td>[Ni(NOP)₂]I⁺⁺</td>
<td>P₁ P₂ O N I</td>
<td>-43.0</td>
<td>90</td>
</tr>
<tr>
<td>Co(N₃S)(NCS)₂⁻</td>
<td>N₄ N₁ N₃ N₂ N₃</td>
<td>+38.7</td>
<td>92</td>
</tr>
<tr>
<td>Ni[C₆H₅P(CH₃)₂]₂Br₃</td>
<td>P₃ P₂ Br₃ Br₂ Br₄</td>
<td>+49.4</td>
<td>24</td>
</tr>
<tr>
<td>Ni[C₆H₅P(OCC₆H₅)₂]₃(CN)₂</td>
<td>C₂ C₁ P¹ P₂ P₃</td>
<td>+11.6</td>
<td>22</td>
</tr>
<tr>
<td>Ni[C₆H₅P(CH₃)₂]₃(CN)₂</td>
<td>C₂ C₁ P₂ P₃ P₁</td>
<td>+39.9</td>
<td>23</td>
</tr>
<tr>
<td>[Ni(TSP)Cl]ClO₄⁻</td>
<td>P Cl S₁ S₂ S₃</td>
<td>+46.0</td>
<td>94</td>
</tr>
<tr>
<td>Ni(CN)₅S⁻</td>
<td>C₂ C₄ C₁ C₅ C₃</td>
<td>-54.1</td>
<td>8</td>
</tr>
<tr>
<td>Compound</td>
<td>Atom Position Numbers</td>
<td>Bond Angle</td>
<td>Dipole Moment (D)</td>
</tr>
<tr>
<td>-------------------</td>
<td>-----------------------</td>
<td>------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Ni(CN)₅³⁻</td>
<td>C₃ C₅ C₁ C₂ C₄</td>
<td>+14.6</td>
<td>8</td>
</tr>
<tr>
<td>Ni(DSP)I₂</td>
<td>I₂ P S₁ S₂ I₁</td>
<td>-55.7</td>
<td>75</td>
</tr>
</tbody>
</table>

*a* The Atom position numbers refer to the position of Xₙ in Figure 1. The subscript numbers (n) of the donor atoms are those of the original authors.

*b* Two 'slightly different' structures are present in the unit cell.

*c* NNN= 6,6'-dimethyldi-(2-pyridylmethyl)amine.

*d* ONN= 1-(o-methoxyphenyl)-2,6-diazaoctane.

*e* NOP₂= bis(2-diphenylphosphinoethyl)-2-methoxyethylamine.

*f* N₂S= bis(2-diethylaminoethyl)-2-methylthioethylamine; the sulfur atom is uncoordinated.

*g* TSP= tris(o-methylthiophenyl)phosphine.

*h* DSP= bis(o-methylthiophenyl)phenylphosphine.
APPENDIX B

Attempts at Other Phosphine Ligands

Introduction:

The preparation of multidentate ligands and the study of their metal complexes has received much interest in the past decade. Of particular interest are those ligands which contain phosphorous donors, since metal-phosphine complexes often exhibit unique and extraordinary properties; pentacoordination, stabilization of unusual metal oxidation states and stabilization of metal alkyl or aryl bonds, and catalytic properties are among those unusual properties that could be cited. Hence, the preparation of new multidentate ligands in which the donor atoms or the donor atom basicity are varied, and the study of their metal complexes would provide new information for the phenomena cited above, and might provide totally new avenues of research.
Results

1. Preparation of Tris(2-diphenylphosphinoethyl)phosphite, $P[OCH_2CH_2P(C_6H_5)_2]_3$

Treatment of potassium diphenylphosphide in p-dioxane/ether with ethylene oxide followed by hydrolysis and work-up yielded 2-diphenylphosphinoethanol, $(C_6H_5)_2PCH_2CH_2OH$, b.p. 165-170°/1 torr. (Lit.\textsuperscript{128} b.p. 178-184°/18 torr). Tris(dimethylamino)phosphine and phosphino-alcohol were refluxed at 110° for two days. The evolution of dimethyl amine was followed by bubbling the effluent gas through a dilute HCl solution and by passing the gas over wet litmus. When these tests indicated no more dimethyl amine was being produced, the reaction was stopped. No distillate was obtained when the residue was heated to 80°/1 torr, indicating the absence of tris(dimethylamino)phosphine. The water-clear, mobile residue exhibited no absorptions in the infrared attributable to O-H, indicating that the phosphino-alcohol had completely reacted. Furthermore, the infrared spectrum exhibited bands which could only be assigned to $[(C_6H_5)_2PCH_2CH_2O]_3P$. The yield was quantitative.

Attempted preparation of the sulfide, oxide, and methiodide derivatives led to intractable oils. Presumably, the reaction conditions lead to the hydrolysis products of the phosphite—\,(C_6H_5)_2PCH_2CH_2OH and P(OH)$_3$.\)
The reaction of \( \text{Ni(H}_2\text{O)}_6\text{I}_2 \) with the ligand in acetone resulted in a deep purple solution, and a purple powder was isolated from ethanol.

**Anal. Calcd.** for \( \text{C}_{42}\text{H}_{42}\text{I}_3\text{Ni}_0\text{P}_4r \):

- \( \text{C}, \) 48.88; \( \text{H}, \) 4.07; \( \text{I}, \) 24.64; \( \text{P}, \) 12.0.

**Found:**
- \( \text{C}, \) 49.13; \( \text{H}, \) 4.35; \( \text{I}, \) 26.88; \( \text{P}, \) 12.2.

The analyses indicate that the complex is slightly impure, and subsequent recrystallizations did not give a complex which exhibited satisfactory analyses. Reaction of the ligand with other Ni(II) salts and with Co(II) salts yielded deeply colored oils or powders which exhibited inconsistent analyses.

A similar reaction sequence was followed in an attempt to prepare \( [(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{O}]_2\text{P} \). After the evolution of dimethylamine had ceased, an attempt was made to vacuum distill the product. However, when the temperature reached \( \sim100^\circ \) the liquid suddenly pyrolyzed, and the distillation apparatus was filled with a yellow solid.

2. **Attempted preparation of** \( (\text{CH}_3)_2\text{P(0)CH}_2\text{CH}_2\text{CH}_2\text{Cl} \).

The preparation of 3-chloropropyldimethylphosphine oxide was attempted according to the following reaction sequence:

\[
(i-\text{C}_3\text{H}_7\text{O})_3\text{P} + \text{BrCH}_2\text{CH}_2\text{CH}_2\text{Cl} \rightarrow (i-\text{C}_3\text{H}_7\text{O})_2\text{P(0)CH}_2\text{CH}_2\text{CH}_2\text{Cl} \tag{1}
\]

\[
(i-\text{C}_3\text{H}_7\text{O})_2\text{P(0)CH}_2\text{CH}_2\text{CH}_2\text{Cl} + 2\text{PCl}_5 \xrightarrow{\text{CHCl}_3} \text{Cl}_2\text{P(0)CH}_2\text{CH}_2\text{CH}_2\text{Cl} \tag{2}
\]
$$\text{Cl}_2\text{P(0)CH}_2\text{CH}_2\text{CH}_2\text{Cl} + 3\text{CH}_3\text{MgBr} \xrightarrow{(\text{C}_2\text{H}_5)\text{\_}_2^0} (\text{CH}_3)_2\text{P(0)CH}_2\text{CH}_2\text{CH}_2\text{Cl} \quad (3)$$

The products in Equations (1) and (2) were characterized by their infrared and $^1\text{H}$ nmr spectra. In (3), the Grignard reagent was added to the $\text{Cl}_2\text{P(0)CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ in ether. The reaction is complicated by the precipitation of the complex formed between Grignard reagent and the phosphoryl moiety. This precipitate is a gummy, white solid, and interferes with the mechanical stirrer. A NaHCO$_3$ wash was employed in the work-up to destroy this complex; after the work-up, a water-clear, liquid was isolated, which was distilled at $90^\circ/\text{<1 torr}$. The $^1\text{H}$ nmr spectrum was consistent with that expected for the proposed product, exhibiting a doublet centered at 0.40$\tau$ (methyl), a multiplet centered at 7.95$\tau$ ($\alpha$ and $\beta$ methylene), and a triplet centered at 6.25$\tau$ ($\gamma$ methylene). The integrated intensity ratio (3:2:1) was in agreement with theory. The infrared spectrum contains no absorptions which cannot be attributed to bands expected for $(\text{CH}_3)_2\text{P(0)CH}_2\text{CH}_2\text{CH}_2\text{Cl}$. No further characterizations or reactions were undertaken.

3. **Preparations of 1,2-Bis(diphenylphosphino)ethane.**

2-Chloroethylidiphenylphosphine did not react with magnesium chips in dry tetrahydrofuran at room temperature, even in the presence of 1,2-dibromoethane or a crystal of iodine. When warmed in reflux with a heat gun, a reaction was initiated, as indicated by a vigorous frothing of the solution. The remaining ClCH$_2$CH$_2$P(C$_6$H$_5$)$_2$ solution
was added at such a rate to maintain a gentle frothing of the solution. The product isolated after the work-up of this reaction solution, was 1,2-bis(diphenylphosphino)ethane. This bis-phosphine was identified through its infrared and $^1$H nmr spectra, and a mixed melting point.

When three molar equivalents potassium diphenylphosphide in p-dioxane was treated with one molar equivalent of P(OCH$_2$CH$_2$Cl)$_3$, the deep red color of the phosphide solution faded to colorless after $\sim\frac{1}{2}$ of the P(OCH$_2$CH$_2$Cl)$_3$ solution had been added. The addition was halted, and after work-up of the reaction mixture, a gummy solid was isolated. This solid was dissolved in ethanol, and a small amount (~30% yield) of white crystals were isolated. These were identified as 1,2-bis(diphenylphosphino)ethane, as above.

4. Attempted Preparation of 1,3-Bis[(3-ethylthiopropyl)phenylphosphino]propane.

The deep red color of C$_6$H$_5$(Na)P(CH$_2$)$_3$P(Na)C$_6$H$_5$ in liquid NH$_3$/THF$^{127}$ was discharged on the dropwise addition of two moles of ClCH$_2$CH$_2$CH$_2$SCH$_2$H$_5$ $^{128}$. A pale yellow liquid was isolated after work-up, from which no distillate could be isolated (C$_6$H$_5$(H)P(CH$_2$)$_3$P(H)C$_6$H$_5$ distills at 174$^\circ$/0.8 torr). The attempted preparations of the sulfide and methiodide derivatives led to intractable oils. The deeply colored
solutions formed when the crude product and Ni(H$_2$O)$_6$I$_2$ are mixed in ethanol slowly deposits green crystals, presumably of the original Ni(II) salt.
REFERENCES


4. The tetragonal pyramid discussed here is the one adopted by J.K. Stalick and J.A. Ibers, in reference 22. Their C₁-Ni-C₂ angle should read 160° instead of 180°.


6. A situation which is almost invariably found in tetragonal pyramids. See reference 4 and the discussion therein.


177
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   9, 1215.
   (1963), 3930.


103. J.R. Ferraro, to be published.


120. J.W. Dawson, B.C. Lane, R.J. Mynott, and L.M. Venanzi, to be published.


