1983

NMR studies of phosphorus ligand complexes of silver and cobalt

Steven Mark Socol
Iowa State University

Recommended Citation

Socol, Steven Mark, "NMR studies of phosphorus ligand complexes of silver and cobalt " (1983). *Retrospective Theses and Dissertations*. 8962.
https://lib.dr.iastate.edu/rtd/8962

INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.
2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of "sectioning" the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.

University
Microfilms
International

300 N. Zeeb Road
Ann Arbor, MI 48106

8407126

Socol, Steven Mark

NMR STUDIES OF PHOSPHORUS LIGAND COMPLEXES OF SILVER AND COBALT

Iowa State University PH.D. 1983

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

NMR studies of phosphorus ligand complexes of silver and cobalt

by

Steven Mark Socol

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1983

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PREFACE

Phosphorus ligands are of a wide range of sizes and basicities. The size of phosphorus ligands can vary from small constrained bicyclic phosphites of the type $P(OCH_2)_3CR$ to very bulky 2,6 disubstituted triarylphosphines. The basicity of phosphorus ligands ranges from $P(\underline{t}\text{-}Bu)_3$, the most basic phosphine as shown by comparison of the A_1 CO stretches in $Ni(CO)_3L$ complexes, to PF_3 which has a basicity comparable to CO. The research described in this dissertation involves the study of the consequences of steric size and lone pair basicity on the relative extent of coordination of phosphorus ligands toward silver(I) and on the ligand field in $[Co(P)_6]^{3+}$ complexes where P is a phosphorus donor. In addition, the effect of the symmetry of the phosphorus ligands on the electric field gradient at Co in $[Co(P)_6]^{3+}$ complexes is investigated.

A list of phosphorus ligands discussed in this dissertation is included in Table 1.

Table 1. Phosphorus compounds discussed in this dissertation

1	$\mathrm{PF_3}$	24	$\mathrm{P(O\text{-}2,6\text{-}C_6H_3Me_2)_3}$
2	$\mathrm{P(OEt)_3}$	25	$\mathrm{CH_3O\overline{POCH_2C(CH_3)_2CH_2O}}$
3	$\mathrm{P(\underline{p}\text{-}tolyl)_3}$	26	$\mathrm{\overline{P(OCH_2)_2CHO}}$
4	$\mathrm{P(\underline{t}\text{-}Bu)_3}$	27	$\mathrm{MeO\overline{POCH_2CH_2O}}$
5	$\mathrm{P(2,4,6\text{-}C_6H_2Me_3)_3}$	28	$\mathrm{P(CH_3)_3}$
6	$\mathrm{P(\underline{n}\text{-}Bu)_3}$	29	$\mathrm{P(\underline{i}\text{-}Pr)_3}$
7	$\mathrm{P(NMe_2)_3}$	30	$\mathrm{\underline{o}\text{-}(P(OMe)_2)_2C_6H_4}$
8	$\mathrm{P(NH_2)_3}$	31	$\mathrm{\underline{o}\text{-}(P(OEt)_2)_2C_6H_4}$
9	$\mathrm{P(OMe)_3}$	32	$\mathrm{(CH_3)_2PCH_2CH_2P(CH_3)_2}$
10	$\mathrm{P(OCH_2CH_2Cl)_3}$	33	$\mathrm{PhP(OEt)_2}$
11	$\mathrm{P(OPh)_3}$	34	$\mathrm{PPhCl_2}$
12	$\mathrm{PPh_3}$	35	$\mathrm{PEtCl_2}$
13	$\mathrm{P(O\text{-}\underline{o}\text{-}tolyl)_3}$	36	$\mathrm{Cl_2PCH_2CH_2PCl_2}$
14	$\mathrm{PEt_3}$	37	$\mathrm{Cl\overline{POCH_2CH_2O}}$
15	$\mathrm{PMe_2Ph}$	38	$\mathrm{EtO\overline{POCH_2CH_2O}}$
16	$\mathrm{PMePh_2}$	39	$\mathrm{\underline{n}\text{-}PrO\overline{POCH_2CH_2O}}$
17	$\mathrm{P(OCH_2)_3CC_2H_5}$	40	$\mathrm{\underline{n}\text{-}BuO\overline{POCH_2CH_2O}}$
18	$\mathrm{P(OCH_2)_3CCH_3}$	41	$\mathrm{\underline{i}\text{-}PrO\overline{POCH_2CH_2O}}$
19	$\mathrm{P(\overline{NCH_2C}H_2)_3}$	42	$\mathrm{\underline{i}\text{-}BuO\overline{POCH_2CH_2O}}$
20	$\mathrm{P(OCH_2CCl_3)_3}$	43	$\mathrm{\underline{sec}\text{-}BuO\overline{POCH_2CH_2O}}$
21	$\mathrm{P(OCH(CH_3)_2)_3}$	44	$\mathrm{\underline{t}\text{-}BuO\overline{POCH_2CH_2O}}$
22	$\mathrm{P(NMeCH_2)_3CCH_3}$	45	$\mathrm{PhO\overline{POCH_2CH_2O}}$
23	$\mathrm{P(O\text{-}\underline{t}\text{-}Bu)_3}$	46	$\mathrm{CF_3CH_2O\overline{POCH_2CH_2O}}$

Table 1. Continued

47	$\mathrm{O(CH_2CH_2)_2N\overline{POCH_2CH_2O}}$	63	$\mathrm{MeO\overline{POCH_2CH_2S}}$
48	$\mathrm{MeO\overline{POCH_2CHCH_3O}}$	64	$\mathrm{PhO\overline{POCH_2CH_2S}}$
49	*dl*-*meso*-$\mathrm{Cl\overline{POCHCH_3CHCH_3O}}$	65	$\mathrm{C_6H_4}$-*o*-$\mathrm{O_2PCl}$
50	*dl*-$\mathrm{MeO\overline{POCHCH_3CHCH_3O}}$	66	$\mathrm{C_6H_4}$-*o*-$\mathrm{O_2POMe}$
51	*dl*-$\mathrm{EtO\overline{POCHCH_3CHCH_3O}}$	67	$\mathrm{P(CH_2CH_2CN)_3}$
52	*dl*-*n*-$\mathrm{PrO\overline{POCHCH_3CHCH_3O}}$	68	$\mathrm{(MeO)_2PCH_2CH_2P(OMe)_2}$
53	*dl*-*i*-$\mathrm{PrO\overline{POCHCH_3CHCH_3O}}$	69	$\mathrm{P(OCH)_3(CH_2)_3}$
54	$\mathrm{MeO\overline{POC(CH_3)_2C(CH_3)_2O}}$	70	$\mathrm{\underline{CH_2O\overline{POCH_2CH_2}}\overline{CHO}}$
55	$\mathrm{F\overline{POCH_2CH_2O}}$	71	ax-$\mathrm{MeO\overline{POCH(CH_3)_{eq}CH_2CH(CH_3)_{eq}O}}$
56	$\mathrm{Ph\overline{POCH_2CH_2O}}$	72	eq-$\mathrm{MeO\overline{POCH(CH_3)_{eq}CH_2CH(CH_3)_{eq}O}}$
57	$\mathrm{Et\overline{POCH_2CH_2O}}$	73	ax-$\mathrm{MeO\overline{POCH(CH_3)_{eq}CH_2CH_2O}}$
58	$\mathrm{OC(NMe\overline{POCH_2CH_2O})_2}$	74	ax-*n*-$\mathrm{PrO\overline{POCH(CH_3)_{eq}CH_2CH_2O}}$
59	$\mathrm{P(SMe)_3}$	75	eq-$\mathrm{MeO\overline{POCH(CH_3)_{eq}CH_2CH_2O}}$
60	$\mathrm{As(OMe)_3}$	76	eq-*n*-$\mathrm{PrO\overline{POCH(CH_3)_{eq}CH_2CH_2O}}$
61	$\mathrm{As(OCH_2)_3CCH_3}$	77	$\mathrm{MeO\overline{POCH_2CH_2CH_2O}}$
62	$\mathrm{Cl\overline{POCH_2CH_2S}}$	78	$\mathrm{PPhH_2}$
		79	$\mathrm{MeOP(OCH_2)_2C(CH_2O)_2POMe}$
		80	$\mathrm{P(OCH_2)_3CCH_2Br}$
		81	*meso*-$\mathrm{MeO\overline{POCHPhCHPhO}}$

PART I. COORDINATION OF PHOSPHORUS LIGANDS TO SILVER(I)

INTRODUCTION

It has long been recognized that changing the substituents on phosphorus ligands can have profound influences on the properties of the free ligands as well as on their behavior as complexing agents. These changes can be of either a steric or an electronic nature. Until 1970, the properties of phosphorus ligands were discussed exclusively in terms of electronic considerations and steric effects were for the most part ignored (1).

Electronic effects are manifested in the basicity of the phosphorus lone pair. In general, the basicity at the phosphorus lone pair decreases with increasing electronegativity of the substituents on phosphorus. That is, phosphines are more basic than aminophosphines which are more basic than phosphites which are more basic than $\underline{1}$. The poor basicity of $\underline{1}$ is such that the donor/acceptor properties of this ligand have been compared to that of CO. Experimental evidence for this comparison comes from the CO stretches in $Mo(CO)_3(\underline{1})_3$ from which Cotton concluded that $\underline{1}$ was a better π acceptor than CO (2). Green and co-workers later reached this same conclusion on the basis of their interpretation of the photoelectron spectra of $Ni(\underline{1})_4$ and $Ni(CO)_4$ (3).

The electronic properties of phosphorus ligands can be compared in relation to a number of criteria based on either measurements of CO stretching frequencies in metal carbonyl complexes or of phosphorus coupling constants. Tolman quantifies the donor/acceptor properties of phosphorus ligands by observing the A_1 CO stretch of $Ni(CO)_3L$ complexes.

He defines the substituent additivity contribution χ_i for phosphorus ligands $PX_1X_2X_3$ as

$$\nu = [2056.1 + \sum_{i=1}^{3} \chi_i]\ \mathrm{cm}^{-1} \qquad (1)$$

where ν is the A_1 stretch of a $Ni(CO)_3L$ complex (4). Protonation studies have also been used to study the relative basicity of phosphines and phosphites. The value of ^1JPH has been related to the s character of the P-H bond (5). It has also been found that more basic phosphorus ligands have a smaller value of ^1JPH due to the s electrons being more diffuse because of a smaller positive charge on phosphorus (6). For the same reasons ^{31}P-^{77}Se one-bond couplings in the corresponding selenides can be used as a measure of phosphorus basicity (7). A good correlation is seen between ^1JPH in the protonated phosphorus ligand and $^1J^{77}Se$-^{31}P in the corresponding selenophosphate (7). Moreover, $^1J^{77}Se$-^{31}P values for the corresponding selenophosphates correlate very well with the B-H stretching frequencies in the analogous phosphite borane adducts (7). It has also been noted that a linear correlation exists between the electronegativity of the substituents on phosphorus and the $^1J^{31}P$-^{77}Se value of the corresponding selenophosphate (7).

Recently, the importance of steric considerations in the coordination of phosphorus ligands has become recognized (1,8). Experiments conducted by Tolman demonstrated that the affinity of Ni(0) for phosphorus ligands is dominated by steric effects with electronic considerations being of little importance. For example, the positions of equilibria of the type 2 below

$$NiL_4 + 4L' \rightleftharpoons NiL_{4-n}L'_n + (4-n)L' + nL \qquad (2)$$

are a function of the steric size of L and L′ with Ni(0) binding to smaller ligands preferentially (9). The extent of ligand dissociation in NiL_4 complexes (Equation 3) was also found to be dependent on the

$$NiL_4 \overset{k_d}{\rightleftharpoons} NiL_3 + L \qquad (3)$$

size of L, with larger ligands dissociating to a greater extent (10). In another set of experiments a linear relationship was found between the degree of substitution of carbonyl groups from $Ni(CO)_4$ upon reaction of excess ligand in a sealed tube and the size of the ligands, with smaller ligands displacing CO to a greater extent (9).

Since the ability of phosphorus ligands to compete for Ni(0) could not be adequately rationalized in terms of electronic properties but could be explained with steric arguments, it became desirable to quantitate these steric properties. Tolman defined the ligand cone angle, θ, for symmetric ligands as the apex angle of a cylindrical cone, centered 2.28 Å from the center of the phosphorus atom, which just touches the outermost substituent van der Waals radii as shown in Figure 1. If there are internal degrees of freedom, the substituents are oriented to give a minimum cone angle (9).

It was deemed of interest to compare the results obtained with Ni(0) complexes to that of a positively charged metal ion wherein electronic effects would be expected to be of greater importance. The silver(I) ion

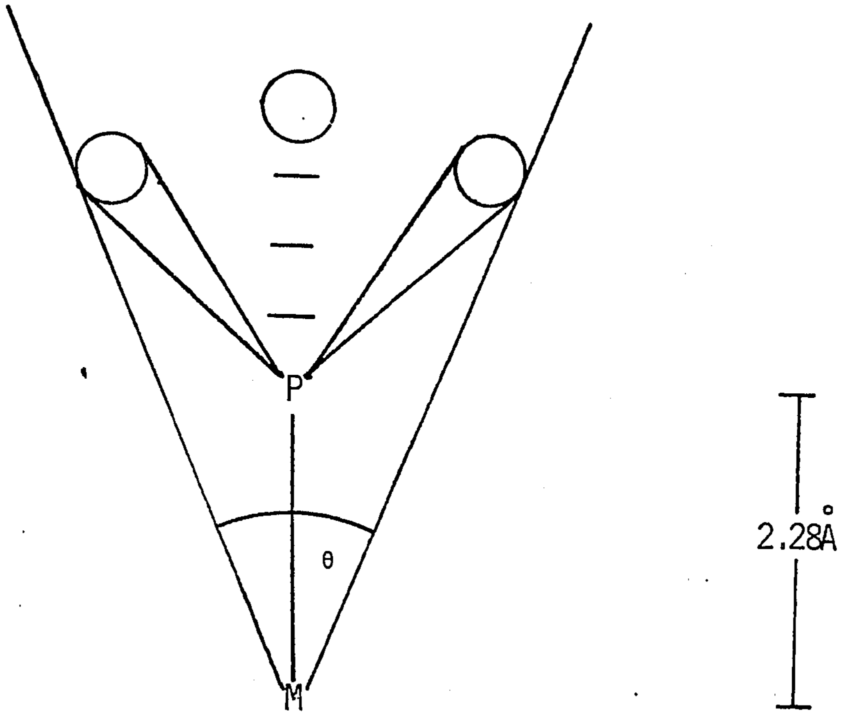


Figure 1. The phosphorus ligand cone angle as defined by Tolman

is an excellent candidate for such a comparison. Compared to Ni(0), the silver(I) ion has a slightly larger radius in addition to possessing a positive charge (11). Both of these factors should make Ag(I) more sensitive to electronic compared to steric effects.

Previous work has hinted that this may indeed be true. Muetterties found that 2 which is smaller but less basic than 3, competes about equally as well as 3 for Ag(I) (11). The role of steric effects in limiting the extent of coordination of phosphorus ligands to Ag(I) has also been demonstrated. Although ionic four-coordinate Ag(I) complexes of phosphorus ligands have long been known (11-16), it has been observed that large phosphine ligands do not form four-coordinate complexes with this metal ion. For example, only two molecules of 4 coordinate to Ag(I) either in the solid state or in solution (17). Likewise, a crystal structure determination of a two-coordinate complex of a large phosphorus ligand $[Ag(\underline{5})_2]PF_6$ has been shown to be sterically crowded owing to interligand methyl group repulsions (18).

The majority of silver(I) complexes of phosphorus ligands show a temperature dependence in their $^{31}P\{H\}$ NMR spectra. At room temperature, singlets are observed because the phosphorus atoms are decoupled from the silver atoms due to rapid intermolecular exchange. As the temperature is lowered, the exchange is frozen out and the $^{31}P\{H\}$ NMR spectrum appears as a doublet of doublets. The doublet of doublet pattern results from the two silver nuclei at spin 1/2 which in nature are each approximately 50% abundant with $\mu^{109}Ag/\mu^{107}Ag = 1.15$ as seen in Table 2.

Table 2. NMR properties of nuclei

Isotope	Natural Abundance %	Spin I	Magnetogyric ratio ($\gamma/10^7$ rad $T^{-1}s^{-1}$)	Relative receptivity[a]
^1H	99.985	1/2	26.7510	1.000
^{13}C	1.108	1/2	6.7263	1.59×10^{-2}
^{31}P	100.0	1/2	10.829	6.64×10^{-2}
^{107}Ag	51.82	1/2	-1.0835	6.69×10^{-5}
^{109}Ag	48.18	1/2	-1.2449	1.01×10^{-4}

[a] For equal number of nuclei at constant field.

The magnitude of Ag-P coupling is dependent on the coordination number of Ag(I) as well as the electronegativity of the substituents attached to phosphorus. This is to be expected from theory. Following the method of Pople and Santry, the Fermi contact term for spin-spin coupling between two nuclei A and B is given by

$$J_{AB} = k\, \alpha_A^{\,2} \alpha_B^{\,2} |\psi_A(0)|^2 |\psi_B(0)|^2 / {}^3\Delta E \qquad (4)$$

where k is a constant for the group of compounds in question, the α factors represent the localized hybrid bond s-character in a valance bond description, the $|\psi_A(0)|$ and $|\psi_B(0)|$ terms refer to the s-electron densities at the nucleus of A and B and $^3\Delta E$ is the singlet triplet excitation energy (19,20). A reduced coupling constant K_{AB} which is independent of the nuclear magnetic moments of A and B can be defined by

$$K_{AB} = (2\pi/\hbar\ \gamma_A\gamma_B)\cdot J_{AB} \qquad (5)$$

where γ_A and γ_B are the magnetogyric ratios of A and B (21). For the remainder of this work only J couplings will be discussed. Equation 4 predicts that one-bond phosphorus couplings should increase upon placing more electronegative groups on phosphorus since a larger positive charge on phosphorus will tend to increase $|\psi_P(0)|$. Indeed, an increase of phosphorus coupling constants with increasing electronegativity of the substituents on phosphorus has been previously noted in P-C, P-H, P=Se, P-W and P=O couplings (22). Likewise, the Ag-P coupling for Ag(I) complexes of phosphite ligands has been shown to be greater than for phosphine ligands of the same stoichiometry (11). As n increases in AgL_nX where X can be either a coordinating or a noncoordinating anion, silver-phosphorus coupling decreases due to the decrease in s character in the silver hydridization (11,23,24). In fact, plots of $^1J_{Ag-P}$ *vs* 1/n for $[Ag(\underline{2})_n]^+$, $[Ag(\underline{3})_n]^+$ and $[Ag(\underline{6})_n]^+$ (n = 2-4) are nearly linear (23).

During the course of this study, the crystalline compound $[Ag(\underline{7})_2]BPh_4$ was isolated. Since this compound appeared to be a unique example of a complex whose ligands do not sterically demand an apparent coordination number of two, an x-ray crystal and molecular structural investigation was undertaken to determine if coordination of the anion was perhaps involved. Such a study also offered the opportunity to compare the conformations of ligand $\underline{7}$ in a monovalent metal complex with those in zero-valent iron complexes reported earlier (25,26).

The preferred conformation of tris(dialkylamino)phosphines has been a topic of recent interest. Of the five conformations which have been proposed for these molecules (A-E in Figure 2), the two that have drawn theoretical support for being the most stable are structures C and D. Recent ab initio molecular orbital calculations on 8 suggest that C represents the most stable conformation with only a slight energy difference between this structure and D (26). The same conclusion was reached in an MNDO study of 7 (27). Unfortunately, 8 exists only as its borane adduct (28,29) and most uncomplexed acyclic tris(dialkylamino)-phosphines such as 7 are liquids at room temperature which become glasses at low temperature. Recently, however, a number of structures have appeared of coordinated 7 (25,26) or of larger systems containing the PN_3 moiety (30-36). In these structures, the aminophosphines adopt conformations closely resembling either C or D. For example, the ligand in $Fe(7)(CO)_4$ adopts conformation C (25) as does one of the ligands in trans-$Fe(7)_2(CO)_3$ (26). The second ligand in the latter complex possesses the symmetry of D. A common phenomenon observed in these structures is that one of the nitrogens is more pyramidal than the remaining two. The P-N bond to the more pyramidal nitrogen is the longest of the three presumably due to the presence of less s character. This trend appears to be more pronounced in ligands having the C_s symmetry of D. It is thought that the presence of three electron donating NR_2 groups renders phosphorus insufficiently electronegative to maintain planarity in all three nitrogens (37). Support of this postulate comes from structural data of $OP(NR_2)_3$ molecules. As expected, the nitrogens are more planar in

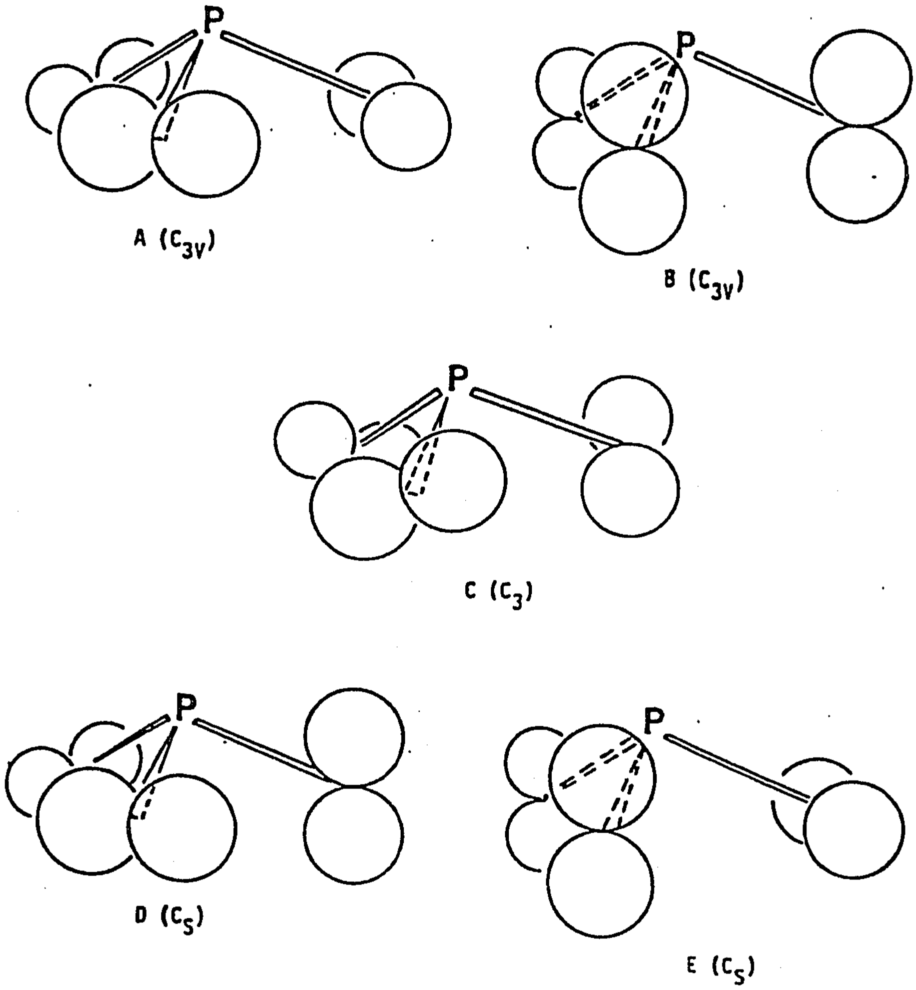


Figure 2. Some possible conformations of tris(dialkylamino)phosphines

$OP[N(CH_2CH_2)_2O]_3$ than in $SeP[N(CH_2CH_2)_2O]_3$ wherein the phosphorus is less electronegative (33). In the weak adduct formed from $OP(NMe_2)_3$ and $SAsMePh_2$, the aminophosphine derivative adopts the propeller-like conformation C with essentially planar nitrogens and equal phosphorus-nitrogen bond lengths (32).

Coordination number 2 is quite uncommon for metal complexes and it is largely limited to relatively few compounds of monovalent copper, silver and gold and of divalent mercury (38). The only previously reported structure of Ag(I) complexed to two phosphorus ligands in a two coordinate cation is $[Ag(\underline{5})_2]PF_6$ (18). A comparison of the Ag-P bond lengths in $[Ag(\underline{5})_2]PF_6$ and $[Ag(\underline{7})_2]BPh_4$ is of interest since $\underline{7}$ is less sterically demanding, but it is also less basic than $\underline{5}$.

It will be shown in this section that in contrast to Ni(0) wherein the coordination properties of phosphorus ligands are determined mainly by steric consideratons, electronic effects gain importance in the Ag(I) system. Likewise, it will be shown that the extent of coordination of phosphorus ligands to Ag(I) can be limited by poor phosphorus lone pair basicity in addition to large steric size.

EXPERIMENTAL

Procedures

Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Conductivities were measured with an Industrial Instruments Inc. Model RA 16B2 conductivity bridge. ^1H (89.55 MHz) and ^{13}C (22.5 MHz) NMR spectra were obtained with a JEOL FX-90Q spectrometer operating in the FT mode while locked on the ^2H resonance of deuterated solvents and were referenced to internal Me_4Si. All ^{13}C and ^1H NMR spectra were recorded at ambient temperatures unless otherwise indicated. The ^{31}P NMR spectra were obtained with either a Bruker HX-90 spectrometer operating at 36.44 MHz or a Bruker WM-300 spectrometer operating at 121.51 MHz in the FT mode while locked on the ^2H resonance of a deuterated solvent. The external standard was PCl_3 (219.4 ppm) and the chemical shifts are reported with respect to 85% H_3PO_4. All ^{31}P NMR samples were run in 75% CH_2Cl_2/25% d_6-acetone at -95° unless stated otherwise. Spectra of silver complexes which were later run unlocked in 100% CH_2Cl_2 showed essentially the same values of $^1J_{Ag-P}$ and chemical shifts. Molecular weights were obtained using a Knaur Vapor Pressure Osmometer at 37°.

Materials

All solvents were reagent grade or better. Acetone was dried over molecular sieves. Ether was distilled from potassium/benzophenone while methylene chloride was distilled from P_4O_{10}.

Silver tetrafluoroborate was purchased from Alfa Inorganics. Silver nitrate and silver chloride were purchased from Fisher Chemical Company. Silver cyanide was purchased from Mallinckrodt and silver iodide was supplied by Allied Chemical. All silver salts were used as received. The ligands $P(OMe)_3$ (9), $P(OEt)_3$ (2), $P(OCH_2CH_2Cl)_3$ (10), $P(OPh)_3$ (11), PPh_3 (12), and $P(NMe_2)_3$ (7) (Aldrich); P(O-*o*-tolyl)$_3$ (13) (Eastman) and PF_3 (1), PEt_3 (14) PMe_2Ph (15) and $PMePh_2$ (16) (Strem) were obtained from commercial sources. All ligands obtained from commercial sources, except (1) which is a gas and was used as received, were purified by distillation or recrystallization.

Preparation of Compounds

$P(OCH_2)_3CC_2H_5$ (17)

This compound was prepared by the general method which Verkade and Heitsch used to prepare 18 (39).

KSeCN

This compound was prepared by the method of Waitkins and Shutt (40).

$P(NCH_2CH_2)_3$ (19)

A literature method was followed for the preparation of this compound (41). Purification by distillation was not carried out because of a previous explosion reported when this was attempted (42). The crude product was judged to be greater than 90% pure by ^{31}P NMR spectroscopy (^{31}P NMR $((CD_3)_2CO)$ 131.3, lit. 129 (42)).

$P(OCH_2CCl_3)$ (20)

This ligand was prepared by the method of Gerrard *et al.* (43) (b_5 = 160°, lit. $b_{0.5}$ = 122° (43); ^{31}P NMR ($(CD_3)_2CO$) 136.6).

$P(OCH(CH_3)_2)_3$ (21)

This phosphite was prepared as originally described by Ford-Moore and Williams (44) (b_5 = 40°, lit. b_{11} = 63-64 (45); ^{31}P NMR ($(CD_3)_2CO$) 140.6, lit. 138 (46)).

$P(NMeCH_2)_3CCH_3$ (22)

This ligand was synthesized using the procedures of Kroshefsky *et al.* (7).

P(O-*t*-Bu)$_3$ (23)

This water stable but extremely acid sensitive ligand was prepared using the method of Cox and Newton (47) (b_1 = 62-64, lit. b_3 = 67-69 (47); ^{31}P NMR ($(CD_3)_2CO$) 138.4, lit. 138.2 (48)).

$P(O\text{-}2,6\text{-}C_6H_3Me_2)_3$ (24)

Although the preparation of this compound has previously been reported in the literature (49), the following procedure was found to be an improvement. To a solution of PCl_3 (14.7 g, 10.7 mMol) and Et_3N (43.5 g, 43.0 mMol) in 500 ml of Et_2O was added dropwise a solution of 2,6-dimethylphenol (41.3 g, 38.8 mMol) in 200 ml of Et_2O. The solution was kept at 5° with an ice bath. The precipitated $NEt_3{\cdot}HCl$ was removed by filtration after which the solvent was removed under reduced pressure at room temperature. Excess phenol was removed by distillation at 45° and 5 mm Hg. Two recrystallizations from hexanes yielded 24 in 83% yield as white flakes (mp = 93.0, lit. 83-84 (49); ^1H NMR ($CDCl_3$) 2.2s 2H CH_3, 6.9m 1H C_6H_3; ^{31}P NMR ($(CD_3)_2CO$) 143.9).

$CH_3O\overline{POCH_2C(CH_3)_2CH_2O}$ (25)

This phosphite was prepared as previously described (50).

$\overline{P(OCH_2)_2CHO}$ (26)

This phosphite was prepared as previously described (51).

$MeO\overline{POCH_2CH_2O}$ (27)

This phosphite was prepared as previously described (7).

$SeP(O\text{-}\underline{t}\text{-}Bu)_3$, $SeP(OCH_2CCl_3)$, $SeP(OC_6H_5)_3$, $SeP(O\text{-}2,6\text{-}C_6H_3Me_2)_3$ and $SeP(O\text{-}\underline{o}\text{-}tolyl)_3$

These selenophosphates were prepared by the procedure given by P. Nicpon and D. W. Meek for the preparation of phosphine selenides (52). A solution of phosphite (0.4 mMol) and KSeCN (0.4 mMol) was stirred in acetonitrile for 30 minutes. The selenophosphates were then extracted with benzene after removal of solvent. $SeP(OCH_2CCl_3)_3$ was further purified by sublimation at 100° and 1 torr ($SeP(O\text{-}\underline{t}\text{-}Bu)_3$, ^{31}P NMR ($(CD_3)_2CO$) 31.8, lit. 31.1 (47); $SeP(OCH_2CCl_3)_3$, mp = 77-79, ^1H NMR ($CDCl_3$) 4.7d JPH = 8 Hz, ^{31}P NMR ($(CD_3)_2CO$) 71.7, low resolution mass spectrum showed peaks in the parent ion region in the expected abundance ratio due to the isotope abundance of Se; $SeP(OC_6H_5)_3$, ^{31}P NMR ($CDCl_3$) 59.7, lit. 58 (53); $SeP(O\text{-}2,6\text{-}C_6H_3Me_2)_3$, ^{31}P NMR (CD_3CN) 51.0; $SeP(O\text{-}\underline{o}\text{-}tolyl)_3$, ^{31}P NMR ($(CD_3)_2CO$) 55.0).

$[Ag(\underline{9})_4]BF_4$

To a solution of $AgBF_4$ (0.302 g, 1.55 mMol) in 50 ml of acetone was injected 9 (3.20 g, 25.8 mMol). Addition of Et_2O resulted in the precipitation of the product which was recrystallized by slow addition of Et_2O into an acetone solution to give a 74% yield of $[Ag(\underline{9})_4]BF_4$ (^1H NMR ($(CD_3)_2CO$, 25°) 3.69d JPH = 11.7 Hz; ^1H NMR ($(CD_3)_2CO$, -65°) 3.67s; Anal. Calcd. for $C_{12}H_{36}BF_4O_{12}P_4$: C, 20.85; H, 5.21. Found: C, 21.00; H 5.47). Prepared in a similar manner in comparable yields were $[AgL_4]BF_4$ complexes where L is 17 or 10 or 2.

$[Ag(\underline{12})_4]BF_4$

This complex was prepared by using the procedure Cotton and Goodgame reported for the perchlorate salt (13) except that acetone was used as a solvent instead of ethanol. An 81% yield was obtained upon recrystallization from acetonitrile/ether. Prepared in a similar manner were $[Ag(\underline{15})_4]BF_4$ and $[Ag(\underline{16})_4]BF_4$ which were obtained in comparable yields after recrystallization from acetone/ether.

$[Ag(\underline{11})_3]BF_4$

To a solution of $AgBF_4$ (0.173 g, 0.891 mMol) in 15 ml of acetone was injected 11 (2.18 g, 7.63 mMol). The solution was filtered and the product was obtained in 74% yield after washing with Et_2O. This compound could be recrystallized by slow addition of ether into an acetone solution (Anal. Calcd. for $C_{54}H_{45}AgBF_4O_9P_3$: C, 57.61; H, 4.00; P, 8.27. Found: C, 58.31; H, 4.25; P, 8.26).

$[Ag(\underline{21})_3]BPh_4$

To a solution of $AgBF_4$ (0.219 g, 1.12 mMol) in 20 ml of EtOH was added <u>21</u> (1.20 g, 5.76 mMol). The solution was allowed to stir for 2 minutes before $NaBPh_4$ (0.500 g, 1.46 mMol) was added. The product crystallized upon cooling to -20° for a period of 2 hrs. The product was washed with EtOH and then placed under vacuum for 1/2 hr. A yield of 97% was obtained (^1H NMR ($(CD_3)_2CO$) 6.5-7.5m 20H C_6H_5, 4.7m 9H CH, 1.30d 54H CH_3 $^2JHH = 6.3$ Hz).

$[Ag(\underline{21})_4]BPh_4$

To a solution of $AgBF_4$ (0.339 g, 1.74 mMol) in 30 ml of $(CH_3)_2CHOH$ was added <u>21</u> (3.45 g, 16.6 mMol). After the solution was allowed to stir for 2 minutes $NaBPh_4$ (0.660 g, 1.93 mMol) was added to precipitate the product which was subsequently recrystallized in 89% yield from acetone/ether (^1H NMR ($(CD_3)_2CO$) 6.5-7.5m 20H C_6H_5, 4.78m 12H CH, 1.30d 72H CH_3 $^2JHH = 6.3$ Hz).

$Ag(\underline{24})BF_4$

In 30 ml of CH_2Cl_2 was dissolved $AgBF_4$ (10.2 g, 1.02 mMol) and <u>24</u> (0.450 g, 1.14 mMol). The mixture was allowed to stir for 5 minutes. The product was precipitated by the addition of 20 ml of ether followed by slow addition of hexanes. A yield of 69% was obtained after recrystallization by slow addition of hexanes into a solution of 50% CH_2Cl_2 in Et_2O (^1H NMR (CD_3CN) 6.9m 1H C_6H_3, 2.1s 2H CH_3).

$[Ag(23)_2]BF_4$

To a solution of $AgBF_4$ (0.213 g, 1.10 mMol) in 20 ml of acetone was added 23 (1.50 g, 6.60 mMol). The solution was allowed to stir for 10 minutes. Addition of Et_2O (10 ml) and hexanes (50 ml) resulted in the precipitation of $[Ag(23)_2]BF_4$ in 67% yield (^1H NMR ($(CD_3)_2CO$) 1.4s).

Ag(23)X

Complexes where X = Cl, CN or I were prepared by reacting four equivalents of 23 with a suspension of the corresponding silver salt. For example, Ag(23)Cl was prepared by adding 23 (2.23 g, 8.92 mMol) to a suspension of AgCl (0.319 g, 2.22 mMol) in Et_2O. The AgCl went into solution over a period of 10 minutes. Hexanes were then added and the solution was cooled to -70° overnight to precipitate the product. A yield of 69% was obtained after recrystallization from hexanes (^1H NMR ($CDCl_3$) 1.4s; Anal. Calcd. for $C_{12}H_{27}O_3ClPAg$: C 36.6, H 6.9; Found: C 37.8, H 7.8.) Prepared in a similar manner were Ag(23)I which could only be isolated as an oil in 55% yield upon attempted recrystallization from hexanes (^1H NMR ($CDCl_3$) 1.4s) and Ag(23)CN which was recrystallized from hexanes in 51% yield (^1H NMR ($CDCl_3$) 1.4s).

Ag(23)$_2$NO$_3$

To a suspension of AgNO$_3$ (0.30 g, 1.76 mMol) in 20 ml of ether was injected 23 (2.50 g, 10.0 mMol). The mixture was allowed to stir as the AgNO$_3$ reacted and went into solution. Cooling to -70° resulted in the precipitation of colorless needles in 59% yield (^{1}H NMR (CDCl$_3$) 1.4s; Anal. Calcd. for $C_{24}H_{54}AgO_9NP_2$: C, 42.99; H, 8.06. Found: C, 43.19; H, 8.39).

[Ag(7)$_2$]BPh$_4$

To a solution of AgBF$_4$ (0.210 g, 1.10 mMol) in 30 ml of EtOH was injected 7 (0.360 g, 2.21 mMol). After the mixture was allowed to stir for 30 seconds, NaBPh$_4$ (0.450 g, 1.40 mMol) was added to precipitate the product which was isolated in 50% yield after recrystallization by slow diffusion of Et$_2$O vapor into a saturated solution of [Ag(7)$_2$]BPh$_4$ in CH$_2$Cl$_2$. (^{1}H NMR (CD$_2$Cl$_2$, -45°) 2.61t 36H NCH$_3$$|{}^2\mathrm{JPH} + {}^4\mathrm{JPH}|$ = 11.4 Hz, 6.8-7.2m 20H C$_6$H$_5$.)

[Ag(7)$_3$]BPh$_4$

To a solution of AgBF$_4$ (0.124 g, 0.634 mMol) in 30 ml of ethanol, was injected 7 (0.692 g, 4.25 mMol). After the solution was allowed to stir for 30 seconds, NaBPh$_4$ (0.250 g, 0.731 mMol) was added to precipitate [Ag(7)$_3$]BPh$_4$. After washing with ethanol a yield of 72% was realized. ^{1}H NMR ((CD$_3$)$_2$CO) 2.57d 54H NCH$_3$ ^{2}JPH = 10.5 Hz, 6.8-7.2m 20H C$_6$H$_5$).

An attempt at recrystallizing $[Ag(\underline{7})_3]BPh_4$ from CH_2Cl_2/Et_2O resulted in the precipitation of a mixture of $[Ag(\underline{7})_2]BPh_4$ and $[Ag(\underline{7})_3]BPh_4$ as shown by low temperature ^{31}P NMR spectroscopy (vide infra).

$[Ag(\underline{22})_3]BPh_4$

Into a solution of $AgBF_4$ (0.157 g, 0.0807 mMol) in 20 ml of ethanol was injected $\underline{22}$ (0.573 g, 2.90 mMol). Addition of $NaBPh_4$ (0.320 g, 0.936 mMol) resulted in precipitation of $[Ag(\underline{22})_3]BPh_4$ in 72% yield after washing with ethanol. This compound could be recrystallized without loss of ligand from acetone/EtOH (^1H NMR ($(CD_3)_2CO$) 0.90s 9H C-CH_3; 2.63d 27H NCH_3 ^3JPH = 18.1 Hz, 2.79d 18H CH_2 ^3JPH = 4.9 Hz, 6.8-7.2m 20H C_6H_5).

$[Ag(\underline{7})_2X]$

Complexes where X = Cl, CN, I or NO_3 were prepared by reacting 8.0 or more molar equivalents of ligand with an ether suspension of the corresponding Ag(I) salt. As an example $[Ag(\underline{7})_2Cl]$ was prepared by injecting $\underline{7}$ (3.50 g, 21.6 mMol) into a suspension of AgCl (0.362 g, 2.36 mMol) in 50 ml of Et_2O whereupon the AgCl slowly dissolved. Slow evaporation of some of the solvent under a nitrogen atmosphere caused precipitation of the product, which was subsequently obtained in 72% yield as colorless needles after recrystallization from Et_2O (^1H NMR ($(CD_3)_2CO$) 2.62d ^2JPH = 10.2; Anal. Calcd. for $C_{12}H_{36}N_6P_2ClAg$: C, 30.68; N, 17.90. Found: C, 31.08; N, 17.88). The same procedure was used to prepare $Ag(\underline{7})_2I$, $Ag(\underline{7})_2CN$ and $Ag(\underline{7})_2NO_3$ in yields at 68, 89 and 75%, respectively.

[Ag(<u>19</u>)$_4$]BF$_4$

Addition of approximately 14 molar equivalents of <u>19</u> to a solution of AgBF$_4$ (0.155 g, 0.796 mMol) in 20 ml of EtOH resulted in the immediate precipitation of [Ag(<u>19</u>)$_4$]BF$_4$. This heat and light sensitive compound is insoluble in ethanol and acetone but is soluble in CH$_2$Cl$_2$. A 76% yield of product was obtained after recrystallization from CH$_2$Cl$_2$/Et$_2$O (^{1}H NMR (CDCl$_3$) 2.16d ^{3}JPH = 11.7; Anal. Calcd. for $C_{24}H_{48}AgBF_4P_4N_{12}$: C, 35.01; H, 5.83; N, 20.42. Found: C, 35.07; H, 6.28; N, 18.66).

[Ag(<u>19</u>)$_4$]X

Approximately 10 molar equivalents of <u>19</u> was injected into a suspension of AgI (0.417 g, 1.78 mMol) in 50 ml of Et$_2$O. The yellow color of the AgI disappeared within two minutes and the solution became a cloudy white. The solution was stored at -65° overnight whereupon the product precipitated from solution. The product was obtained as a slightly oily white powder in 80% yield after filtration and washing with Et$_2$O and hexanes. An attempt at recrystallization of [Ag(<u>19</u>)$_4$]I from CH$_2$Cl$_2$/Et$_2$O in the presence of a molar equivalent of free ligand did not improve the physical appearance of the compound (^{1}H NMR (CDCl$_3$) 2.1d ^{3}JPH = 11.0). [Ag(<u>19</u>)]$_4$Cl, which could only be isolated as an oil, was prepared by using essentially the same procedure (^{1}H NMR (CDCl$_3$) 2.1d ^{3}JPH = 10.8).

X-ray Data for [Ag(P(NMe$_2$)$_3$)$_2$]BPh$_4$

Crystals of [Ag(<u>7</u>)$_2$]BPh$_4$ were grown by slow diffusion of Et$_2$O into a saturated solution of the complex in CH$_2$Cl$_2$. A crystal was cut to dimensions of approximately 0.2 x 0.2 x 0.2 mm and was mounted and sealed in a Lindemann capillary. The crystal was indexed in an automatic indexing procedure (54) using 12 independent reflections. It was found to be monoclinic with $\underline{a} = 11.975(3)$, $\underline{b} = 17.325(3)$, $\underline{c} = 20.079(5)$ Å and $\beta = 107.08(3)°$ with four molecules of $[Ag(\underline{7})_2]BPh_4$ per unit cell. A density of 1.26 g/cc was computed based on a cell volume of 3981(1) $Å^3$. Systematic absences (h0l absent if l = 2n + 1, 0k0 absent if k = 2n + 1) indicated space group $P2_{1/c}$.

Data collection was carried out using an automated four-circle diffractometer built in the Ames Laboratory which was equipped with a scintillation counter and interfaced to a PDP-15 computer. Employing a procedure described previously (55), data were collected with graphite monochromated MoKα radiation from four octants within a sphere of $2\theta < 50°$ yielding 8432 measured intensities. There was little crystal decomposition as judged by repeated measurements of three standard reflections. Corrections for Lorentz polarization effects and averaging of equivalent data yielded 4523 observed reflections ($F_o > 3\sigma F$). Lattice constants were obtained by a least squares refinement of $\pm 2\theta$ for 15 high-angle reflections.

The silver atom was positioned from a Patterson map. Electron density maps generated by the program ALLS (56) were used to locate the remaining nonhydrogen atoms. Isotropic refinement of these positions by block matrix least squares techniques followed by three cycles of anisotropic refinement using full matrix techniques gave a conventional residual index (R) of 5.5 and a weighed R factor of 8.9. Phenyl hydrogen positions were calculated assuming a carbon-hydrogen bond length of 1.05 Å. Hydrogen atom temperature factors were set at 1.0 Å greater than that of the corresponding carbon. The scattering factors (57) were modified for anomalous dispersion effects (58) and hydrogens were included but not refined. Final atom positional parameters (Table A1) and thermal parameters (Table A2) are summarized as indicated.

RESULTS AND DISCUSSION

Cationic Phosphorus Ligand Complexes of Silver(I)

The extent of ligation of Ag(I) by phosphorus ligands can be limited either by the steric bulk of the ligand or a lack of basicity of the lone pair on phosphorus. A prime example of the latter is the coordination of 26 to silver(I). The very poor basicity of 26 compared to 9 and 18 is illustrated by the energies of CO stretches in metal carbonyl complexes (59), the values of $^{1}J^{77}SeP$ and ^{1}JHP in the protonated and selenated ligands, respectively (6,7), the energies of the P=O stretches of the corresponding phosphates (60) and the energies of the B-H stretch of their BH_3 adducts (61).

Addition of one equivalent of 26 to a solution of $AgBF_4$ at -95° resulted in the observation of the AgL^+ species in solution at 118.0 ppm with a $J^{107}Ag^{31}P$ value of 1057 Hz. Addition of more 26 results in the growth of an unsplit resonance at 112 ppm due to uncomplexed ligand. These results suggest that Ag(I) tolerates only one poorly ligating 26 in its coordination sphere despite the small size of the ligand. It may be that 26 is acting as a Lewis acid for Ag(I) and that coordination of one 26 ligand enhances the positive charge on Ag(I) such that a second ligand will not coordinate. No evidence of coordination of 1 to Ag(I) could be seen in the ^{31}P NMR at -90° of a saturated solution of PF_3 in acetone which was 0.1 M in $AgBF_4$. This result is not unexpected in view of the fact that the $\Sigma\chi$ value for 1, 56.3, is significantly greater than for phosphorus ligands which do coordinate to silver(I) (Table 3). The poor basicity of PF_3 compared to phosphites and phosphines has also been demonstrated by the high value of ^1JPH in $[H\text{-}PF_3]^+$ (62).

As another example of this type of behavior ^{31}P NMR evidence shows that 20, which has a cone angle of 115°, will form only a three-coordinate ionic complex with Ag(I) in solution. For a solution which is 0.3 M in $AgBF_4$ containing 7 equivalents of ligand, the only signals which are observed in the ^{31}P NMR are an unsplit signal due to free ligand at 140.1 ppm and a species absorbing at 128.3 ppm showing a $^1J^{107}Ag^{31}P$ value of 508 Hz which is assignable to $[AgL_3]^+$ by comparison with the values in Table 4. Even though 12 and 21 have cone angles of 130° and 145°, respectively, ionic four-coordinate Ag(I) complexes of these ligands can be isolated. This is undoubtedly due to their greater basicity compared to 20, as shown by their $\Sigma\chi$ values and $^1J^{77}Se^{31}P$ couplings in their corresponding selenophosphates (Table 3).

Although 11 has a cone angle of (127°), within a few degrees of 21 (130°), only $[Ag(\underline{11})_3]BF_4$ was isolated in the solid state after reacting 9 equivalents of 11 with one equivalent of $AgBF_4$. The four-coordinate $[Ag(\underline{11})_4]BF_4$ species could be observed in the low-temperature ^{31}P NMR, however, upon addition of four or more equivalents of 11 to a solution of $AgBF_4$. Similar occurrences have been noted in Au(I) chemistry. For example, Mays and Vergnano observed $[Au(\underline{14})_n]^+$ (n = 2, 3 or 4) in solution but could only crystallize $[Au(\underline{14})_2]PF_6$ even in the presence of a five-fold excess of ligand (63). For the $[Au(\underline{3})_n]^+$ system, it was found that if ClO_4^- is the counter anion, only the bis and tris ligand cations can be

Table 3. Ligand cone angles, sum of ligand substituent contributions to $\nu(CO)(A_1)$ in $Ni(CO)_3L$, $^{31}P-^{77}Se$ coupling of corresponding ligand selenides and maximum value of n in $[AgL_n]^+$

				Max n	
Ligand	Cone Angle[a] (°)	$\Sigma\chi$[b]	$^1J_{Se-P}$ (Hz)	Isol. solid	Soln at -95°C
26	< 101	---	1099[c]	---	1
17	101	33.9[d]	1053[c]	4	4
9	107	23.1	954[c]	4	4
19	108	---	851[e]	4	4
2	109	20.4	935[f]	4	4
10	110	27.9	955[f]	4	4
20	115	35.7	1018	---	3
15	122	9.5	710[g]	4	4
11	128	29.1	1025	3	4
21	130	18.9	912[f]	4	4

---

[a] Values taken from reference 1 except for 26 which was an estimate.

[b] Determined by measuring $\nu_{(CO)}(A_1)$ of $Ni(CO)_3L$ in CH_2Cl_2. For $PX_1X_2X_3$ $\nu = (2056.1 + \sum_{i=1}^{3} \chi_i)$ cm^{-1}. Values calculated from data given in reference 1 unless otherwise indicated.

[c] Reference 7.

[d] J. G. Verkade, R. E. McCarley, D. G. Hendricker and R. W. King, Inorg. Chem. 4, 228 (1965).

[e] Reference 42.

[f] W. J. Stec, A. Okruszek, B. Uznański and J. Michalski, Phosphorus 2, 97 (1972).

[g] W. McFarlane and D. S. Rycroft, J. Chem. Soc., Dalton Trans., 2162 (1973).

Table 3. (Continued)

Ligand	Cone Angle[a] (°)	$\Sigma\chi$[b]	$^1J_{Se-P}$ (Hz)	Max n Isol. Solid	Soln at -95°C
14	132	5.4	705[f]	---	4
16	136	11.2	725[g]	4	4
13	141	27.9	1022	---	3
12	145	12.9	735[g]	4	4
3	145	10.5	723[h]	4[i]	4[i]
7	157	5.7	805[c]	3	3
22	---	6.5	854[c]	3	3
23	172	---	924	2	3
4	182	0.0	712[j]	2[k]	2[k]
24	190	---	1012	1	2
5	212	---	---	2[l]	2[l]

---

[h] R. P. Pinnell, C. A. Megerle, S. L. Manatt and P. A. Kroon, J. Am. Chem. Soc. 95, 977 (1973).

[i] Reference 11.

[j] W.-W. DuMont and H.-J. Kroth, J. Organomet. Chem. 113, C35 (1976).

[k] Reference 17.

[l] E. C. Alyea, S. A. Dias and S. Stevens, Inorg. Chim. Acta 44, L203 (1980).

Table 4. ^{31}P NMR chemical shifts and silver(107)-phosphorus(31) couplings as a function of L and n in $[AgL_n]^+X^-$ complexes

L	X	$\delta\,^{31}P^{a,b}$	$[AgL_n]X$ $\delta\,^{31}P^{a}/J_{Ag-P}^{c}$			
		free ligand	n = 1	2	3	4
3[d]	PF_6	1.1		13.1 503	10.6 321	5.6 225
14	BF_4	-20.0	10.3 712	8.9 482	1.9 304	7.5 211
6[e]	BF_4	-32.5	--- 759	32.9 470	26.6 304	15.5 219
5[f]	PF_6	-39.1		-25.8 513		
12	BF_4	-7.4				7.5 222
16	BF_4	-28.0				-16.0 230
15	BF_4	-47.0				-31.6 212
4[g]	BF_4	60.8		80.0 444		

---

[a] In ppm relative to 85% H_3PO_4.

[b] Measured at ambient temperature.

[c] Values precise to ±2 Hz.

[d] Reference 11.

[e] Reference 21.

[f] E. C. Alyea, S. A. Dias and S. Stevens, Inorg. Chim. Acta, 44, L203 (1980).

[g] Reference 17.

Table 4. (Continued)

L	X	$\delta^{31}P^{a,b}$	$[AgL_n]X$ $\delta^{31}P^{a}/JAgP^{c}$			
		free ligand	n = 1	2	3	4
19	BF_4	131.3	186.6 801			118.3 303
7	BF_4	121.4	121.5 910			
7	BPh_4			115.4 610	122.1 393	
22	BF_4	83.8	90.2 811	90.4 603		
22	BPh_4				101.1 394	
2	BF_4	139.8	125.4 1038			
2[d]	ClO_4			123 756	129 472	133 341
11	BF_4	127.5	120.0 992	116.8 667	115.7 505	116.5 345
23	BF_4	138.5	102.1 1118	102.7 747	113.8 469	
20	BF_4	136.6	129.7 989	125.3 691	126.3 509	
13	BF_4	129.1	122.4 992	115.8 692	114.9 500	
24	BF_4	143.9	127.4 1063	120 700±20		
21	BPh_4	140.6			134.8 472	130.2 343

Table 4. (Continued)

			[AgL$_n$]X			
L	X	$\delta^{31}P^{a,b}$		$\delta^{31}P^{a}$/J_{AgP}^{c}		
		free ligand	n = 1	2	3	4
26	BF_4	106.1	118.0 1057			
9	BF_4	139.8				133.7 341
17	BF_4	91.8				101.5 369
10	BF_4	138.9				131.1 346

isolated (64), while with $B_9H_{12}S$ all three cations $[Au(3)_n]^+$ (n = 2, 3 or 4) could be isolated; however, with $B_9H_{14}^-$, $B_{10}H_{15}^-$ or $B_{11}H_{14}^-$ only $[Au(3)_4]^+$ was isolated (65,66). The trend seen here is that smaller anions favor the crystallization of smaller cations while large anions favor isolation of larger cations (67). An attempt was made to prepare $[Ag(11)_4]BPh_4$ by reacting 10 equivalents of 11 to one equivalent of $AgBF_4$ in EtOH and then adding $NaBPh_4$ to crystallize the BPh_4 salt. This resulted, however, in obtaining a product which was insoluble in all common organic solvents and was not further characterized. The low conductivity of $[Ag(11)_3]BF_4$ in CH_2Cl_2 (Table 5) possibly indicates that the less basic ligands enhance the positive charge on silver(I) which

Table 5. Melting point and conductance data for isolated ionic silver complexes

	Molar conductance (ohm^{-1} cm^2 $mole^{-1}$)[a]	mp (°C)
$[Ag(\underline{9})_4]BF_4$	50.8	97-8
$[Ag(\underline{19})_4]BF_4$	57.1	170
$[Ag(\underline{10})_4BF_4$	49.5	66-7
$[Ag(\underline{17})_4]BF_4$	135[b]	---
$[Ag(\underline{21})_3]BPh_4$	139[b]	66-8
$[Ag(\underline{21})_4]BPh_4$	139[b]	55-7
$[Ag(\underline{12})_4]BF_4$	107.3[b]	278-8
$[Ag(\underline{16})_4]BF_4$	126.0[b]	174-5
$[Ag(\underline{15})_4]BF_4$	115.3[b]	75-7
$[Ag(\underline{7})_2]BPh_4$	59.8	115-6
$[Ag(\underline{7})_3]BPh_4$	54.1	125-6
$[Ag(\underline{22})_3]BPh_4$	45.1	155-8
$[Ag(\underline{2})_4]BF_4$	57.8	113
$[Ag(\underline{24})]BF_4$	7.3	127
$[Ag(\underline{11})_3]BF_4$	14.2[c]	95-9

[a] For 10^{-3} M solutions in CH_2Cl_2 at 25° unless otherwise indicated.

[b] For 10^{-3} M solution in CH_3CN at 25°.

[c] A conductance of 25.0 ohm^{-1} cm^2 $mole^{-1}$ was measured in nitrobenzene wherein a 1:1 electrolyte typically has a conductance of 20-30 ohm^{-1} cm^2 $mole^{-1}$.

allows interaction between the BF_4 anion and the coordinatively unsaturated Ag(I) ion. Upon addition of 12 molar equivalents of 13 (a phosphite of basicity similar to 11) to a 0.3 M solution of $AgBF_4$, a resonance at 114.9 ppm with a ^{107}Ag-^{31}P coupling of 500 Hz assignable to $[Ag(P(OR)_3)_3]^+$ as well as an unsplit peak due to free ligand at 129.1 ppm is seen in the ^{31}P NMR spectrum. The inability of 13 to form a four-coordinate complex is undoubtedly due to the larger steric demands of 13 compared to 11.

Previously it was found that the extent of coordination of large phosphine ligands can be limited by their steric bulk (17,18). The two aminophosphine ligands 7 and 22 are of a size intermediate between 4 and 5 (which have cone angles of 182 and 212°, respectively) and smaller ligands such as 9 (whose cone angle measured 107°) which can form $[AgL_4]^+$ complexes. The aminophosphine ligands 7 and 22 form ionic Ag(I) complexes which contain an upper limit of three ligands which can be observed by $^{31}P\{H\}$ NMR spectroscopy, both in the solid state and in solution. When 7 is added to $AgBF_4$ in a 2:1 molar ratio, $[Ag(7)_2]^+$ is formed which can be isolated in 50% yield as a crystalline tetraphenylborate salt. In the presence of a seven-fold excess of 7, a 72% yield of $[Ag(7)_3]BPh_4$ is realized. Attempts to recrystallize this salt resulted in partial loss of ligand to precipitate a mixture of two and three-coordinate complexes as shown by ^{31}P NMR spectroscopy. Like 7, 22 is capable of forming an isolable three-coordinate complex $[Ag(22)_3]BPh_4$ in high yield (72%).

Upon successive addition of molar equivalents of 7 to a 0.3 M solution of $AgBF_4$ in $CH_2Cl_2/(CD_3)_2CO$ (75/25), progressively smaller ^1JAgP

values are observed at the corresponding chemical shifts given in Table 4. Addition of a fourth equivalent of 7 resulted in the appearance of an extremely broad resonance at 122 ppm, suggesting that $[Ag(7)_3]^+$ undergoes ligand exchange by an S_N2 mechanism in the presence of free ligand. The same observation was made with the two-coordinate complex $[Ag(23)_2]^+$ reported earlier by others (17). Analogous experiments with 22 revealed that $[Ag(22)_2]BF_4$ disproportionates to a small extent to $[Ag(22)_3]BF_4$ and $Ag(22)BF_4$ which may explain the failure of attempts to isolate $[Ag(22)_2]BPh_4$. Addition of a fourth molar equivalent of 22 to a solution of $AgBF_4$ caused collapse of the ^{31}P NMR doublets to a broad singlet at 96 ppm indicating that $[Ag(22)_3]^+$ also probably undergoes exchange by an S_N2 mechanism in the presence of free ligand.

The formulation of the 1:1 complexes in the aforementioned NMR experiments as $[Ag(7)]BF_4$ and $Ag(22)BF_4$ are deduced from low temperature conductivity studies which are now described. The insolubility of $AgBF_4$ in CH_2Cl_2 and its incomplete reaction with 7 and 22 precluded conductivity studies in this solvent. Because of decomposition, difficulties were encountered in maintaining completely clear solutions in acetone at 25°. However, measurements could be carried out in acetone at -22°. Correlation of our conductivity results in this solvent with the NMR data is not unreasonable since 25% acetone in CH_2Cl_2 was the solvent system used in the NMR experiments. Using approximately 10^{-2} M $AgBF_4$ in acetone at -22°, the conductivity of the solution was found to decrease 26% upon the addition of 22, but rose to the original value upon addition of a second equivalent. This suggests that the complexes present at -95° in

Me_2CO in CH_2Cl_2 is a weakly or nonconducting Ag(22)BF_4 species. It is interesting in this respect that previous workers have reported complexes of the type [$R_3PAgClO_4$] (wherein the ligand is a bulky trialkyphosphine or a triaryl-phosphine) which are two-coordinate in methylene chloride and in the solid state owing to coordination of the anion (68). With 7 no decrease in conductivity was observed which is indicative of [Ag(7)]BF_4 wherein the more basic aminophosphine ligand (probably in conjunction with ligated solvent molecules) is capable of satisfying the coordination requirements of the silver without anion participation. Moreover, the anomalously large $^1J^{107}Ag^{31}P$ coupling of 910 Hz for this complex would appear to suggest the presence of substantial [Ag(7)]BF_4 in equilibrium with Ag(7)BF_4 while the 811 Hz value for the corresponding complex of 22 can be construed to indicate a larger fraction of two-coordinate Ag(22)BF_4 which would have less s character in the Ag-P bond. Coordination of BF_4^- has been verified crystallographically in the solid state structures of Cu(12)$_3BF_4$ (69) and [Ni(en)$_2$(H_2O)BF_4]BF_4 (70) and has been suggested by IR and conductivity measurements in a number of other complexes (71-74). The solid state structure of Ag(2,4,6-t-$Bu_3C_6H_2CN$)$_2PF_6$ was also found to be four-coordinate with the PF_6 moiety functioning as a fluoride chelate (75). This complex was found to be a 1:1 electrolyte in DMSO, however.

Isolated three-coordinate complexes of the type $[Ag(L)_3]^+$ are still rare. Previously, a number of complexes of the type AgL_3X (where L = 2 and 3 and X = halide, pseudohalide, B_3H_8, S_2PF_2, O_2CCF_3, NO_3, PF_6, ClO_4 or $B_9H_{12}S$) were described (11). Many of these complexes disproportionate according to reaction 6 with the extent of disproportionation varying with the coordinating ability of X. Analogous disproportionation products of $[Ag(\underline{7})_3]^+$ and $[Ag(\underline{22})_3]^+$ were not detected in their ^{31}P NMR spectra at

$$2[AgL_3]X \rightleftarrows [AgL_4]X + [AgL_2]X \text{ (or } AgL_2X) \qquad (6)$$

-95°. This is not unexpected since $[Ag(\underline{7})_4]^+$ and $[Ag(\underline{22})_4]^+$ are not observed in the ^{31}P NMR spectra at this temperature in the presence of excess ligand (vide supra). However, since the ^{31}P NMR resonances for $[Ag(\underline{7})_3]^+$ and $[Ag(\underline{22})_3]^+$ broaden upon adding ligand at -95°, the corresponding $[AgL_4]^+$ species could well be intermediates in an S_N2 associative ligand exchange process. Reaction 6 cannot be ruled out as a pathway for ligand exchange at higher temperatures.

In contrast to 7 and 22, addition of successive equivalents of the aminophosphine 19 to solutions of $AgBF_4$ allowed the observation of $Ag(\underline{19})BF_4$ and $[Ag(\underline{19})_{2-4}]BF_4$ in solution. The 1:1 complex is formulated as nonconducting on the basis of its low $^1J^{107}Ag^{31}P$ coupling and the fact that addition of a molar equivalent of 19 to an acetone solution of $AgBF_4$ at -22° resulted in a 39% decrease in conductance.

The coordination chemistries of the large phosphite ligand 23 and the large phosphine 4 with silver(I) are rather different although an $[AgL_2]BF_4$ complex is isolated after reacting excess L with $AgBF_4$ for both ligands. Others have reported that $[Ag(\underline{4})_2]BF_4$ shows Ag-P coupling in its ^{31}P NMR spectra at room temperature (17). However, the spectra of solutions containing an equimolar mixture of complex and free ligand consisted of a singlet at room temperature while at -90° separate signals due to free phosphine and $[Ag(\underline{4})_2]^+$ were observed (17). In contrast, low temperatures are necessary to observe coupling in $[Ag(\underline{23})_2]BF_4$. A ^{31}P NMR taken of a solution which was 0.2 M in $[Ag(\underline{23})_2]BF_4$ and contained two molar equivalents of $\underline{23}$ consisted of signals assignable to $[Ag(\underline{23})_3]BF_4$ and free ligand. It is thus seen that $[Ag(\underline{4})_2]^+$ does not exchange in solution at room temperature and $[Ag(\underline{4})_3]^+$ cannot be observed in the NMR spectrum, while $[Ag(\underline{23})_2]BF_4$ does undergo rapid ligand exchange at room temperature and $[Ag(\underline{23})_3]BF_4$ can be observed in the NMR spectrum. This indicates that an associative step is involved in the exchange of these two-coordinate complexes as suggested earlier (17). Since $[Ag(\underline{4})_3]^+$ is unstable, $[Ag(\underline{4})_2]^+$ undergoes exchange rather slowly.

In an attempt to make a two-coordinate cationic silver complex of a phosphite ligand which would not exchange at room temperature, complexes of $\underline{24}$ were investigated. It was thought that the greater steric requirements of $\underline{24}$ as opposed to $\underline{23}$ would destabilize a three-coordinate cation and hence retard the intermolecular exchange of a two-coordinate cation. When four equivalents of $\underline{24}$ were added to a methylene chloride solution of $AgBF_4$, however, $Ag(\underline{24})BF_4$ precipitated from solution upon addition of hexanes. As expected, this complex showed a relatively low conductivity in CH_2Cl_2 (Table 5) which suggested coordination of the BF_4 anion. No difference was seen in the ^{19}F NMR of this complex from that reported for ionic BF_4 (76) down to temperature of -95°, however.

In addition to the conductivity measurements, evidence for the two coordinate nature of $Ag(\underline{24})BF_4$ comes from solid state ^{31}P NMR spectroscopy. The two coordinate nature of $[Ag(\underline{7})_2]BPh_4$ in the solid state is shown by crystallographic studies (vide infra), while conductivity data show this complex to be a 1:1 electrolyte in CH_2Cl_2 at 25°. The ^{31}P NMR chemical shifts and silver-phosphorus coupling of this compound measured in the solid state and in solution at -95° are comparable. Conversely, the solution and solid state ^{31}P NMR of Ag(24)BF_4 are rather different with a significant decrease in silver-phosphorus coupling (Table 6).

Table 6. Comparison of solution and solid state ^{31}P NMR for [Ag(7)$_2$]BPh_4 and Ag(24)BF_4

	$\delta^{31}P$ (ppm)	$J^{107}Ag^{31}P$ (Hz)	Molar conductance (ohm^{-1} cm^2 $mole^{-1}$)[a]
[Ag(7)$_2$]BPh_4 (solution)	115.4	610	59.8
[Ag(7)$_2$]BPh_4[b] (solid)	115.2	603	
Ag(24)BF_4 (solution)	127.4	1068	7.3
Ag(24)BF_4[b] (solid)	112.6	803	

[a] For 10^{-3} M solutions in 25°C in CH_2Cl_2.

[b] Jim Frye of the Regional NMR Center at Colorado State University is thanked for these measurements.

Addition of 0.8 molar equivalents of 24 to a solution of $AgBF_4$ in 95% CH_2Cl_2/5% d_6-acetone resulted in the appearance of a ^{31}P NMR signal at 250K which was assigned to Ag(24)BF_4 (Table 6). The ligand exchange in

Ag(24)BF_4 at 250K is slow compared to other isolated silver complexes of phosphite ligands which are two-, three-, or four-coordinate and which require low temperatures (<190K) to observe coupling. At 250K, silver-phosphorus coupling is completely resolved in Ag(24)BF_4. Introduction of additional 24 resulted in the collapse of the silver-phosphorus coupling seen at 250K. For a solution which is 0.15 M in $AgBF_4$ and 0.50 M in 24, peaks are seen in the ^{31}P NMR at 194K corresponding to free ligand, monoligated Ag(I) and diligated Ag(I) in an area ratio of 1:1.3:1. The peaks due to the monoligated Ag(I) species are better resolved than that for the diligated species showing, as expected, that the more sterically crowded species exchanges at a faster rate. Although $[Ag(24)_2]BF_4$ could not be isolated, a two-coordinate cation of a larger ligand $[Ag(5)_2]^+$ has previously been shown to exist (18). This apparent paradox can be explained by either the greater basicity of the phosphine 5 compared to phosphite 24 or by relative sizes of 5 and 24 which are different from those predicted by models. Crystallographic support for the latter explanation will be given later (Section III).

In a number of other d^{10} metal complexes of phosphine ligands, it was noted that a large downfield coordination chemical shift is observed in the ^{31}P NMR spectrum which decreases upon increasing coordination number (64, 77-79). The upfield shift upon increasing coordination number in Ag(I) complexes of 3 and the phosphite 2 was also seen by Muetterties although the trend was less pronounced and complexation of the phosphite 2 led to an upfield coordination chemical shift (11). Further examination of silver(I) complexes of phosphorus ligands shows that the trend of downfield coordination chemical shifts which decrease upon increasing coordination number is not a general trend as seen in Table 7. In fact, the coordination chemical shift in [Ag(23)]BF_4 is -36 ppm.

The ^1H NMR spectra of the exchanging silver(I) complexes, like the ^{31}P spectra, are also temperature dependent. For three- and four-coordinate complexes, an effective decoupling of phosphorus to the α hydrogens is seen as the temperature is lowered. For example, the proton resonances in [Ag(9)$_4$]BF_4 and

Table 7. ^{31}P NMR chemical shifts[a] as a function of coordination number n in complexes of d^{10} metals

	n			
	2	3	4	Reference
Hg(28)$_n^{2+}$	13.0	2.5	-17.5	77
Pd(29)$_n$	49.3	9.0	---	78
Pd(14)$_n$	---	9.6	-1.5	78
Pt(29)$_n$	70.7	64.4	---	78
Pt(14)$_n$	---	64.0	4.6	78
Au(14)$_n^+$	43.3	38.3	5.7	62
Au(16)$_n^+$	26.0	13.8	-5.8	77

[a] In ppm downfield of 85% H_3PO_4.

$[Ag(\underline{7})_3]BPh_4$ are singlets below -65°C. Previously, it was reported that the ^1H NMR spectrum of $[Cu(\underline{9})_4]^+$ at -15° in methylene chloride solution is characteristic of the $[A_9X]_4$ spin system with A = ^1H and X = ^{31}P (80). At this temperature, the ^1H NMR consists of two sharp outer lines ($|^3JPH + 3(^5JPH| = 11.2$ Hz)) arising from species in which the phosphorus spin states are all α or all β along with a broad band between the two outer peaks (80). At 23° mixing of these spin states was sufficient for the two sharp lines to collapse into the broad band. Ligand exchange had no effect here since copper-phosphorus coupling was seen in the ^{31}P NMR at both temperatures.

The appearance of the α protons in these three- and four-coordinate complexes will be a function of ^2JPP, ^3JPH and ^5JPH (81,82). The value of ^2JPP will significantly decrease as the P-Ag-P angle decreases as shown in studies of complexes of the type $Ag\{P(O)(OEt)_2(\underline{6})_n\}$, n = 1, 2, 3 (83). It was decided not to do a detailed ^1H NMR examination of the three- and four-coordinate ionic silver(I) complexes due to the number of factors involved in determining the shape of the α hydrogen resonance.

The ^1H NMR spectrum of the linear two coordinate complex $[Ag(\underline{7})_2]BPh_4$ is more readily explainable. As the temperature is lowered the proton resonance becomes a triplet owing to the chemically equivalent protons on each ligand which are magnetically inequivalent because of strong three-bond couling to a phosphorus which is in turn strongly coupled to the second phosphorus in the intact two-coordinate complex. Similarly, the ^{13}C peaks become a triplet which is consistent with $|JAX-JAX'|^2<8JXX'\nu_{1/2}$ where A = ^{13}C and X,X' = ^{31}P (81,82).

Neutral Complexes of Silver(I) Complexed to Phosphorus Ligands

Analogously to cationic complexes of Ag(I), the extent of coordination of phosphorus ligands in complexes of Ag(I) wherein the anion coordinates can be limited by the size of the phosphorus ligand. Previously, others have shown that equilibrium 7 exists in solution when L is 2 or 3, but four-coordinate ionic complexes could not be isolated

$$[L_4Ag]^+X^- \leftrightarrows L_3AgX + L \qquad (7)$$

in the solid state where L was either of these ligands (11). Later, the isolation of $[Ag(28)_4]Cl$ was reported but this compound is rather unstable (84).

Aminophosphine 19, which is sterically smaller than 28, also forms isolable ionic four coordinate complexes with Ag(I). In solution at -88° $[Ag(19)_4]I$ dissociates according to equation 7 and resonances assignable to $[Ag(19)_4]I$, $Ag(19)_3I$ and free ligand can be assigned in the ^{31}P NMR spectrum as shown in Figure 3. At 25° the virtually zero conductance observed in a 10^{-3} M solution of $[Ag(19)_4]I$ in CH_2Cl_2 is probably due to entropy effects which shift equilibrium 7 to the right. Upon lowering the temperature of the solution to -65°, a small but definitely measureable conductance is observed despite the tendency for conductances to decrease with decreasing temperature owing to lower ionic mobility. The chloride ion has been shown to be a weaker ligand toward Ag(I) than I^- (11). In accord with this observation, $[Ag(19)_4]Cl$, which could only be

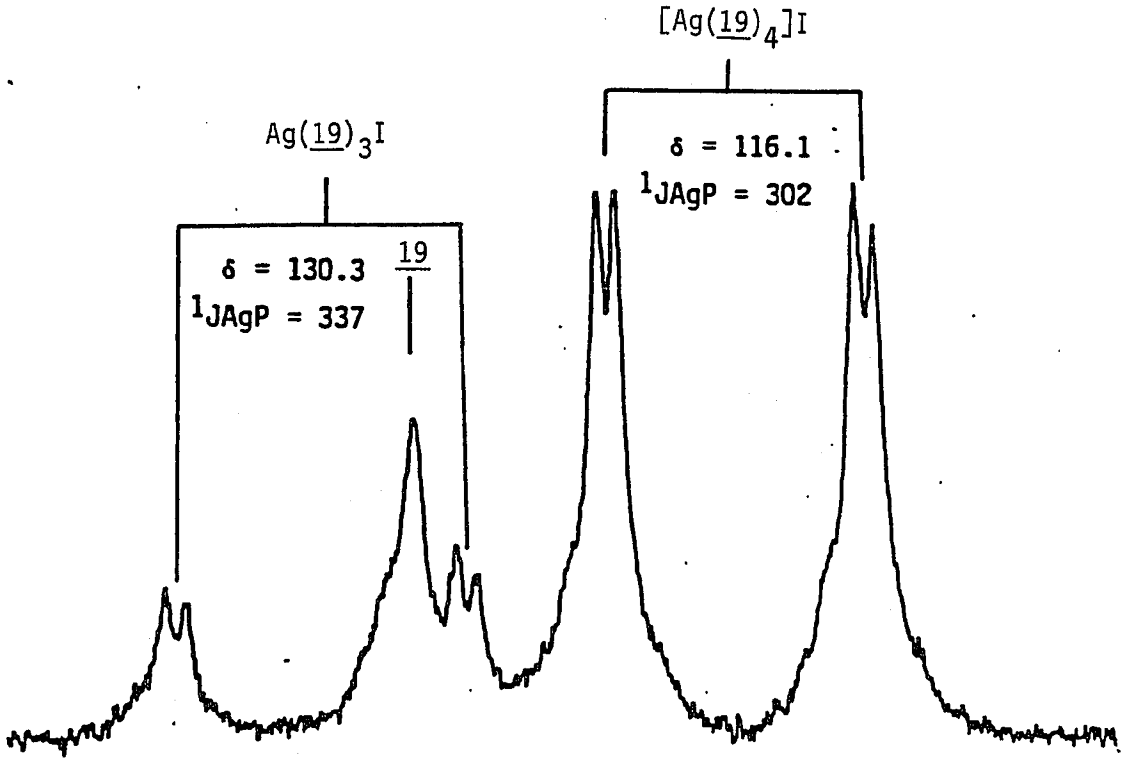


Figure 3. ^{31}P NMR spectrum of [Ag(19)$_4$]I at -88°C in 75/25 CH_2Cl_2/d_6-acetone. The Ag-P coupling constants refer to the ^{107}Ag nucleus

isolated as an oil, shows no evidence for equilibrium 7 in the low temperature ^{31}P NMR spectrum.

As was observed with the cationic complexes, only two 7 ligands coordinate to Ag(I) when the anion coordinates. Addition of 10 molar equivalents of 7 to ether suspensions of AgX where X is Cl, I, NO_3 or CN resulted in the formation of $Ag(7)_2X$ upon crystallization. These complexes were nonconductors in CH_2Cl_2 with the exception of the NO_3^- salt which shows slight conductance. The decrease in silver-phosphorus coupling in the order X = NO_3 > Cl > I > CN (Table 8) parallels that seen previously with $AgL_{2,3}X$ where L was 2 or 3 (11) and in Ag(4)X complexes (17). Addition of less than 1/4 molar equivalent of ligand to 0.2 M solutions the $Ag(7)_2X$ complexes at -95° leads to collapse of the ^{31}P NMR coupling pattern, which shows that $Ag(7)_2X$ complexes can undergo ligand exchange via an S_N2 type mechanism in the presence of excess ligand.

The ^1H NMR spectra of the $Ag(7)_2X$ complexes show a doublet at room temperature and a singlet at -95°. The proton doublet is consistent with rapidly dissociating ligand while the low temperature proton singlet could arise from opposite signs of approximately equal values of ^3JPH and ^5JPH in the intact AgL_2X complex (81,82).

For both 4 and 23, complexes of the type AgLX (X = CN, Cl or I) are isolated after reacting excess ligand with suspensions of the silver halides in ether. The temperature-dependent $^{31}P\{H\}$ NMR spectra of the phosphine and phosphite complexes are different, however. When L is 4 silver-phosphorus splitting is observed at room temperature (17), while Ag(23)X complexes show a singlet in the ^{31}P NMR spectrum at room

Table 8. ^{31}P NMR, melting point, conductivity and molecular weight data of non or slightly conducting silver complexes

	$\delta^{31}P^{a}$ (ppm)	$^{1}J^{107}Ag^{31}P^{a}$ (Hz)	Molar conductance^{b} (ohm^{-1} cm^{2} mole^{-1})	mp (°C)	Molecular weight Calcd.	Found
$Ag(19)_4Cl$	117.7	302	---	---	---	---
$Ag(19)_4I$	116.1	302	2.6^{c}	---	---	---
$Ag(19)_3I^{d}$	130.3	337	---	---	---	---
$Ag(7)_2CN$	124.3	437	0	68-9	450	282^{e}
$Ag(7)_2I$	119.3	507	0	85-8	561	581^{f}
$Ag(7)_2Cl$	121.2	535	0	82-3	470	529^{f}
$Ag(7)_2NO_3$	118.6	592	4.5	79-81	---	---
$Ag(23)Cl$	114.4	888	0	145-6	393	402^{e}
$Ag(23)_2Cl^{d}$	118.4	614	---	---	---	---
$Ag(23)I$	106.0	719	0	---	---	---
$Ag(23)_2I^{d}$	123.4	570	---	---	---	---
$Ag(23)CN$	115.1	658	0	146	384	305^{e}
$Ag(23)_2NO_3$	121.1	717	7.3	137	---	---

[a] Measured in 75% CH_2Cl_2/25% d_6-acetone at -95°.

[b] For 10^{-3} M solutions at 25° in CH_2Cl_2.

[c] Conductance was measured at -65°. Essentially zero conductance was measured at 25°.

[d] Species was not isolated, but was observed in solution.

[e] Measured in 1,2-dichloroethane.

[f] Measured in THF.

temperature and low temperature spectra are needed to observe coupling. In contrast to $\mathrm{Ag}(\underline{4})\mathrm{X}$ complexes where addition of two equivalents of phosphine resulted in the appearance of peaks in the $^{31}\mathrm{P}\{\mathrm{H}\}$ NMR at -95° assignable to $[\mathrm{Ag}(\underline{4})_2]^+$ and free ligand (17), addition of two molar equivalents of $\underline{23}$ to a solution of $\mathrm{Ag}(\underline{23})\mathrm{Cl}$ resulted in the observation of peaks assignable to free ligand and $\mathrm{Ag}(\underline{23})_2\mathrm{Cl}$ at -95° in the $^{31}\mathrm{P}$ NMR spectrum. Upon addition of 10 molar equivalents of $\underline{23}$ to a solution of $\mathrm{Ag}(\underline{23})\mathrm{I}$, $\mathrm{Ag}(23)_2\mathrm{I}$ and $\underline{23}$ were seen in the $^{31}\mathrm{P}$ NMR spectrum. Between 180K and 200K, an equilibrium of type 8 was observed between $\underline{23}$, $\mathrm{Ag}(\underline{23})\mathrm{I}$ and $\mathrm{Ag}(\underline{23})_2\mathrm{I}$ with $\mathrm{Ag}(\underline{23})_2\mathrm{I}$ being favored at low temperatures. The $\mathrm{Ag}(\underline{23})_2\mathrm{Cl}$

$$\mathrm{Ag}(\underline{23})\mathrm{I} + \underline{23} \rightleftharpoons \mathrm{Ag}(\underline{23})_2\mathrm{I} \qquad (8)$$

and $\mathrm{Ag}(\underline{23})_2\mathrm{I}$ species are assigned on the basis of their $^{31}\mathrm{P}$ NMR spectra as nonconducting species in which the halide is coordinated. Both the $^{31}\mathrm{P}$ NMR chemical shift and silver-phosphorus coupling for these two molecules differ as would be expected if the anions were coordinated. The silver-phosphorus couplings in both molecules are significantly less than in $[\mathrm{Ag}(\underline{23})_2]\mathrm{BF}_4$ (Table 4) which also suggests the anions are coordinated. The $^{31}\mathrm{P}$ NMR of $\mathrm{Ag}(\underline{23})\mathrm{CN}$ with added free ligand could not be completely frozen out down to 178K. These results show that while $\underline{23}$ may not have the necessary basicity to displace halide from the inner coordination sphere as does $\underline{4}$, it is small enough to form tricoordinate complexes as in $\mathrm{Ag}(\underline{23})_2\mathrm{Cl}$.

The possibility of dimerization of the Ag(7)$_2$X and Ag(23)X complexes in solution as well as in the solid state exists. Molecular weight measurements suggest that little if any association occurs in solution (Table 8). It is unwarranted, however, to draw any conclusions regarding the solution structure of these complexes at -95° from the osmometric data which were taken in different solvents and at a temperature 132° higher than that at which the NMR studies were performed. The monomeric character of these complexes at -95° is implied, however, by the value of the ^{107}Ag-^{31}P coupling constants which for halide bridged four-coordinate dimeric complexes of the type [AgX(7)$_2$]$_2$ are estimated to be 300-400 Hz and 400-500 Hz for [AgX(23)]$_2$. Also supportive of monomeric species is the lack of four-bond metal-phosphorus coupling which is observed for halide bridged $L_2Pt_2X_4$ dimers (85).

Addition of excess 7 or 23 to ether suspensions of $AgNO_3$ resulted in the isolation of Ag(7)$_2$NO$_3$ and Ag(23)$_2$NO$_3$. In contrast to [Ag(4)$_4$]NO$_3$, which was shown to be a 1:1 electrolyte in CH_2Cl_2 (17), solutions of Ag(7)$_2$NO$_3$ and Ag(23)$_2$NO$_3$ conduct to a much lesser extent as shown in Table 9. The nitrate ion in these latter two complexes can be considered to be weakly coordinated. A relationship is seen between the cone angle of L and the conductivity of an AgL_2NO_3 complex in CH_2Cl_2 (Table 9) in which these parameters rise monotonically with each other until a large increase in equivalent conductance is realized with 4.

Table 9. Conductivity of AgL_2NO_3 complexes as a function of the cone angle of L

L	Cone Angle	Equivalent Conductance of AgL_2NO_3[a]
2[b]	109	0.9
3[b]	145	3.9
7	157	4.5
23	172	7.3
4[c]	182	52.6

[a] In units of $\Omega^{-1}cm^2equiv^{-1}$ for 1×10^{-3} M solutions in CH_2Cl_2 at 25°.

[b] Reference 11.

[c] Reference 17.

Ligand Competition Experiments

In an attempt to determine the relative importance of steric and electronic effects in the coordination of phosphorus ligands to silver(I), equilibrium experiments were performed in which four molar equivalents of a ligand L' were added to a solution of an $[AgL_4]^+$ complex. These experiments were followed by low temperature ^{31}P NMR spectral examination. In these experiments, the ^{31}P NMR signals for the bound ligands were never cleanly resolved doublet-of-doublet patterns, but were always somewhat broadened. Since the signals for bound ligand in these ligand competition experiments were rather broad and the coordination chemical shifts for phosphorus ligands to Ag(I) are as a rule small, it was necessary that L and L' have ^{31}P NMR chemical shifts separated by about 15 ppm.

The results obtained from these experiments show that while both steric and electronic effects are of importance in determining the relative affinity of phosphorus ligands for Ag(I), electronic effects are somewhat more important as illustrated by the ligation order: 15 > 25 ≈ 27 ≈ 14 > 9 > 12 > 17 > 26.

It has previously been established that because of orbital constraint on the esteratic oxygens of phosphorus esters, basicity in addition to steric requirements decrease with increasing constraint in the order: 9 > 25 > 27 > 17 > 26 (6,59). However, no trend was seen in the relative affinity of Ag(I) for phosphorus ligands upon constraint, which shows that more favorable steric properties are counterbalanced by less favorable electronic properties upon constraint. The phosphines 12 and 14 have their more favorable basicity compared to the phosphite ligands offset by a larger steric requirement. The fact that 9 displaces 17 from $[Ag(17)_4]^+$ is especially noteworthy in view of the fact that the opposite result was observed in the Ni(0) system (8).

The importance of both steric and electronic effects was also illustrated in competition experiments between 11, 17 and 21. The cone angles of 11 and 21 are essentially the same, with 21 being significantly more basic (Table 3). The steric requirement of 17 is less than the aforementioned two but its basicity is less than that of 11. Ligand displacement studies show that in the affinity for Ag(I): 21 > 11, 17 > 11, 21 > 17. These results again illustrate the preferential binding of

Ag(I) to ligands which are small and basic. In the competition between 21 and 11 and 17 and 11, coordination to the ligand which is more basic or is smaller was more favored as expected. In the competition between 21 and 17 where one ligand is more basic and one is smaller, the higher basicity of 21 overcame the steric advantage of 17.

The three aminophosphine ligands 7, 19 and 22 offer another set of ligands of differing steric and electronic properties for comparing binding strengths to Ag(I). Molecular models show 7 and 22 to be of nearly the same steric size while the cone angle of 19 is reported to be much smaller than that of 7 (Table 3). The value of $^{1}J\,^{31}P-^{77}Se$ for the corresponding selenides show that the order of basicity of these aminophosphines is $7 > 19 \approx 22$ (Table 3). Ligand competition experiments show that both 7 and 19 will displace 22 from Ag(I) demonstrating again that Ag(I) prefers igands which are small and basic.

Addition of 4 molar equivalents of 9 to a solution of $[Ag(23)_2]BF_4$ results in the complete displacement of 23 to form $[Ag(9)_4]BF_4$, while addition of large excesses of 9 to $[Ag(7)_2]BPh_4$ does not result in the displacement of the more basic 7. Examination of the ^{31}P NMR of a solution which contains equivalent amounts of $[Ag(7)_2]BPh_4$ and 9 shows that the resonance for 9 is a much broadened singlet at 130 ppm (10 ppm upfield of the shift of the free ligand). This is indicative of weak interaction between 9 and $[Ag(7)_2]^+$. Addition of more 9 shifted the position of the resonance back toward 140 ppm.

X-ray Structure of $[Ag(P(NMe_2)_3)_2]BPh_4$

The solid state structure of the cation in $[Ag(\underline{7})_2]BPh_4$ is shown in Figure 4 and a drawing of the molecule is shown in Figure 5. The P-Ag-P moiety is bent with an angle of 167° and the silver-phosphorus distance is 2.395(3)Å (Tables 10 and 11). The cause of the bend is not apparent. Coordination of the tetraphenylborate anion would not be unprecedented (86,87), but no intermolecular contacts were found between the anion and the cation. In the structure of the two-coordinate silver(I) complex $[Ag(\underline{4})_2]BF_4$, the P-Ag-P angle is nearly linear (179.4°) with a silver-phosphorus bond distance of 2.461(6)Å (18). It is believed that the extremely large cone angle of $\underline{4}$ precludes any bending of the P-Ag-P bond (18) although in $[Au(\underline{16})_2]PF_6$ where the ligand is small enough to permit additional coordination, the P-Au-P angle is also linear (88). The shorter Ag-P bond distance in $[Ag(\underline{7})_2]BPh_4$ is ascribed at least in part to the smaller steric requirements of $\underline{7}$ compared to $\underline{4}$.

Both of the ligands in $[Ag(\underline{7})_2]BPh_4$ are in an approximately C_s configuration (D) similar to one of the ligands in <u>trans</u>-$Fe(CO)_3(\underline{7})_2$ wherein the most tetrahedral nitrogen has its lone pair roughly anti to the Ag-P bond while the other nearly planar Me_2N groups are twisted in opposite directions (26). As was noted previously, a relationship exists between the sum of the bond angles around nitrogen (ΣN) and the nitrogen-phosphorus bond lengths (Table 12). For example, ΣN_{1A} is 346.9° and the N_{1A}-P1 distance is 1.683Å while the more planar nitrogen N_{1C} (ΣN_{IC} = 356.2°) is only 1.651Å from P1, presumably because of more s character in its bond to P1.

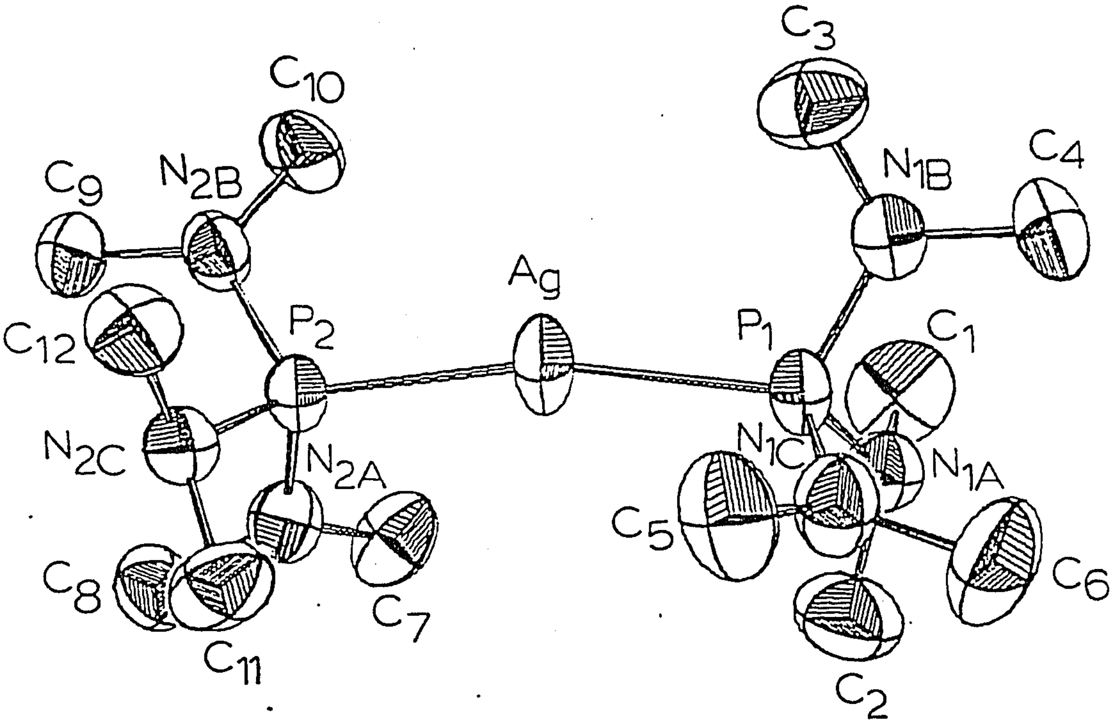


Figure 4. ORTEP drawing of $[Ag(\underline{7})_2]^+$ cation

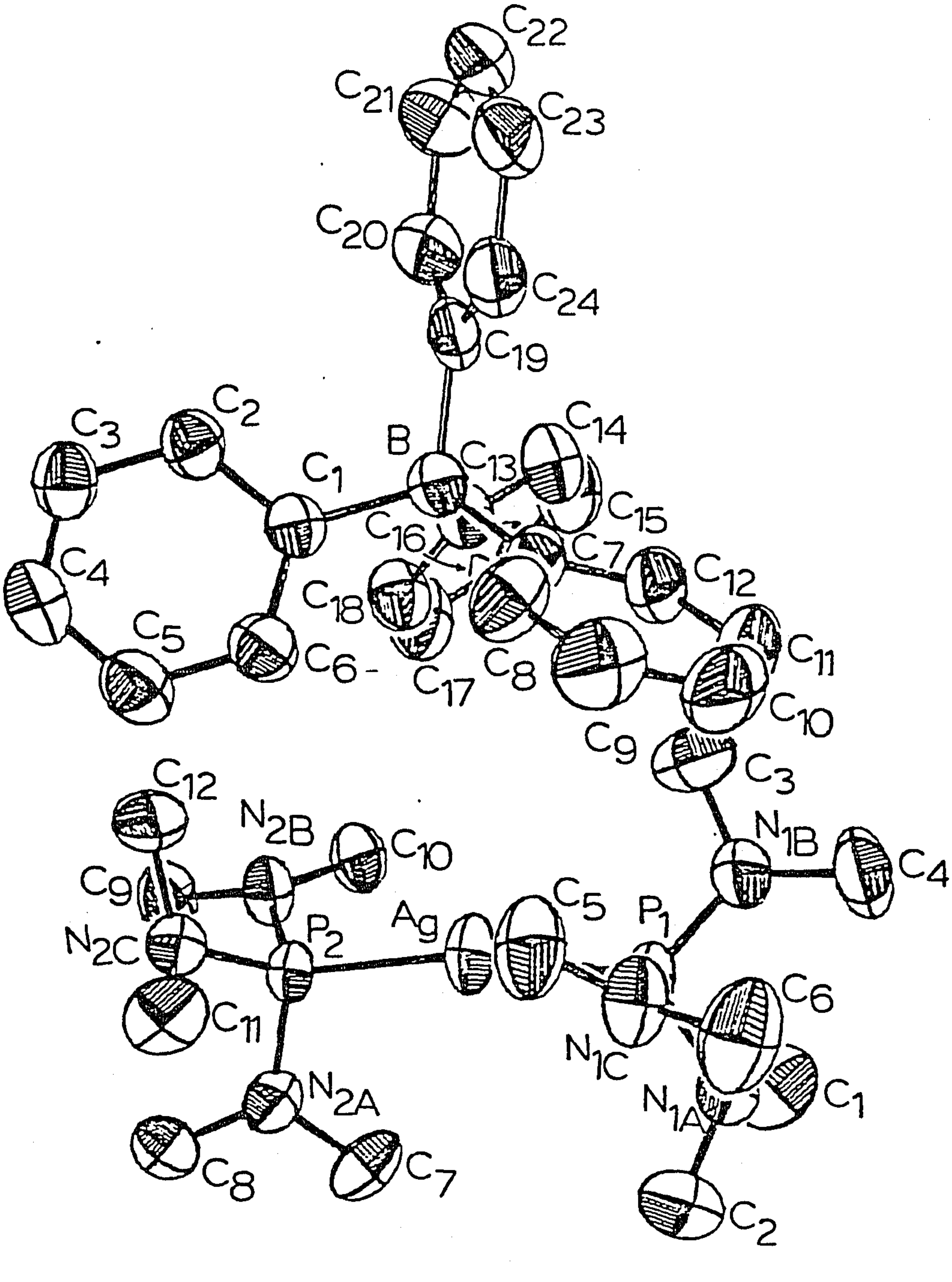


Figure 5. ORTEP drawing of $[Ag(\underline{7})_2]BPh_4$

Table 10. Interatomic distances and selected intramolecular contacts (Å) and their estimated standard deviations (in parentheses) for $[Ag(P(NMe_2)_3)_2]BPh_4$

$[Ag(P(NMe_2)_3)_2]^+$		$B(C_6H_5)_4^{-1}$	
$Ag - P_1$	2.395(2)	$B - C_1$	1.643(9)
$Ag - P_2$	2.393(2)	$B - C_6$	1.642(10)
$P_1 - N_{1A}$	1.683(7)	$B - C_{13}$	1.653(10)
$P_1 - N_{1B}$	1.658(6)	$B - C_{19}$	1.641(11)
$P_1 - N_{1C}$	1.651(6)	$C_1 - C_2$	1.399(10)
$P_2 - N_{2A}$	1.655(6)	$C_1 - C_6$	1.405(9)
$P_2 - N_{2B}$	1.658(5)	$C_2 - C_3$	1.401(9)
$P_2 - N_{2C}$	1.681(6)	$C_3 - C_4$	1.380(10)
$N_{1A} - C_1$	1.473(11)	$C_4 - C_5$	1.369(11)
$N_{1A} - C_2$	1.475(11)	$C_5 - C_6$	1.389(9)
$N_{1B} - C_3$	1.482(11)	$C_7 - C_8$	1.406(10)
$N_{1B} - C_4$	1.462(9)	$C_7 - C_{12}$	1.403(11)
$N_{1C} - C_5$	1.474(12)	$C_8 - C_9$	1.380(11)
$N_{1C} - C_6$	1.479(9)	$C_9 - C_{10}$	1.392(14)
$N_{2A} - C_7$	1.490(11)	$C_{10} - C_{11}$	1.363(15)
$N_{2A} - C_8$	1.465(9)	$C_{11} - C_{12}$	1.396(10)
$N_{2B} - C_9$	1.485(8)	$C_{13} - C_{14}$	1.397(10)
$N_{2B} - C_{10}$	1.475(9)	$C_{13} - C_{18}$	1.405(9)
$N_{2C} - C_{11}$	1.482(9)	$C_{14} - C_{15}$	1.415(11)
$N_{2C} - C_{12}$	1.504(10)	$C_{15} - C_{16}$	1.358(12)
$C_1 \cdots C_3$	4.161(12)	$C_{16} - C_{17}$	1.382(13)
$C_1 \cdots C_4$	3.316(12)	$C_{17} - C_{18}$	1.404(10)
$C_2 \cdots C_5$	4.193(13)	$C_{19} - C_{20}$	1.400(10)
$C_2 \cdots C_6$	3.363(14)	$C_{19} - C_{24}$	1.412(9)
$C_3 \cdots C_5$	4.210(12)	$C_{20} - C_{21}$	1.380(14)
$C_4 \cdots C_6$	3.386(13)	$C_{21} - C_{22}$	1.392(15)
$C_7 \cdots C_{10}$	4.076(11)	$C_{22} - C_{23}$	1.364(15)
$C_7 \cdots C_{11}$	4.252(11)	$C_{23} - C_{24}$	1.387(12)
$C_8 \cdots C_9$	3.410(10)		
$C_8 \cdots C_{11}$	3.369(11)		
$C_9 \cdots C_{12}$	3.427(11)		

Table 11. Bond angles (deg) and their standard deviations (in parentheses) for $[Ag(P(NMe_2)_3)_2]BPh_4$

$[Ag(P(NMe_2)_3)_2]^+$		$B(C_6H_5)_4^{-1}$	
P_2 - Ag - P_1	166.9(1)	C_1 - B - C_7	110.5(5)
Ag - P_1 - N_{1A}	116.4(2)	C_1 - B - C_{13}	108.3(5)
Ag - P_1 - N_{1B}	113.2(2)	C_1 - B - C_{19}	109.5(6)
Ag - P_1 - N_{1C}	109.1(2)	C_7 - B - C_{13}	110.4(6)
N_{1A} - P_1 - N_{1B}	100.6(3)	C_7 - B - C_{19}	108.5(5)
N_{1A} - P_1 - N_{1C}	101.4(3)	C_{13} - B - C_{19}	109.7(5)
N_{1B} - P_1 - N_{1C}	115.6(3)	B - C_1 - C_2	123.1(6)
Ag - P_2 - N_{2A}	108.2(2)	B - C_1 - C_6	122.5(6)
Ag - P_2 - N_{2B}	114.8(2)	C_1 - C_2 - C_3	123.0(6)
Ag - P_2 - N_{2C}	116.5(2)	C_2 - C_3 - C_4	119.7(7)
N_{2A} - P_2 - N_{2B}	114.2(3)	C_3 - C_4 - C_5	119.4(6)
N_{2A} - P_2 - N_{2C}	100.9(3)	C_4 - C_5 - C_6	120.3(7)
N_{2B} - P_2 - N_{2C}	101.7(3)	C_5 - C_6 - C_1	123.1(7)
C_1 - N_{1A} - C_2	112.8(7)	C_6 - C_1 - C_2	114.4(6)
C_1 - N_{1A} - P_1	117.3(5)	B - C_7 - C_8	122.8(6)
C_2 - N_{1A} - P_1	116.8(6)	B - C_7 - C_{12}	122.4(6)
C_3 - B_{1B} - C_4	114.1(6)	C_7 - C_8 - C_9	123.1(8)
C_3 - N_{1B} - P_1	118.8(5)	C_8 - C_9 - C_{10}	120.0(8)
C_4 - N_{1B} - P_1	121.5(5)	C_9 - C_{10} - C_{11}	119.2(8)
C_5 - N_{1C} - C_6	113.8(6)	C_{10} - C_{11} - C_{12}	120.3(9)
C_5 - N_{1C} - P_1	119.8(5)	C_{11} - C_{12} - C_7	122.7(7)
C_6 - N_{1C} - P_1	122.6(6)	C_{12} - C_7 - C_8	114.7(6)
C_7 - N_{2A} - C_8	113.4(6)	B - C_{13} - C_{14}	123.6(6)
C_7 - N_{2A} - P_2	118.7(5)	B - C_{13} - C_{18}	122.1(6)
C_8 - N_{2A} - P_2	124.3(5)	C_{13} - C_{14} - C_{15}	123.1(6)
C_9 - N_{2B} - C_{10}	113.0(5)	C_{14} - C_{15} - C_{16}	120.0(8)
C_9 - N_{2B} - P_2	120.9(4)	C_{15} - C_{16} - C_{17}	119.8(8)
C_{10} - N_{2B} - P_2	118.4(5)	C_{16} - C_{17} - C_{18}	119.6(7)
C_{11} - N_{2C} - C_{12}	110.9(5)	C_{17} - C_{18} - C_{13}	123.3(7)

Table 11. (Continued)

$[Ag(P(NMe_2)_3)_2]^+$		$B(C_6H_5)_4^{-1}$	
C_{11} - N_{2C} - P_2	115.2(5)	C_{18} - C_{13} - C_{14}	114.3(6)
C_{12} - N_{2C} - P_2	116.4(4)	B - C_{19} - C_{20}	122.7(6)
		B - C_{19} - C_{24}	121.9(6)
		C_{19} - C_{20} - C_{21}	121.8(7)
		C_{20} - C_{21} - C_{22}	120.8(9)
		C_{21} - C_{22} - C_{23}	119.4(10)
		C_{22} - C_{23} - C_{24}	119.6(8)
		C_{23} - C_{24} - C_{19}	123.0(7)
		C_{24} - C_{19} - C_{20}	115.4(7)

Table 12. Phosphorus-nitrogen bond distances (Å) and sum of angles around nitrogen (deg) in $[Ag(\underline{7})_2]BPh_4$

	P-N	ΣN
N_{1A}	1.683	346.9
N_{1B}	1.658	354.4
N_{1C}	1.651	356.2
N_{2A}	1.655	356.4
N_{2B}	1.658	352.3
N_{2C}	1.681	342.5

The P-N bond lengths show evidence of π bonding between the phosphorus and nitrogens. From the Schomaker-Stevenson empirical correlation

$$r_{AB} = r_A + r_B - 0.09\ (X_A - X_B) \tag{9}$$

r_A, r_B = covalent radii X_A, X_B = electronegativities

it is estimated that a nitrogen-phosphorus single bond has a length of 1.76 Å (89), while the average P-N distance in $[Ag(\underline{7})_2]BPh_4$ is 1.66 Å, suggesting that the phosphorus-nitrogen bond is strengthened by π interaction. The poor π acceptor properties of tris(dialkylamino)-phosphines have been attributed to the fact that the d orbitals on phosphorus in these ligands are involved in π interaction with the nitrogens which renders the ligands poor π acids in their metal complexes (90-92). It is seen that the ΣX values for 7 and 22 in Table 3 are smaller than those of some phosphines while the $^1J^{77}SeP$ values for the corresponding selenides lie between the value seen for phosphines and phosphites as expected. The reason for this may be that ΣX is a partial measure of π acceptor ability of the ligand while the selenium-phosphorus coupling constant measures the positive charge on phosphorus. It is possible that nitrogen-phosphorus π bonding affects the former more than the latter.

Cowley argues that the longer average P-N bond distance (1.673Å) in trans-$Fe(CO)_3(\underline{7})_2$ compared to that in $Fe(CO)_4(\underline{7})$ (1.664Å) is due to increased Fe-P π bonding in trans-$Fe(CO)_3(\underline{7})_2$ which leads to decreased P-N π bonding (25). On the basis of this model, one might expect the P-N bond distance in $[Ag(\underline{7})_2]BPh_4$ to be shorter than in $Fe(CO)_4(\underline{7})$ since the positively-charged silver(I) might be expected to be a poorer π base than Fe(0). The average P-N distance in $[Ag(\underline{7})_2]BPh_4$ (1.664Å) is essentially the same as in $Fe(CO)_4(\underline{7})$, however.

Both ligands in $[Ag(\underline{7})_2]BPh_4$ exhibit one larger and two smaller N-P-N bond angles (Table 11). In each ligand the largest N-P-N bond angle is between nitrogen atoms which are closest to trigonal-planar geometry. This large NPN angle arises from the greater repulsion of the predominantly 2p lone pairs which are pointed toward one other. This trend was also noted by others (25,26,30,31,33,34,36). On each ligand, two of the carbons are involved in two rather short intramolecular carbon-carbon contacts (C_4, C_6, C_8 and C_9). It is seen that these four carbons have the four largest P-N-C angles which may be due to a crowding effect (Table 10, Table 11). This relationship is not seen, however, in the two structured Fe complexes of $\underline{7}$ (24,25).

From the structural data it can be concluded that because of similarities in the structures of various PN_3 compounds, the ligand conformations observed are not determined by lattice effects. The present results also lend further credence to conclusions from theoretical work which suggest that structures C and D are the most stable conformations of tris(dialkylamino)phosphines with the energy difference between the two being rather small. Finally, the bulk of the structural data indicates that tris(dialkylamino)phosphines are not idealized symmetrical structures but that at least in the solid state they prefer a configuration where one of the nitrogens is pyramidal.

PART II. NMR STUDIES OF PHOSPHORUS LIGAND COMPLEXES OF COBALT

INTRODUCTION

The ^{59}Co nucleus at least in a historical sense can be considered as one of the most important nuclei in the development of NMR spectroscopy. In 1951, six years after the discovery of the NMR experiment, Proctor and Yu found that the resonance frequency of cobalt compounds could vary as much as 1 part in 100 depending on the compound selected for measurement. Since they were attempting to measure the magnetogyric ratio of ^{59}Co, this effect was thought to be a nuisance and was called the most derogatory term the two scientists could think of, namely, "the chemical shift". The development of the many applications of NMR spectroscopy by chemists stems from a phenomenon which annoyed two physicists (93,94).

The properties of the ^{59}Co nucleus make it idealy suited for NMR observation. In addition to a 100% natural abundance it has a rather large magnetic moment, giving it a relative sensitivity of 0.281 with respect to ^{1}H for equal numbers of nuclei of constant field. These two factors place ^{59}Co in the top six nuclei for ease in detection. A nuclear spin of 7/2 along with a quadrupole moment of 0.40×10^{-28} m^{2} makes ^{59}Co NMR linewidths sensitive to electric field gradients at the ^{59}Co nucleus. The absence of reports of ^{59}Co NMR data for Co(I) compounds can be attributed to the large electric field gradients expected for these five-coordinate complexes.

Chemical shifts of ^{59}Co compounds span a very wide range. The chemical shift of $[Co(CO_3)_3]^{3-}$ is the furthest downfield ever reported (14,000 ppm downfield from $[Co(CN)_6]^{3-}$) with the shift of $[Co(PF_3)_4]^-$

(-1,400 ppm) being the most upfield (94). The wide range in chemical shifts is due to the large variance in the paramagnetic term in the shielding tensor

$$\sigma_p = (-32\beta^2/\Delta E < r_d\text{-}3>) \tag{10}$$

Inclusion of the diamagnetic contribution of the cobalt ion (which is thought to be constant) into equation 10 gives

$$\delta^{59}\text{Co} = \sigma_d + \sigma_p = (e^2/3mc^2\sum_i <r_i\text{-}1> + 32\beta^2(\kappa)^2<r_d\text{-}3>\Delta E^{-1} \tag{11}$$

where i denotes all doubly occupied orbitals, κ (the orbital reduction factor) is the coefficient of the d_z2 and $d_x2_{-y}2$ atomic orbitals, r_d is the cobalt d-orbital radius, β is the Bohr magneton, and ΔE is the singlet triplet excitation energy. From equation 10, it is seen that a plot of the ^{59}Co NMR chemical shift vs the lowest energy d-d transition for a series of cobalt complexes should have a slope of $32\beta^2(\kappa)^2<r_d\text{-}3>$ and an intercept of σ_d, the shielding of a hypothetical Co^{3+} ion with a spherically symmetrical charge distribution for which the σ_p term is zero.

Indeed, many early workers in the field noted a rather linear relationship between the energy of the lowest energy d-d transition and the ^{59}Co NMR resonance for Co(III) complexed to six carbon, nitrogen or oxygen donors (94). Later, a number of authors noted departures from the above correlation for S, Se and As donor ligands. These deviations from the first-row donor plot were associated with an increase in the metal-ligand distance corresponding to a decrease in $<r_d\text{-}3>$ where r_d is the cobalt d-orbital radius (94). The inclusion of data for $[Co(P(OR)_3)_6]^{3+}$

compounds showed that the intercepts of the plots of the first and second period ligators were not the same (95). The ratio of the intercepts of the first and second row elements given by $\sum_i \langle r_i\text{-}1\rangle_1/\sum_i \langle r_i\text{-}1\rangle_2 = 1.60$ strongly suggested that cobalt radius changes are important in comparing correlations involving ligands from different periods (95).

Juranić later noted that the difference between the intercepts of the first- and second-row ligators corresponds to a difference in the dimagnetic shielding constant which is as large as 0.005 while a previous estimate of the diamagnetic shielding constant value gives $\sigma_d = 0.0021$ (96,97). He thus suggests that one or both of the correlations are accidental (96).

Recently, Juranić noted that in complexes which contain a greater amount of covalency in the cobalt ligand bond, the paramagnetic circulation from the $T_{1g} \longleftarrow A_{1g}$ electronic transition deshields the cobalt nucleus less effectively because the circulation is driven away from the ligands. He defined a term which he called the circulation-removing ratio which was dependent on the electronegativity of the donor atoms. For ligators of the same electronegativity, plots can be drawn of ^{59}Co NMR chemical shift against the energy of the lowest d-d transition which all have the same intercept. Thus, for example, the line containing phosphorus and arsenic donors has a correlation coefficient of 0.98 (98). It is for this reason that ^{59}Co NMR can be used as a probe of ligand field in complexes of the type $[Co(P)_6]^{3+}$ where P refers to a phosphorus donor atom.

It was of interest to study the ligand field properties of phosphites in complexes of the type $[Co(P(OR)_3)_6]^{3+}$ to see if a relationship could be found between the effective ligand field of the complexes and the steric and/or electronic properties of the ligands. The complexes studied herein were prepared by the disproportionation reaction 12 which was first reported in 1962 for an analogous reaction where 18 was reacted with $[Co(H_2O)_6](ClO_4)_2$ (14). Since that time, it has been found that

$$2[Co(H_2O)_6](BF_4)_2 + 11L \xrightarrow[\text{2,2-dimethoxypropane}]{\text{acetone}} [CoL_6](BF_4)_3 + [CoL_5]BF_4 \tag{12}$$

reaction 12 proceeds with other bicyclic phosphites (99,100), monocyclic phosphites (95), the acyclic phosphite (9) (15), as well as the chelating phosphonites 30 and 31 (101). The absence of $[Co(PR_3)_6]^{3+}$ complexes has been attributed to the relatively poor pi bonding capability of phosphines in spite of their high sigma basicity (102). Recently, however, a complex of the bidentate phosphine 32 of the type $[CoL_3]^{3+}$ has been reported (103). The instability of $[Co(PF_3)_6]^{3+}$ has been rationalized as being due to the insufficient basicity of PF_3 to neutralize the charge on the metal (102).

In addition to the aforementioned examples, the only other report of Co(III) coordinated to phosphite ligands has been in complexes prepared by reactions 13 and 14 (104). The finding that 2 and 33 do not react with

$$Co(SCN)_2 + 9(\underline{9}) \longrightarrow [Co(\underline{9})_5]^+ + [\underline{cis}\text{-}Co(NCS)_2(\underline{9})_4]^+ + 2\ SCN^- \tag{13}$$

$$2\ Co(NCS)L_4 + 2NO \longrightarrow [CoL_2(NO)_2]^+ + [Co(NCS)_2L_4]^+ + 2\ L \tag{14}$$

$Co(SCN)_2$ by equation 13 probably stems from the larger steric requirement of these ligands compared to 9.

In metal complexes wherein the ligands have empty pi orbitals of higher energy than the metal T_{2g} orbitals, an interaction can take place which stabilizes the metal T_{2g} orbitals with respect to the metal Eg^* orbitals. The net result of this interaction is an increase in ligand field. Although phosphite ligands are thought to be good pi acceptors, it is questionable whether the small highly charged Co(III) ion is sufficiently pi basic for this effect to be seen. Steric factors can also have consequences in terms of the ligand field of metal complexes. For example, increasing methyl substitution on a diamine chelate shifts λ_{max} to lower energies in complexes of the type $[CuL_2](ClO_4)_2$ (105) and $[NiL_3](ClO_4)_2$ (106). The small size of the Co(III) ion should serve to enhance the importance of steric efects.

Since a ^{59}Co NMR shift can be measured to a greater degree of precision than a uv band (and many $[Co(P(OR)_3)_6]^{3+}$ complexes display their lowest energy d-d bands in or near the charge transfer region of the uv) a ^{59}Co NMR study of $[Co(P(OR)_3)_6]^{3+}$ complexes was undertaken to investigate the relative importance of steric and electronic properties in determining the effective ligand field in $[Co(P(OR)_3)_6]^{3+}$ complexes.

Recently, some work along these same lines has appeared. An investigation of the effect of steric and electronic properties of phosphorus ligands on metal NMR shifts has been reported by Rehder and coworkers (107). Complexes of the type $[M(CO)_{6-n}L_n]^q$ (M = V,Nb: q = - 1; M = Mn: q = + 1; n = 0 - 6), η^5-$C_5H_5M(CO)_{4-n}L_n$ (M = V,Nb; n = 0 - 4) and η^5-$C_5H_5M(L')_2L$ (M = V, L' = NO; M = Mn, L' = CO) were studied by ^{51}V, ^{55}Mn and ^{93}Nb NMR, respectively. In general, it was found that there is a decrease in shielding with decreasing pi acceptor ability of the ligand and increasing ligand bulkiness. An interesting exception was found in η^5-$C_5H_5Mn(CO)_2L$ complexes where the ^{55}Mn NMR chemical shift was virtually independent of the ligand L. This was attributed to the large splitting of the Mn-3d orbitals in these complexes (108) which reduces the changes in ΔE upon subsitution of L. It is of interest to compare the results obtained by these authors on complexes which are for the most part low symmetry, low valent organometallic complexes to $[CoP_6]^{3+}$ complexes where more pronounced trends may be expected since the coordination of six sites can be varied in contrast to only one or two and the range of ^{59}Co NMR chemical shifts is much larger than those of ^{51}V, ^{55}Mn and ^{93}Nb NMR (94).

EXPERIMENTAL

Procedures

UV-visible spectra were recorded on a Perkin Elmer 320 spectrometer. Cobalt-59 (70.85 MHz) and ^{31}P (121.51 MHz) NMR spectra were recorded on a Bruker WM-300 spectrometer operating in the Fourier mode while locked on the ^{2}H resonance of deuterated solvents and referenced to aqueous $K_3[Co(CN)_6]$ and 85% H_3PO_4, respectively, with positive shifts defined as being downfield. Carbon-13 (23.5 MHz) and ^{1}H (89.55 MHz) NMR spectra were recorded on a JEOL FX-90Q spectrometer operating in the Fourier mode and referenced to Me_4Si.

The T_1 values of ^{59}Co and ^{31}P were measured by the 180-τ-90 technique as described by Becker (109). For the measurements of T_1 of ^{59}Co a sweepwidth of 100,000 Hz was used incorporating 8192 data points with an acquisition time of 0.082 sec while for the measurements of T_1 of ^{31}P, a sweepwidth of 10,000 Hz was used incorporating 16,486 data points with an acquisition time of 0.819 sec. Recovery times were chosen that were a minimum of 5 times the T_1 values. Data acquisition was performed by the computer T_1 program. The peak heights were measured by hand. Analysis of the data was accomplished by least-squares fitting of the semilog plot $\ln(S_\infty - S_t)$ against t, whence the inverse slope provides the $-T_1$ value (S_∞ = equilibrium signal intensity, S_t = signal intensity at time t).

Materials

All solvents were dried over molecular sieves before use. Et_2O was distilled from potassium/benzophenone. $[Co(H_2O)_6](BF_4)_2$ was obtained from Alfa Products. 2,2-Dimethoxypropane and 34 were purchased from Aldrich Chemical, while 32, 35 and 36 were purchased from Strem Chemicals. N,N'-dimethylurea was purchased from Fluka.

Preparation of Compounds

$Cl\overline{POCH_2CH_2O}$ (37)

This phosphorochloridite was prepared as described by Lucas and coworkers (110) with the exception that the glycol was slowly added to a solution of PCl_3 instead of simultaneous addition of the two reactants.

$RO\overline{POCH_2CH_2O}$ (R = Et(38), R = *n*-Pr(39), R = *n*-Bu(40), R = *i*-Pr(41), R = *i*-Bu(42), R = *sec*-Bu(43), R = *t*-Bu(44), R = Ph(45), R = CF_3CH_2(46) R = $N(CH_2CH_2)_2O$ (47)

These ligands were prepared from 37 and the appropriate alcohol or amine in yields of approximately 80% following the method of Lucas (110). Boiling points and ^{31}P NMR are given in Table 13.

$CH_3O\overline{POCH_2CH(CH_3)O}$ (48a,b)

This monocyclic phosphite was prepared as described by Denney and coworkers (111). Although the separation of the two possible isomers (*cis* and *trans* methyl to methoxy) can be achieved by gas-liquid chromatography

Table 13. Boiling points and ^{31}P NMR chemical shifts of 2-substituted-1,3,2-dioxaphospholanes

	Bp °C	Bp °C (lit)	δ ^{31}P^{a}	δ ^{31}P (lit)
37	b_1 = 40	b_{15} = 46.5^{b}	167.3	166.6 - 168.4^{c}
27	b_5 = 35	b_{35} = 60-2^{b}	130.4	131.6 - 132.4^{c}
38	b_1 = 40	b_{21} = 60-61^{b}	131.6	131-4^{c}
39	b_5 = 45	b_{30} = 84-6^{b}	131.8	132.0, 134.4^{c}
40	b_1 = 55	b_{25} = 90^{b}	131.8	132-3^{c}
41	b_{10} = 75	b_{20} = 64-6^{b}	132.1	---
42	b_5 = 52	b_{25} = 97^{b}	131.2	134.1^{c}
43	b_3 = 50	b_{25} = 83^{b}	132.3	---
44	b_5 = 52	b_{25} = 74^{b}	132.9	---
45	b_1 = 90-100	$b_{0.3}$ = 73^{d}	128.5	120 - 29^{c}
46	b_3 = 37	---	137.6	---
47	---	---	137.9	---
48	b_5 = 50-2	b_{23} = 53-59^{e}	137.6, 141.3^{f}	139, 142^{e}
49	b_3 = 45	---	170.9, 171.8	---
50	b_5 = 45-50	---	140.0	140^{e}
51	$b_{3.5}$ = 52-5	---	140.1	---
52	b_3 = 52	---	139.0	---

---

[a] In ppm downfield from 85% H_3PO_4. Measured in $(CD_3)_2CO$ unless otherwise indicated.

[b] Reference 110.

[c] Reference 53.

[d] D. C. Ayres and H. N. Rydon, J. Chem. Soc., 1109 (1957).

[e] Reference 111.

[f] Measured in $CDCl_3$.

Table 13. (Continued)

	Bp °C	Bp °C (lit)	$\delta\ ^{31}P^a$	$\delta\ ^{31}P$ (lit)
53	$b_2 = 45$	---	139.8	---
54	$b_6 = 50$	$b_6 = 33^e$	148.1	147^e
55	$b_{100} = 35$	$b_{170} = 48^g$	124.1^h	$124.4^{g,i}$
56	$b_1 = 85$	---	162.0	162
57	$b_1 = 40$	---	191.7	---

[g] Reference 112.

[h] $^1J_{PF}$ = 1223 Hz.

[i] $^1J_{PF}$ = 1260 Hz.

for analytical purposes (111), separation of the macroscopic quantities required herein was not carried out.

dl-meso-ClPOCHCH$_3$CHCH$_3$O (49)

This phosphorochloridite was prepared from PCl$_3$ and 2,4-pentanediol by the method of Denney and co-workers (111) with the modification that Et$_3$N was used as a base instead of N,N-dimethylanaline.

dl-MeOPOCHCH$_3$CHCH$_3$O (50)

This phosphite was prepared in 17% yield by transesterification of 9 with 2,4-butanediol as described by Denney and co-workers (111).

Distillation through a 2" Vigreaux column resulted in the *dl* isomer being obtained in greater than 95% isomeric purity.

dl-$ROPOCHCH_3CHCH_3O$ (R = Et (51), R = *n*-Pr (52), R = *i*-Pr (53)

These phosphites were prepared by the reaction of equivalent amounts of 49 and the appropriate alcohol in ether in the presence of Et_3N as described by Denney and co-workers (111). Distillation through a 2" Vigreaux column resulted in obtaining the *dl* phosphites in greater than 95% isomeric purity.

$CH_3OPOC(CH_3)_2C(CH_3)_2O$ (54)

This phosphite was prepared by using the modification described by Vande Griend (59) of the procedure originally described by Denney and co-workers (111).

$FPOCH_2CH_2O$ (55)

This compound was prepared by the method of Schmutzler (112).

$PhPOCH_2CH_2O$ (56)

To a solution of $PPhCl_2$ (20.3 g, 113 mMol) in 500 ml of Et_2O and 40 ml of Et_3N was added dropwise over a period of 15 minutes ethylene glycol (7.01 g, 113 mMol). The product was distilled in 79% yield after filtration of the precipitated $Et_3N{\cdot}HCl$ (b_1 = 85; ^{31}P NMR ($CDCl_3$) 162, lit. 162 (113)).

$EtPOCH_2CH_2O$ (57)

To a solution of $PEtCl_2$ (9.0 g, 69.2 mMol) in 300 ml of Et_2O and 20 ml of Et_3N was added dropwise ethylene glycol (4.5 g, 72.5 mMol). The $Et_3N{\cdot}HCl$ was filtered and the very air sensitive compound was distilled in 48% yield.

$O{=}C(NMePOCH_2CH_2O)_2$ (58)

In a 1000 ml round bottom flask was dissolved 38 (31.6 g, 250 mMol) in 300 ml of CH_2Cl_2. To this solution was added Et_3N (29.0 g, 286 mMol). Then N,N'-dimethylurea (10.0 g, 114 mMol) in 50 ml at CH_2Cl_2 was added dropwise over a period of one-half hour. After the addition was complete, 50 ml of Et_2O was added. The precipitated $Et_3N{\cdot}HCl$ was filtered and the solvent was evaporated under reduced pressure. The product was obtained in 66% yield following recrystallization from a solution of 15% CH_3CN, 55% Et_2O and 30% hexanes (^{31}P NMR (CD_3CN) 138.0; ^1H NMR (CD_3CN) 4.4-4.0m 4H OCH_2, 2.63t 3H NCH_3 $|{}^2JPH + {}^4JPH| = 1.7$ Hz; ^{13}C NMR (CD_3CN) 118.2 C=0, 66.5 CH_2, 29.1 CH_3; a parent ion could not be seen in the mass spectrum).

$P(SMe)_3$ (59)

This ligand was prepared as described previously (114) ($b_1 = 65°$; ^{31}P NMR ($(CD_3)_2CO$) 123.9, lit. 125.6 (115)).

$As(OMe)_3$ (60)

This ligand was prepared in 18% yield by the method described by Moedritzer and Van Wazer (116) (b_{760} = 130-4, lit. b_{760} = 129-30 (116)).

$As(OCH_2)_3CCH_3$ (61)

This ligand was kindly supplied by Dr. R. A. Montag who used a procedure described previously to prepare it (117).

$Cl\overline{POCH_2CH_2S}$ (62)

This phosphorochloridite was prepared as described by Bergesen, Bjorøy and Gramstad (118) (b_2 = 65°, lit. $b_{0.4}$ = 57° (118)).

$MeO\overline{POCH_2CH_2S}$ (63)

In 200 ml of Et_2O and 25 ml of Et_3N was dissolved 62 (15.0 g, 102 mMol). To this solution was added MeOH (4.50 g, 140 mMol). After filtering off the precipitated $Et_3N{\cdot}HCl$ 63 could be distilled in 82% yield. Although two peaks were reported for the ^{31}P NMR of 64 (119) which was attributed to two configurations of the five-membered ring (118,119); only one peak was seen in the ^{31}P NMR of 63 (b_1 = 60°; ^{31}P NMR ($CDCl_3$) 170.3).

C_6H_4-o-O_2PCl (65)

This precursor was prepared by the method of Crofts, Markes and Rydon (120) (b_2 = 65°, lit. b_{20} = 90° (120); ^{31}P NMR (C_6D_6) 172.8).

C_6H_4-*o*-O_2POMe (66)

This phosphite was prepared as originally described by Arbuzov and Valitova (121) (b_2 = 55-7, lit. b_8 = 73 (121); ^{31}P NMR ($(CD_3)_2CO$) 127.7).

$P(CH_2CH_2CN)_3$ (67)

This ligand was kindly supplied by Dr. Phil M. Stricklen who used the method of Vullo to prepare it (122).

$(MeO)_2PCH_2CH_2P(OMe)_2$ (68)

This diphosphonite was prepared from 36 and MeOH by using the method of King and Rhee (123) ($b_{0.6}$ = 66-70, lit. $b_{0.07}$ = 60-64 (123)).

$P(OCH_2)_3CCH_3$ (18)

This bicyclic phosphite was prepared as was previously described (39).

$P(OCH)_3(CH_2)_3$ (69)

This phosphite was prepared as previously described (124).

$CH_2OPOCH_2CH_2CHO$ (70)

This phosphite was also prepared by a literature procedure (125).

ax-$MeOPOCH(CH_3)_{eq}CH_2CH(CH_3)_{eq}O$ (71)

This ligand was synthesized as reported previously (50).

$\text{eq-MeO}\overline{\text{POCH(CH}_3)_{\text{eq}}\text{CH}_2\text{CH(CH}_3)_{\text{eq}}\text{O}}$ (72)

This ligand was synthesized as reported previously (126).

$\text{ax-MeO}\overline{\text{POCH(CH}_3)_{\text{eq}}\text{CH}_2\text{CH}_2\text{O}}$ (73), $\text{ax-}n\text{-PrO}\overline{\text{POCH(CH}_3)_{\text{eq}}\text{CH}_2\text{CH}_2\text{O}}$ (74), $\text{eq-MeO}\overline{\text{POCH(CH}_3)_{\text{eq}}\text{CH}_2\text{CH}_2\text{O}}$ (75), $\text{eq-}n\text{-PrO}\overline{\text{POCH(CH}_3)_{\text{eq}}\text{CH}_2\text{CH}_2\text{O}}$ (76)

These compounds were prepared by the general method of Bodkin and Simpson (127)for the preparation of 2-alkoxy-4-methyl-1,3,2-dioxaphosphorinanes with the modification that p-toluenesulfonic acid was used to isomerize the unstable to the stable isomers (74, ^{31}P NMR $(CD_3)_2CO$) 125.7; 76, ^{31}P NMR ($(CD_3)_2CO$) 130.5).

$\text{MeO}\overline{\text{POCH}_2\text{CH}_2\text{CH}_2\text{O}}$ (77)

This phosphite was prepared according to a literature method (7).

$[Co(30)_3]_3(BF_4)_3$ and $[Co(31)_3]_3(BF_4)_3$

These complexes were prepared by Dr. Richard Weiss following the procedure described by Meiners (128).

$[Co(32)_3](ClO_4)_3$

This complex was prepared as previously described (103).

$[Co(DMSO)_6](BF_4)_2$

This compound was prepared as previously described (129) for the perchlorate salt.

$W(CO)_4$(58)

In 15 ml of dry degassed THF was dissolved $W(CO)_6$ (0.100 g, 0.284 mMol) and 58 (0.200 g, 0.746 mMol). This solution was placed in a quartz photolysis tube equipped with a cooling probe and was irradiated with uv light at 254 nm for a period of 3 hrs at room temperature using a reactor obtained from Bradford Scientific, Inc., Marblehead, Mass.. The greenish solution was removed from the photolysis tube and the solvent was removed under reduced pressure. A small amount of colorless residue remained after repeated extraction with CH_3CN (~ 10 mg). This residue was insoluble in all common organic solvents. It was identified as $W(CO)_4$(58) on the basis of parent ion peaks at 562, 564 and 566 m/e in the low resolution mass spectrum.

$SeP(OR)_3$

Selenophosphates were prepared by the method which Kroshefsky used to prepare $SeMeOPOCH_2CH_2O$ (7). Because of the expected instability of the selenides of the five-membered rings (7) and the fact that only NMR parameters were desired from these compounds, they were not purified by sublimation or column chromatography. ^{31}P NMR chemical shifts of the selenophosphates discussed in this section are given in Table 14. When an attempt was made to prepare the diselenide of 68 in this manner, the ^{31}P NMR of the crude product showed the major species had a chemical shift of 108.7 ppm, but two selenium coupling constants were observed in nearly equal intensity (786 and 964 Hz). In comparison, $SeP(CH_3)(OCH_3)_2$ is

Table 14. ^{31}P NMR chemical shifts of selenophosphates

Parent phosphite	δ ^{31}P (ppm)[a]
27	90.5
38	85.5
39	85.5
40	85.8
41	84.9
42	84.6
45	82.9
46	90.4
48a,b	86.9, 87.1
50	82.6
51	82.6
52	82.0
70	80.9
69	70.5
74	70.4

[a] Measured in CD_3CN.

reported to have a ^{31}P NMR chemical shift of 102.3 ppm and a phosphorus-selenium coupling constant of 861 Hz (130). No further characterization of this product(s) was carried out.

$Pt(cod)I_2$

This compound was prepared as described by Clark and Manzer (131).

cis-Pt(41)$_2$I$_2$

In 30 ml of CH_2Cl_2 was dissolved Pt(cod)$_2$I$_2$ (1.26 g, 2.25 mMol). To this solution was added 42 (1.20 g, 8.00 mMol). The reaction was allowed to stir for one-half hour. The solvent was removed under reduced pressure and the product was obtained in 33% yield after chromatography through 30 g of silica using CH_2Cl_2 as eluant (^{31}P NMR ($(CD_3)_2CO$) 92.1 $^1J^{195}Pt^{31}P$ = 5480 Hz; ^1H NMR (CD_3CN) 4.3-4.8m 5H CH CH_2, 1.40d 6H CH_3 ^2JHH = 6 Hz; ^{13}C NMR (CD_3CN) 74.8 CH, 67.7 CH_2, 23.7 CH_3).

[Ni(41)$_5$](ClO$_4$)$_2$

This compound was prepared by a procedure given for the preparation of complexes of the type $[Ni(P(OR)_3)_5](ClO_4)_2$ reported earlier (15). In 10 ml of acetone and 10 ml of 2,2-dimethoxypropane was dissolved $[Ni(H_2O)_6](ClO_4)_2$ (0.220 g, 0.825 mMol). To this solution was injected 41 (1.00 g, 6.67 mMol). Immediately, a yellow precipitate fell from solution. The product was filtered under nitrogen and recrystallized in 85% yield from acetone/ether. (^{31}P NMR ($(CD_3)_2CO$) 100.8; ^{13}C NMR (CD_3CN) 75.5 CH, 68.0 CH_2, 23.6 CH_3; ^1H NMR ($(CD_3)_2CO$) 4.3-4.8m 5H CH CH_2, 1.43d CH_3 6H ^2JHH = 6 Hz).

Preparation of $[Co(P)_6]^{3+}$ and $[Co(P)_5]^+$ Complexes by Disproportionation of Co(II)

Co(II) was disproportionated by two methods. In method A, $[Co(H_2O)_6](BF_4)_2$ was dehydrated with 2,2-dimethoxypropane. In method B,

$[Co(DMSO)_6](BF_4)_2$ was used as the starting complex. An example is given of each method of preparation.

Method A

This method has been described by Piper and Verkade for the preparation of $[Co(\underline{18})_6](ClO_4)_3$ and $[Co(\underline{18})_5]ClO_4$ (14). To a solution of $[Co(H_2O)_6](BF_4)_2$ (1.08 g, 3.17 mMol) in 15 ml of acetone and 15 ml of 2,2-dimethoxypropane was injected 27 (4.74 g, 31.7 mMol). The initially red solution became lemon yellow within 5 seconds after the addition of liquid and yellowish impure $[Co(\underline{27})_6](BF_4)_3$ precipitated from solution. The $[Co(\underline{27})_6](BF_4)_3$ was filtered and washed with CH_2Cl_2. Essentially pure colorless $[Co(\underline{27})_6](BF_4)_3$ was obtained in 82% yield after two recrystallizations from CH_3CN/THF.

The filtrates were combined and the solvent was removed under reduced pressure. The residual yellow $[Co(\underline{27})_5]BF_4$ was redissolved in CH_2Cl_2 and precipitated in 71% yield upon addition of Et_2O.

The following ligands were reacted in this manner to produce $[Co(P)_6]^{3+}$ and $[Co(\underline{P})_5]^+$ compounds: 9, 17, 18, 27, 38, 50, 51, 68, 69, 71, 72, 73, 74, 75 and 77.

Method B

This method avoids the presence of MeOH in the reaction which introduces an interesting phenomenon in certain cases (*vide infra*). To a solution of $[Co(DMSO)_6](BF_4)_2$ (1.60 g, 2.28 mMol) in 20 ml of CH_3CN was injected 41 (3.50 g, 23.3 mMol). The initially red solution quickly became yellow. Addition of 30 ml of THF followed by 20 ml of Et_2O

resulted in the precipitation of impure yellowish $[Co(41)_6](BF_4)_3$. Two careful recrystallizations of the product by slow addition of THF to an acetonitrile solution of the impure product resulted in the precipitation of pure colorless $[Co(41)_6](BF_4)_3$ in 70% yield.

The filtrates were combined and the solvent was removed under reduced pressure. Attempts to crystallize $[Co(41)_5]BF_4$ failed. The following ligands were reacted with Co(II) in this manner to yield $[Co(P)_6]^{3+}$ and $[Co(P)_5]^+$ compounds 39, 40, 41, 42, 52, 53, 70 and 77. In all cases the $[Co(P)_5]BF_4$ compounds prepared by reaction B could not be crystallized, but could be isolated as impure yellow oils upon precipitation from CH_2Cl_2 solution by the addition of Et_2O.

$[Co(41)_5]NO_3$

To a solution of $Co(NO_3)_2 \cdot 6H_2O$ (1.0 g, 3.36 mMol) dissolved in 10 ml of CH_3CN and 20 ml of 2,2-dimethoxypropane was injected 41 (5.00 g, 33.3 mMol). The solution immediately became yellow. Slow addition of Et_2O resulted in the precipitation of the golden yellow $[Co(41)_5]NO_3$ in 80% yield (^{31}P NMR (CD_3CN) 165.3).

RESULTS AND DISCUSSION

Preparation of Phosphorus Ligand Complexes of Cobalt(III)

Complexes of the type $[CoP_6]^{3+}$ were prepared by three methods. The first reaction involves the disproportionation of $[Co(H_2O)_6](BF_4)_2$ by phosphite ligands in acetone/2,2-dimethoxypropane as shown in equation 12. Upon addition of ligand, the less soluble $[Co(P)_6](BF_4)_3$ complex precipitates from solution and thus can be separated from the more soluble $[Co(P)_5]BF_4$ complex.

As will be discussed later, this method was found to be unsuitable for a number of ligands because of catalytic methanolysis of the ligands with the methanol formed by the dehydration of $[Co(H_2O)_6](BF_4)_2$ by 2,2-dimethoxypropane. To circumvent this problem, $[Co(H_2O)_6](BF_4)_2$ was replaced as starting material with $[Co(DMSO)_6](BF_4)_2$ and the reaction was run in acetonitrile solvent. The $[CoL_6](BF_4)_3$ complexes precipitate

$$[Co(DMSO)_6](BF_4)_2 + 11\ L \xrightarrow{CH_3CN} [CoL_6](BF_4)_3 + [CoL_5]BF_4 \qquad (15)$$

from solution upon addition of THF.

The diphosphine complex $[Co(\underline{32})_3](BF_4)_3$ was prepared in a two step procedure as described by Ohishi, Kashiwabara and Fujita wherein Co(II) is oxidized by Cl_2 to Co(III) in the first step (103).

$$2\ \underline{32} + CoCl_2{\cdot}6H_2O + 1/2\ Cl_2 + NaClO_4 \longrightarrow [\underline{trans}\text{-}Co(\underline{32})_2Cl_2]ClO_4 + NaCl \qquad (16)$$

$$[\underline{trans}\text{-}Co(\underline{32})Cl_2]ClO_4 + \underline{32} + 2NaClO_4 \longrightarrow [Co(\underline{32})_3](ClO_4)_3 + 2NaCl \qquad (17)$$

The $Co[P(OR)_3]_6^{3+}$ compounds prepared by these methods are all air-stable over a period of hours and are stable to water. These cobalt(III) compounds are reduced by aqueous base, however. Addition of Et_3N to an aqueous solution of $[Co(\underline{9})_6](BF_4)_3$, for example, results in the initially clear solution taking on a yellow color. The ^{31}P NMR spectrum shows peaks due to $[Co(\underline{9})_5]BF_4$, $\underline{9}$, and $OP(OMe)_3$. The peaks due to free $\underline{9}$ and $OP(OMe)_3$ are in a $\underline{1}$ to $\underline{2}$ intensity ratio while the peak due to $[Co(\underline{9})_5]BF_4$ is much larger than expected (perhaps due to a shorter relaxation time). Addition of Et_3N to a similar solution of $[Co(\underline{17})_6](BF_4)_3$ results in only $[Co(\underline{17})_5]BF_4$ and $\underline{17}$ being seen in the ^{31}P NMR spectrum without any $OP(OCH_2)_3CC_2H_5$ detected. It seems reasonable to suggest that the base serves to react with the protons formed by the oxidation of water. It has

$$2\ H_2O \longrightarrow O_2 + 4\ H^+ + 4e^- \qquad (18)$$

previously been reported that the addition of $\underline{2}$ to solutions of $CoCl_2$ in the presence of stoichiometric amounts of H_2O and NEt_3 results in the formation of $[Co(\underline{2})_5]Cl$ along with the concomitant oxidation of H_2O (85). The lack of observation of $OP(OCH_2)_3CC_2H_5$ is probably due to the poor basicity of this ligand which renders it difficult to oxidize.

Steric and Electronic Influences in the Disproportionation of Co(II) by Phosphorus Ligands

Previously, it was known that $\underline{9}$ along with constrained monocyclic and bicyclic phosphites disproportionates Co(II) by equation 12 (95,128). The lack of reports of larger acyclic phosphites or of phosphines taking part in this reaction suggested that steric factors may be important since phosphines are as a rule larger than phosphites. It was decided to react Co(II) with a series of phosphorus ligands of various sizes and basicities in order to determine the steric as well as the electronic limits on phosphorus ligands which disproportionate Co(II).

The importance of steric properties of phosphorus ligands upon their reaction with Co(II) is seen in the comparison of the reactivities of 9 and its higher homolog 2. The disproportionation of Co(II) by 9 was rather facile. When 2 was introduced into a solution of $[Co(H_2O)_6](BF_4)_2$ in acetone/2,2-dimethoxypropane, however, the immediate yellow color was not followed by precipitation of the Co(III) product from the solution. Upon stirring overnight under nitrogen, the solution reverted to its original red color. This result indicates that the larger size of 2 prevents the formation of a $[CoL_6]^{3+}$ complex and thus inhibits the disproportionation reaction. This result is similar to that reported earlier by Albertin, Pelizzi and Bordignon wherein it was found that 9 will disproportionate $Co(SCN)_2$ by equation 13 while reaction of 2 or 33 resulted in the formation of the Co(II) complexes $Co(NCS)_2L_3$ and/or $[Co(NCS)L_4]^+$ (104). This result was rationalized in part in terms of the relative sizes of the ligands.

It was then decided to investigate a series of 2-alkoxy-1,3,2-dioxaphospholanes (Figure 6) in the disproportionation reaction. These ligands are expected to have similar electronic properties but varying

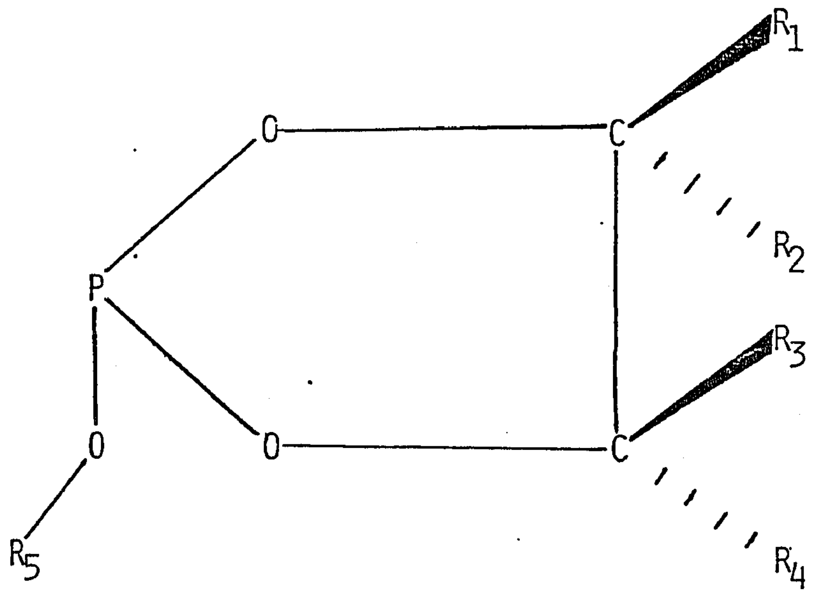


Figure 6. 2-Alkoxy-1,3,2-dioxaphospholanes

steric sizes depending on the nature of the R groups placed on both the ring and the exocyclic position.

When no methyl groups are substituted on the ring (R_1, R_2, R_3, R_4 = H in Figure 6), reaction 15 was found to proceed if R_5 was Me, Et, _n_-Pr, _i_-Pr, _n_-Bu or _i_-Bu. When the exocyclic group was _t_-Bu reaction _15_ was not found to occur. Upon attempts to precipitate a Co(III) product by the addition of THF after the addition of _44_ to a solution of $[Co(DMSO)_6]^{2+}$, a reddish solid fell from solution. Attempts to observe a ^{59}Co NMR signal in the crude reaction mixture failed. Reaction of _43_ led to similar results.

It was also found that _45_ and _46_ did not drive reaction 15. Although the exocyclic group in _46_ is smaller than in _41_ and the size of the exocyclic group in _45_ is comparable to _41_, the selenium-phosphorus coupling constants in the corresponding selenides of _45_ and _46_ (1035 Hz and 1039 Hz, respectively) show them to be poorer bases than the 2-alkoxy-1,3,2-dioxaphospholanes which disproportionate Co(II). The selenium-phosphorus coupling constants for the corresponding selenophosphates of 2-alkoxy-1,3,2-dioxaphospholanes which disproportionate Co(II) are in all cases smaller than 1010 Hz. It will be shown that the bicyclic phosphites _17_, _18_ and _70_, which are poorer bases than _45_ and _46_ do disproportionate Co(II). Thus, it can be concluded that _45_ and _46_ do not disproportionate Co(II) owing to a combination of steric and electronic effects.

When methyl groups are placed in trans positions on the ring in a 2-alkoxy-1,3,2-dioxaphospholane ($R_1 = R_4 = H$, $R_2 = R_3 = Me$ in Figure 6), reaction 15 proceeds if R_5 is Me, Et or _n_-Pr but not _i_-Pr, showing that placing methyl groups on the ring serves to place a smaller limit on the size of the exocyclic group which can be placed on the ring and still drive the reaction. When the five-membered ring is tetrasubstituted with methyl groups as in 54, the reaction will not proceed even when R_5 is Me.

It is rather surprising in this context that 4,6-dimethyl-1,3,2-dioxaphosphorinanes react with Co(II) considering the expected steric demands of the methyl groups on the ring. The compounds $[Co(71)_6](BF_4)_3$ and $[Co(72)_6](BF_4)_3$ have previously been reported in the literature, however (95). A method was needed to study the stereochemistry at phosphorus of these ligands. Reisse and co-workers have demonstrated that ^{13}C NMR spectroscopy can be used as a stereochemical probe of 2-methoxy-1,3,2-dioxaphosphorinanes (132) in that the resonance for the methine carbons in 71 was 3 ppm upfield of that in 72. Likewise, ^3JPC in 72 (13.5 Hz) is significantly greater than in 71 (4.2 Hz) (132).

The ^{13}C NMR results for the 4,6-dimethyl-1,3,2-dioxaphosphorinanes studied here confirm the results of Reisse and show the aforementioned criteria also to be valid for 2-methoxy-4-methyl-1,3,2-dioxaphosphorinanes (Table 15). In the Co(III) complexes of these ligands, the diagnostic carbon is the methoxy carbon. For axially substituted substituents on phosphorus, the position of the methoxy carbon is approximately 4 ppm downfield from that in which the group is in an equatorial position, assuming that the ligands coordinate with retention of configuration. Stereoretentive coordination of 71 and 72 in cis-$Mo(CO)_4L_2$ complexes has been shown previously (133,134).

Table 15. ^{13}C NMR chemical shifts and ^{13}C-^{31}P coupling constants (in parentheses) of 2-methoxy-1,3,2-dioxaphosphorinanes, their $[CoL_6]^{3+}$ complexes and some sulfide derivatives[a]

Compound	C-$\underline{C}H_3$	OCH_3	OCH	C-$\underline{C}H_2$-C	OCH_2
71	22.6(2.5)	49.9(18.3)	65.6(2.5)	42.7(4.9)	---
72	23.9	48.7(11.9)	70.5	41.9(13.5)	---
73	23.2	49.9(17.1)	66.5	36.4(4.9)	60.4
75	23.2	49.3(14.7)	70.2(3.7)	33.9(11.0)	59.3
$S(ax\text{-}CH_3O)\overline{POCH(CH_3)_{eq}CH_2CH_2O}$	22.5(9.8)	54.2(4.9)	77.7(8.5)	33.7(6.1)	68.7(8.6)
$S(eq\text{-}CH_3O)\overline{POCH(CH_3)_{eq}CH_2CH_2O}$	22.2(8.5)	55.6(6.1)	77.3(6.2)	33.9(6.1)	67.8(4.9)
$[Co(\underline{71})_6]^{3+}$	22.5	59.0	80.1,82.1[b]	41.1	---
$[Co(\underline{72})_6]^{3+}$	22.2	54.7	79.6	41.1	---
$[Co(\underline{73})_6]^{3+}$	22.7	59.2	80.6	33.6	71.2
$[Co(\underline{75})_6]^{3+}$	22.8	54.6	80.6	34.2	71.2

[a] In ppm downfield of Me_4Si measured in CD_3CN.

[b] Resonances are of equal intensity.

It was found, however, that addition of $NaBH_4$ to a CH_3CN solution of $[Co(73)_6]^{3+}$ in the presence of S_8 results in the formation of the thiophosphates of 73 and 75 in equal amounts as shown by ^{13}C NMR (Table 15). Reduction of $[Co(75)_6]^{3+}$ in a similar manner resulted in only the formation of the corresponding thiophosphate of 75. It should not be concluded that the Co(III) complex prepared by the reaction of 73 by equation 12 is necessarily coordinated to both 73 and 75 since it is not known if the sulfides were made in a stereospecific process.

No method was developed to monitor the stereochemistry of the Co(I) complexes of 1,3,2-dioxaphosphorinanes. Yarbrough reports that oxidation of $[Co(71)_5]BF_4$ and $[Co(72)_5]BF_4$ with N_2O_4 produced the corresponding phosphates of 72 and 71 in 16/84 and 11/89 ratios, respectively (135), and suggests that the molecular formulas of these complexes which were based on the orientation of the reactant phosphite may not truly reflect the orientation upon coordination. It must be remembered that although N_2O_4 is known to stereoretentively oxidize phosphites to phosphates (126), it has not been proven that N_2O_4 will stereoretentively oxidize coordinated phosphites.

No Co(III) compound could be isolated from the reaction of 25 by reaction 12. This is unexpected since the cone angle of the 25 is expected to be less than 71 and 72 which do form Co(III) complexes. An answer to this apparent paradox can be found by the use of molecular models which show that the hypothetical $[Co(25)_6]^{3+}$ ion would experience severe steric crowding no matter what the conformation of the ligand. If 25 were to coordinate in a boat conformation, unfavorable interactions would be expected between the axial C-methyl group of the ligand and the cobalt atom, whereas if the ligand coordinates in a chair conformation, models show contacts between the equatorial methyl groups and an adjacent ring. Introduction of 25 to a solution of $[Co(H_2O)_6](BF_4)_2$ in acetone/2,2-dimethoxypropane results in a yellow solution. No Co(III) product precipitates, however, and likewise no ^{59}Co NMR could be observed in a spectrum taken of the crude reaction mixture. Although no Co(I) compound could be crystallized from this reaction, a ^{31}P NMR of the material obtained after evaporation of solvent and washing with Et_2O showed a peak at 149 ppm which is assigned to $[Co(\underline{25})_5]BF_4$ by comparison to the shifts previously observed in $[Co(\underline{71})_5]BF_4$ and $[Co(\underline{72})_5]BF_4$ which were also at 149 ppm (135). A number of peaks were observed in the upfield region of the ^{31}P NMR with the largest being at 3 ppm. Only a very small peak was observed at -7 ppm, the resonance reported for $(O)CH_3\overline{POCH_2C(CH_3)_2CH_2O}$ (136). It appears that if a phosphite is not sterically suited to form a hexacoordinate Co(III) complex, the Co(II) will be reduced to Co(I) to form $[CoL_5]^+$ (with water probably being oxidized). Likewise, when 66 is reacted with $[Co(H_2O)_6](BF_4)_2$, the solution turns yellow but no Co(III) compound could be isolated nor could it be observed in a ^{59}Co NMR spectrum of the crude reaction mixture.

The above results show that the steric properties of a phosphite ligand can determine whether a phosphite ligand will disproportionate Co(II). It was also shown that electronic properties are important. It is known that acyclic phosphites are more basic than monocyclic phosphites which are more basic than bicyclic phosphites. It has previously been shown that even the bicyclic phosphites 18 and 70 will disproportionate Co(II) (14,100). The bicyclic phosphite 26, which is an even poorer base than 18 (6), was here found not to disproportionate Co(II), however. Addition of 26 to an acetone/2,2-dimethoxypropane solution of $[Co(H_2O)_6](BF_4)_2$ resulted in the solution becoming lemon yellow which is indicative of Co(I) being formed. No Co(III) compound could be isolated from this reaction nor could a ^{59}Co NMR signal be seen in the crude reaction mixture. A ^{31}P NMR spectrum taken of the crude reaction mixture shows peaks of 157 and 170 ppm in the region where signals due to $[CoL_5]^+$ complexes are usually found as well as a peak at 106 ppm due to free ligand and several peaks from 10-60 ppm, a region in which P=O compounds are usually found. It has been noted that both 26 and $O\overline{P(OCH_2)_2CHO}$ are extremely sensitive to water (51). No ^{59}Co NMR signal could be observed in the crude reaction mixture. Addition of 26 to a solution of $[Co(DMSO)_6](BF_4)_2$ in acetonitrile resulted in the solution taking on a yellowish-brown color. A ^{31}P NMR of this crude reaction mixture showed multiple peaks in all regions of the spectrum. It has previously been suggested that PF_3 fails to form a Co(III) complex because the basicity of the ligand is too poor to neutralize the charge on the Co(III) (102). The results obtained here indicated that the minimum of phosphorus lone pair basicity which is needed to disproportionate Co(II) lies between 18 and 26. The addition of the arsenite esters 60 and 61 as well as the fluorophosphite 55 to solutions of $[Co(H_2O)_6](BF_4)_2$ brought about no changes in color of the solution which is also attributed to the poor basicity of these ligands.

On the other hand, the failure of phosphines to disproportionate Co(II) was attributed to their poor π acceptor behavior (102). In view of the previous results, it was thought that this inability may also be due to the larger steric requirements of phosphines as compared to phosphites. However, addition of 78 (a phosphine which Tolman reports to have a smaller cone angle than 9 (1)) to a solution of $[Co(H_2O)_6](BF_4)_2$ resulted in the solution taking on a blue color. Reaction with 67, a phosphine which recent evidence indicates has phosphite-like electronic properties (137,138) gave the same result. The failure of 67 to disproportionate Co(II) may also be due to its relatively large cone angle, 132° (9).

It was also found that ligands with P-S and P-Cl bonds do not drive reaction 12. Introduction of 59 or 63 to a solution of $[Co(H_2O)_6](BF_4)_2$ results in a green color, while the introduction of PCl_3 or 37 to a solution of $[Co(DMSO)_6](BF_4)_2$ resulted in a blue coloration.

Although the monodentate phosphonites 56 and 57 were found not to disproportionate $[Co(H_2O)_6](BF_4)_2$, it was previously reported that the bidentate phosphonites 30 and 31 do so (101). It was also found herein that the diphosphonite 68 will react in a similar manner. In an attempt to prepare another complex of the type $[CoL_3]^{3+}$, the ligand 58 was synthesized. When 58 was added to a solution of $[Co(H_2O)_6](BF_4)_2$ in acetone 2,2-dimethoxypropane, the solution became yellow, but unfortunately no Co(III) complex could be isolated from this reaction or observed in the ^{59}Co NMR spectrum. Similar results were obtained when the monodentate ligand 47 was reacted with $[Co(H_2O)_6](BF_4)_2$. The comparatively poor ligand properties of 58 compared to 68 are also shown by the fact that reaction of excess 58 with $W(CO)_6$ under photolytic conditions resulted in the formation of $W(CO)_4$(58) while King found that W(68)$_2$(CO)$_2$ could be formed under the same reaction conditions (123).

As another test of the importance of steric and electronic effects of phosphorus ligands on the disproportionation of Co(II), 9 and 17 were simultaneously reacted with $[Co(H_2O)_6](BF_4)_2$. Ten molar equivalents of each ligand were reacted with $[Co(H_2O)_6](BF_4)_2$ after which the Co(III) and Co(I) products were separated. Integration of the peaks in the ^1H NMR of the Co(III) product showed 65% of the ligands complexed to Co(III) to be 9. The Co(I) was analyzed by integrating the peak at 150 ppm in the ^{31}P NMR spectrum corresponding to coordinated 9, against the peak at 138 ppm due to coordinated 17 (135). To the extent that the relaxation times of the coordinated phosphorus in 9 and 17 are nearly the same, this analysis showed 85% of the ligands complexed to Co(I) to be 17. These results indicate that electronic effects dominate steric effects in the distribution of ligands in this reaction. It has been quite well established that the bicyclic ligand 17 is a poorer base than the acyclic 9 because of orbital constraint of the esteratic oxygens (6). In this instance, it appears that because the better π accepting properties of 17 better stabilize the lower oxidation state of Co(I) and the more electropositive 9 better stabilizes the more acidic Co(III), the most effective collisions between Co(II) species leading to electron transfer are those in which the Co(II) intermediate is coordinated to a higher proportion of the more electronegative 17 gain an electron. If steric factors were dominant, the opposite result would have occurred with the smaller Co(III) ion preferring to coordinate to the less sterically demanding 17.

Catalytic Transesterification of Monocyclic Phosphite Esters During the Disproportionation of Co(II)

When an attempt was made to react 41 with Co(II) by equation 12, the ^{59}Co NMR spectrum of the Co(III) product isolated showed 6 peaks which appeared at -720, -804, -879, -990, -1080 and -1157 ppm in an approximate intensity ratio of 1:4:7:5:3:1, respectively. This result indicated that at least two types of ligand were coordinated to Co(III). The gated decoupled ^{13}C NMR of the Co(III) product showed a methine carbon at 80.6 ppm, methylene carbons at 70.3 and 69.7 ppm and methyl carbons at 52.1 and 24.1 ppm suggesting that a portion of the ligands had undergone transesterification with the methanol formed by the dehydration of $[Co(H_2O)_6](BF_4)_2$ with 2,2-dimethoxypropane. This was confirmed by reducing the Co(III) complexes with $NaBH_4$ in the presence of S_8 to form the thiophosphates of 27 and 41. The two thiophosphates were not separated but a ^{13}C and a ^{31}P NMR spectrum of the mixture contained peaks corresponding to authentic samples, and low resolution mass spectra showed both parent ions.

The proportion of transesterified ligand coordinated to Co(I) was greater than to Co(III) in this instance. When 41 was reacted with Co(II) by equation 12, integration of the ^{1}H NMR showed that approximately 40% of the ligands coordinated to Co(III) are 27 while the ^{31}P NMR of the Co(I) from this reaction shows two peaks in a 3:1 area ratio at 168.2 and 165 ppm corresponding to coordinated 27 and 41, respectively.

When 10 molar equivalents of 27 and 10 molar equivalents of 41 were added to [Co(DMSO)$_2$](BF$_4$)$_2$, however, the ^{31}P NMR spectrum showed the Co(I) to be coordinated to the two ligands in equal amounts while integration of the ^{1}H NMR of the Co(III) showed 84% of the coordinated ligand to be 27 and 16% to be 41. It would seem reasonable that steric effects are of importance here since only a small amount of the larger 41 ligand coordinated to the smaller Co(III) ion. Support for this conclusion comes from evidence of significant ligand-ligand repulsion in [Co(41)$_6$](BF$_4$)$_3$ which will be discussed later. This last result possibly suggests that transesterification affects the ligand distribution in the products since in the absence of transesterification the Co(I) was coordinated to a higher proportion of 41. It must be remembered, however, that reactions 12 and 14 are carried out in different media.

A number of additional experiments were performed to prove that transesterification by methanol was occurring. When 41 was reacted by equation 14, the ^{59}Co NMR of the cobalt(III) product obtained showed only one peak at -724 ppm while the gated decoupled ^{13}C NMR showed peaks corresponding to coordinated 41 (Table 16). Unfortunately, [Co(41)$_5$]BF$_4$ could not be obtained pure from this reaction. A ^{13}C NMR spectrum taken of a crude reaction mixture from which the cobalt(III) had been separated showed no methoxy carbons, however, and only one peak (165.7 ppm) was seen in the downfield region of the ^{31}P NMR spectrum.

Table 16. ^{13}C NMR chemical shifts and ^{13}C-^{31}P coupling constants (in parentheses) of 1,3,2-dioxaphospholanes their cobalt complexes and some sulfide derivatives

	$\delta\,^{13}C^{a}(J\,^{13}C\text{-}^{31}P)$		
	CH	CH_2	CH_3
27	---	65.1(9.8)	49.8(7.3)
$SMeO\overline{POCH_2CH_2O}$	---	67.9	56.0(4.9)
$[Co(27)_6](BF_4)_3$	---	69.7	52.1
$[Co(27)_5]BF_4$	---	67.1	52.6
38	---	65.1(8.6)[b] 52.9(9.8)	17.4(4.9)
$[Co(38)_6](BF_4)_3$	---	70.4[b] 69.5	16.0
$[Co(38)_5]BF_4$	---	66.9[b] 65.1	16.0
41	67.0(13.4)	66.4(8.6)	24.2
$S(i\text{-}PrO)\overline{POCH_2CH_2O}$	75.9(4.9)	67.7	21.3(4.8)
$[Co(41)_6](BF_4)_3$	81.1	70.3	24.1
$[Co(41)_5]NO_3$	70.7	66.4	10.5
39	---	65.1 (8.7) 65.1 (8.7) 25.1(3.7)	10.5
$[Co(39)_6](BF_4)_3$	--- --- ---	74.3 70.4 23.9	9.6 --- ---
51	69.8(7.3) 67.3(7.3)	54.3(13.4) ---	14.3(4.9) 7.8(6.1)
$[Co(51)_6](BF_4)_3$	85.2 ---	70.2 ---	16.6 16.0
48a,48b	73.8(9.7) 72.3(8.5)	70.3(7.3) 69.5(8.6)	49.1(11.0) 19.6(4.9) 18.8
$[Co(48)_6](BF_4)_3$	80.7	75.6	58.0 17.4

[a] In ppm downfield from $SiMe_4$. Measured in CD_3CN.

[b] Ring carbons. Assigned on the basis of peak intensity.

When 41 was reacted with $[Co(DMSO)_6](BF_4)_2$ in acetonitrile in the presence of added methanol, both the Co(III) and the Co(I) products obtained contained transesterified ligand. Added ethanol did not transesterify 41, however.

Transesterification also occurred upon the reaction of other 2-alkoxy-1,3,2-dioxaphospholanes with $[Co(H_2O)_6](BF_4)_2$ by reaction 12. Reaction of 44 by equation 12 led to complete transesterification of the ligands in both products as determined by ^{13}C NMR. When 39 was reacted by equation 12, the Co(III) isolated did not contain any transesterified ligand as determined by ^{13}C NMR spectroscopy, but 58% of the ligands complexed to Co(I) were 27 as shown by ^{31}P NMR. No transesterification was seen by ^{13}C NMR spectroscopy in the Co(III) or Co(I) compounds isolated when 38 was reacted with $[Co(H_2O)_6](BF_4)_2$.

Similarly, it was found that $[Co(\underline{51})_6](BF_4)_3$ and $[Co(\underline{51})_5]BF_4$ can be prepared by reaction 12, but when 52 was reacted in this manner the Co(III) was coordinated to both 52 and 50 as shown by ^{13}C NMR. The monocyclic six-membered ring phosphite 76 also undergoes transesterification upon reaction with Co(II). A ^{13}C NMR of the Co(III) product obtained after the reaction of 76 by equation 13 consisted of a methine carbon at 80.4 ppm, methylene carbons at 71.2, 33.9 and 32.9 ppm and methyl carbons at 59.0, 54.9 and 22.5 ppm. The peaks at 33.9 and 32.9 were of about equal intensity as were the peaks at 59.0 and 54.9 ppm. The positions of the latter peaks suggest the presence of two types of methoxy carbons indicative of the simultaneous ligation of both 73 and 75 to cobalt(III) (Table 15) and the absence of ligated 76. Apparently complete transesterification occurred on CoL_6^{3+} but without stereopreference at phosphorus. Because the cobalt(I) complexes from this reaction resisted purification, ^{13}C and ^{31}P NMR spectroscopy were fruitless. Thus, the extent of transesterification could not be determined.

A possible mechanism for the transesterification of 76 when reacted with Co(II) by equation 12 which results in coordination of both 73 and 75 is shown in Figure 7. This mechanism assumes that methanol attacks 76 while it is coordinated to Co(II) and the leaving group in a trigonal-bipyramidal intermediate departs from an axial position as described by the Westheimer rules (139). Methanol may attack the most sterically open site to form intermediate A or may attack in a backside manner with respect to the O-*n*-Pr group (most likely by a MeOH which was previously coordinated to Co(II)) to form intermediate B. Intermediate B can also result from intermediate A following a series of four pseudorotations (Figure 8).

In contrast, the ^{13}C NMR spectrum of the Co(III) product obtained after the reaction of the isomeric phosphite 74 consisted of a methine carbon at 80.6 ppm, methylene carbons at 71.4, 70.9, 33.9 and 24.5 ppm, and methyl carbons at 22.8 and 10.8 ppm, which showed that transesterification did not occur in the Co(III) product. In a similar manner, no transesterified ligand was shown to be coordinated to Co(I) on the basis of the ^{13}C NMR spectrum which showed a methine carbon at 71.0 ppm, methylene carbons at 67.7, 63.8, 34.5 and 24.2 ppm, and methyl carbons at 22.9 and 10.8 ppm.

Figure 7. Possible mechanism of transesterification of <u>76</u> upon reaction with Co(II) by equation 12

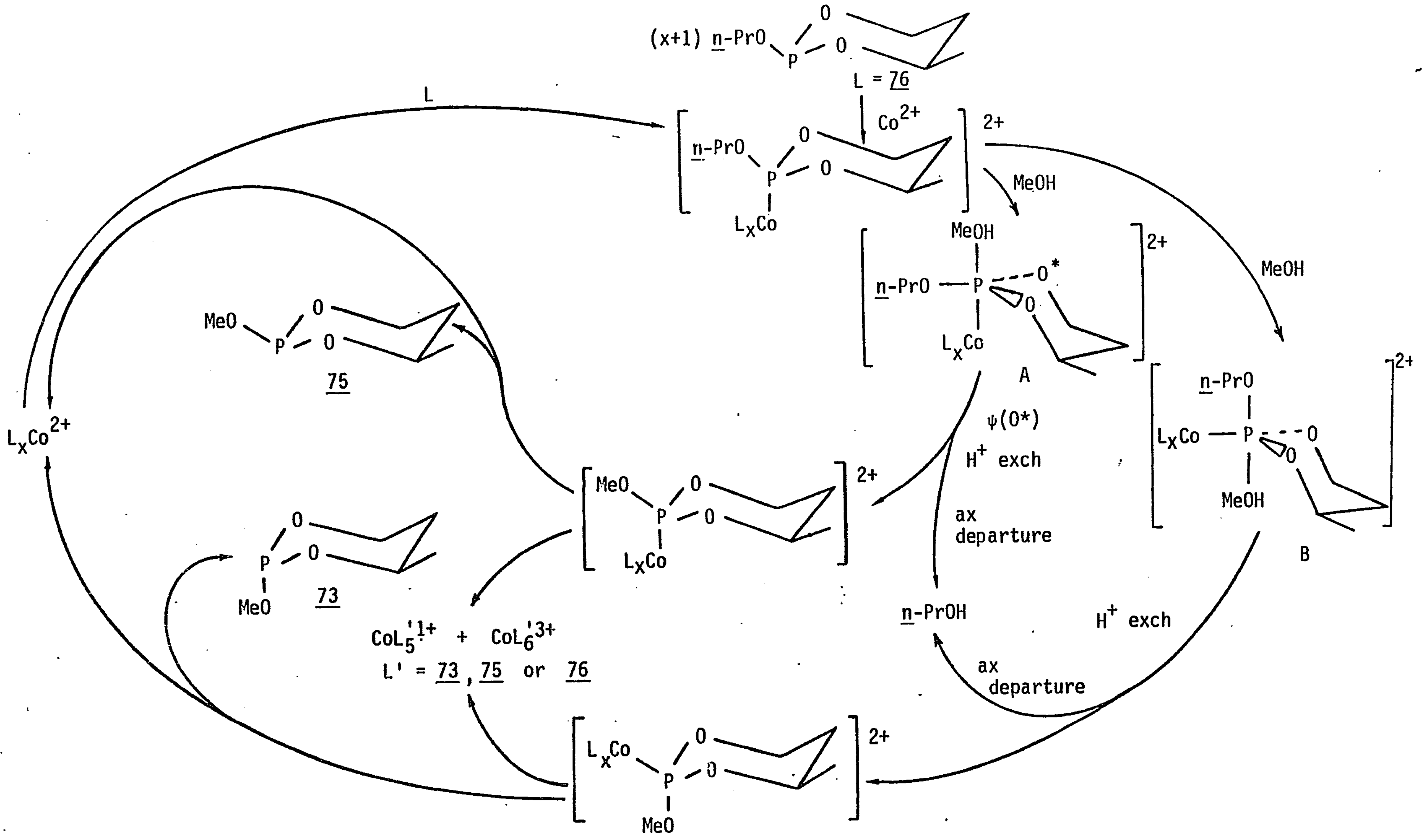
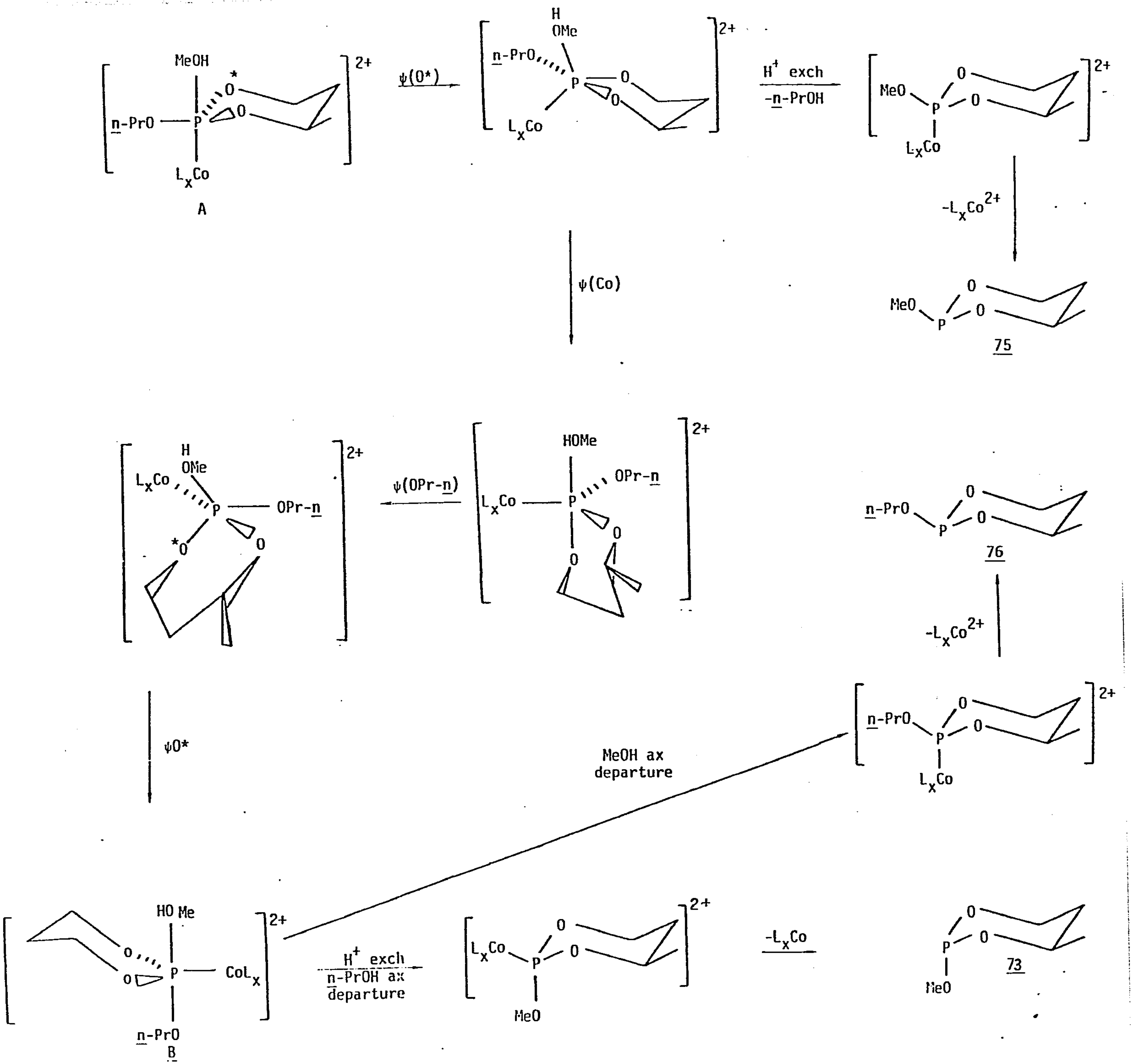

(x+1) n-PrO
L = 76
Co2+
2+
MeOH
L
n-PrO
LxCo
MeOH
n-PrO
O*
LxCo
A
ψ(O*)
H+ exch
ax departure
n-PrOH
MeOH
B
H+ exch
ax departure
LxCo2+
MeO
75
73
CoL'5 1+ + CoL'6 3+
L' = 73, 75 or 76
MeO
LxCo
2+

Figure 8. Series of pseudorotations which isomerize a coordinated 1,3,2-dioxaphosphorinane


MeOH
n-PrO
P
O*
O
LxCo
2+
A
ψ(O*)
H
OMe
n-PrO
P
O
O
LxCo
2+
H+ exch
-n-PrOH
MeO
P
O
O
LxCo
2+
-LxCo2+
MeO
P
O
O
75
ψ(Co)
H
OMe
LxCo
P
OPr-n
*O
O
2+
ψ(OPr-n)
HOMe
LxCo
P
OPr-n
O
O
2+
n-PrO
P
O
O
76
-LxCo2+
ψO*
MeOH ax
departure
n-PrO
P
O
O
LxCo
2+
HO Me
O
O
P
CoLx
n-PrO
2+
B
H+ exch
n-PrOH ax
departure
LxCo
P
O
O
MeO
2+
-LxCo
P
O
O
MeO
73

The reason for the differences which occurred upon the reaction of the two isomeric phosphites 74 and 76 may be of either a steric or an electronic nature. It has been shown that for monocyclic phosphites the positive charge on phosphorus is greater when the lone pair of electrons is in an equatorial as opposed to an axial position (6). On this basis, 74 would be expected to undergo nucleophilic attack by methanol more readily than 76. The reason that 76 transesterifies when reacted with Co(II) by equation 12 and 74 does not may well be due to some rather subtile steric effects which are not readily apparent.

Experimental evidence suggests that the transesterification which takes place is definitely catalyzed and takes place before the electron transfer process. Solutions 0.87 M in 41 and 2.6 M in MeOH monitored by ^{31}P and ^{13}C NMR showed no noticeable transesterification over the period of 15 minutes, while the reaction of $[Co(H_2O)_6](BF_4)_2$ with 41 is complete within 15 seconds. Experiments performed wherein $[Co(\underline{41})_6](BF_4)_3$ or $[Co(\underline{41})_5]BF_4$ were stirred with MeOH resulted in no transesterification. In another experiment, a large excess of $NaBH_4$ was added to a solution of $[Co(\underline{41})_6](BF_4)_3$ in the presence of MeOH. The solution first became green for a period of about 5 seconds then became yellow and was quickly filtered. The $[Co(\underline{41})_5]BF_4$ which was recovered in this reaction in 44% yield showed no evidence of transesterification in the ^{13}C NMR. This result suggests that either electron transfer by disproportionation is necessary for transesterification to occur, or that the lifetime of the Co(II) species in the reduction was too short to permit transesterification. It was previously reported that the reaction of the bicyclic phosphite 18 with $[Co(H_2O)_6](NO_3)_2$ results in the formation of $[Co(\underline{18})_5]NO_3$ without any $[Co(\underline{18})_6](NO_3)_3$ being observed (14). The reason for the anion dependence of the reaction was not determined. Reaction of 41 with $[Co(H_2O)_6](NO_3)_2$ in acetone/2,2-dimethoxypropane solution resulted in an 80% yield of $[Co(\underline{41})_5]NO_3$ based on the Co(II) present. The ^{13}C NMR spectrum of this compound showed only peaks corresponding to coordinated 41 (Table 16). This result shows that either electron transfer by disproportionation is necessary for transesterification to occur as suggested earlier or that the nitrate ion is somehow inhibiting transesterification.

When an excess of 41 was reacted with $[Co(H_2O)_6](BF_4)_2$, analysis of the ^{31}P NMR spectrum of the unreacted ligand revealed the presence of 27 in addition to 41. This result indicates that transesterification happens before electron transfer since the Co(I) and Co(III) products are not labile for the required ligand exchange in this case. The previous experiments suggest the possibility that electron transfer by disproportionation may be necessary for transesterification to occur but this point remains ambiguous. For electron transfer to take place, two ligated Co(II) species need to come in contact. The transesterification may serve to relieve steric crowding in the transition state. Support for this conclusion comes from the result that the extent of transesterification increased with increasing size of the exocyclic group when 1,3,2-dioxaphospholanes were reacted by equation 12.

A number of experiments were performed to see if transesterification could be observed without Co(II) being present. It was at first mistakenly thought that 41 may somehow be rearranging upon reaction with Co(II). It was thus decided to make a complex of Pt(II) by equation 19.

$$\mathrm{Pt(cod)I_2} + \underline{41} \longrightarrow \underline{\mathit{cis}}\text{-}\mathrm{Pt(\underline{41})_2I_2} \qquad (19)$$

In this reaction no redox chemistry takes place and no methanol is present so, as expected, ^{31}P, ^{1}H and ^{13}C NMR all showed that only intact 41 molecules were complexed to platinium. In another experiment, 10 equivalents of 41 were stirred with a 0.03 M solution of $ZnCl_2$ in Et_2O in the presence of 10 equivalents of MeOH for ½ hour. Although a weak interaction between the Zn(II) and added phosphite is to be expected, no evidence was seen for transesterification in the ^{13}C NMR upon recovery of the phosphite.

The reaction of phosphites with $[Ni(H_2O)_6](BF_4)_2$ by reaction 20 when performed in acetone/2,2-dimethoxypropane is similar to reaction 12

$$[\mathrm{Ni(H_2O)_6}](\mathrm{ClO_4})_2 + 5\mathrm{L} \longrightarrow [\mathrm{NiL_5}](\mathrm{ClO_4})_2 \qquad (20)$$

in that a phosphite is reacted with a metal cation which has been dehydrated with 2,2-dimethoxypropane. When 41 was reacted by equation 20, none of the ligands complexed to Ni(II) were transesterified as shown by ^{13}C and ^{31}P NMR.

^{59}Co NMR Studies of Ligand Field and Ligand Conformations in $[Co(P)_6]^{3+}$ Complexes

As expected, larger variances in chemical shift were seen in the ^{59}Co NMR of $[Co(P)_6]^{3+}$ complexes than in the ^{51}V, ^{55}Mn and ^{93}Nb NMR studies reported by Rehder and coworkers (107). For example, the difference in δ^{59}Co between $[Co(\underline{9})_6]^{3+}$ and $[Co(\underline{17})_6]^{3+}$ wherein the ligands in both complexes are phosphites is nearly 950 ppm while the difference in chemical shift between the phosphite complex, $CpV(CO)_3(\underline{9})$, and the phosphine complex, $CpV(CO)_3(\underline{4})$, is only 246 ppm. The trend cited by Rehder of a decrease in metal atom shielding with decreasing ligand pi acceptor ability and increasing ligand bulkiness is also seen in the $[Co(P)_6]^{3+}$ complexes.

Previously, it was reported that the trend among phosphorus ligands to exhibit stronger ligand fields and hence higher field ^{59}Co NMR chemical shifts in $Co[P(OR)_3]_6{}^{3+}$ complexes was $\underline{9} < \underline{71} < \underline{72} < \underline{27} < \underline{18}$ which, except for the reversal of $\underline{71}$ and $\underline{72}$ parallels their decreasing basicity (95). The rise in ligand field with decreasing σ basicity was postulated to be due to either increased π acidity or a decrease in ligand-ligand repulsion. Supporting evidence for the dominance of π acidity effects is the monotonic rise in energy of the lowest d-d transition with decreasing charge in two series of phosphite complexes $NiL_5{}^{2+}$, $CoL_5{}^{+}$ and FeL_5 (140). In the absence of a π acidity effect, 10 D_q is expected to rise with metallic charge.

A more complete analysis of this question herein shows that steric properties of phosphite ligands are indeed of importance in determining the effective ligand field in $[Co(P(OR)_3)_6]^{3+}$ complexes. Evidence for the importance of steric effects comes from investigation of complexes of 2-alkoxy-1,3,2-dioxaphospholanes (Figure 6). These ligands were found to have nearly identical electronic properties as shown by the selenium-phosphorus coupling constants of the corresponding selenophosphates (Table 17), but vary in steric size. When the ring is unsubstituted (R_1, R_2, R_3, R_4 = H in Figure 6), a small but steady downfield shift is obtained upon increasing the size of R_5 from Me to Et to *n*-Pr and *n*-Bu (Table 17). When the exocyclic group is enlarged to *i*-Pr, a large downfield shift is observed. It would seem that placing an *iso*-propoxy group in the exocyclic position results in a significant increase in ligand-ligand repulsion. Support for this postulate comes from the fact that $[Co(\underline{43})_6](BF_4)_3$ and $[Co(\underline{44})_6](BF_4)_3$ (wherein the exocyclic group is even larger) were not formed in detectable amounts in reactions 12 or 15. It was thought that if R_5 was *i*-Bu, the ligand-ligand repulsion should be less than when R_5 was *i*-Pr since the bulky $CH(CH_3)_2$ moiety is further away from phosphorus in the former case. Indeed, the ^{59}Co NMR chemical shift of $[Co(\underline{42})_6](BF_4)_3$ lies between that of $[Co(\underline{27})_6](BF_4)_3$ and $[Co(\underline{41})_6](BF_4)_3$ (Table 17).

As seen in Table 17, two peaks were observed in the ^{59}Co NMR spectrum of $[Co(\underline{39})_6](BF_4)_3$ and $[Co(\underline{40})_6](BF_4)_3$. The two peaks were found to be temperature dependent with the upfield peak being favored at low temperature. The difference in frequency between the two peaks when measured under these conditions (*ca.* 1 x 10^4 Hz) indicates that an exchange rate of 7 x 10^4 Hz would be needed to merge the two peaks (141). The differences in energy between the configurations which correspond to the two peaks were found to be rather small. The thermodynamic parameters for the conversion from the low energy peak to the high energy peak, ΔH = 5 Kcal/mole and ΔS = 15 cal/mole K for $[Co(\underline{39})_6](BF_4)_3$ and ΔS = 6

Table 17. Spectroscopic data for $[Co(P)_6]^{3+}$ complexes and ^1JSeP of selenated ligands

L	$\delta^{59}Co^a$	λ^b	JSeP, Hz
$P(OMe)_3$ 9	-352	340	954^c
eq-$CH_3O\overline{POCH(CH_3)_{eq}CH(CH_3)_{eq}CH_2O}$ 72	-443	337	949^c
ax-$CH_3O\overline{POCH(CH_3)_{eq}CH(CH_3)_{eq}CH_2O}$ 71	-433	339	996^c
eq-$CH_3O\overline{POCH(CH_3)_{eq}CH_2CH_2O}$ 75	-612	333	941^d
ax-$CH_3O\overline{POCH(CH_3)_{eq}CH_2CH_2O}$ 73	-512	337	978^d
ax-n-PrO$\overline{POCH(CH_3)_{eq}CH_2CH_2O}$ 74	+332	350	980
MeO$\overline{POCH_2CH_2O}$ 27	-1202	317	1008
EtO$\overline{POCH_2CH_2O}$ 38	-1182	317	1000
n-Pr$\overline{POCH_2CH_2O}$ 39	-1008,-1160	324	1003
n-Bu$\overline{POCH_2CH_2O}$ 40	-993,-1172	324	1003
i-Pr$\overline{POCH_2CH_2O}$ 41	-724	335	1003
i-Bu$\overline{POCH_2CH_2O}$ 42	-908	327	1001
dl-MeO$\overline{POCH_2CH_3CH_2CH_3O}$ 50	-1085	323	998
dl-EtO$\overline{POCH_2CH_3CH_2CH_3O}$ 51	-1013	327	996
dl-n-PrO$\overline{POCH_2CH_3CH_2CH_3O}$ 52	-694	337	997

---

[a] In ppm from aqueous $K_3[Co(CN)_6]$. Measured in CD_3CN at 25° unless otherwise indicated.

[b] Wavelength in nm of $T_{1g} \longleftarrow A_{1g}$ transition measured in CD_3CN unless otherwise indicated.

[c] Reference 7.

[d] W. J. Stec, Z. Naturforsch. 29B, 109 (1974).

Table 17. (Continued)

L	$\delta^{59}Co^{a}$	λ^{b}	JSeP, Hz
$CH_3OPOCH_2CH(CH_3)O$ 48	-1187	318	1004,1005[e]
$CH_2OPOCH_2CH_2CHO$ 70	-1598	n.o.[f]	1047
$P(OCH_2)_3CC_2H_5$ 17	-1296	n.o.[f]	---
$P(OCH_2)_3CCH_3$ 18	-1308	n.o.[f,g]	1053[c]
$P(OCH)_3(CH_2)_3$ 69	-1201	310	1020
o-$(P(OMe)_2)_2C_6H_4$ 30	-2107	n.o.[f]	---
o-$(P(OEt)_2)_2C_6H_4$ 31	-2060	n.o.[f]	---
$(MeO)_2PCH_2CH_2P(OMe)_2$ 68	-2050	n.o.[f]	---
$(CH_3)_2PCH_2CH_2P(CH_3)_2$ 32	+1250[h]	385[h]	---.

[e] The two coupling constants correspond to the selenides of 48a and 48b.

[f] Obscured by charge transfer band.

[g] Previously the $T_{1g} \leftarrow A_{1g}$ transition in an aqueous solution of $[Co(\underline{18})_6](ClO_4)_3$ was estimated by gaussian analysis to be at 325 nm (14).

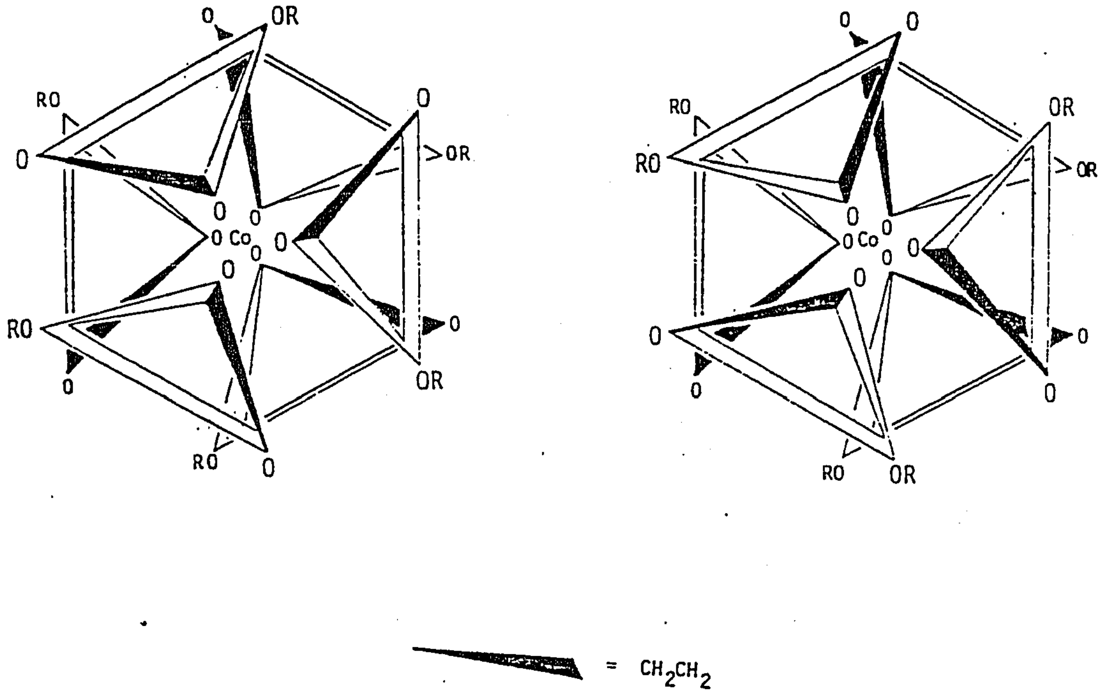
[h] Measured in DMSO.

Kcal/mole and ΔS = 18 cal/mole K for $[Co(\underline{40})_6](BF_4)_3$ were calculated by measuring peak areas at various temperatures (Table 18). These estimates are rather crude and the precision is probably no better than ±20%. ^{13}C NMR spectra of these complexes showed only one set of peaks. The reason for seeing two ^{59}Co NMR peaks for these complexes is still obscure

Table 18. Configurational equilibrium data for $[Co(\underline{39})_6]^{3+}$ and $[Co(\underline{40})_6]^{3+}$

$[Co(\underline{39})_6]^{3+}$		$Co[(\underline{40})_6]^{3+}$	
$\frac{1}{T}$ (K^{-1})	$\ln(\frac{\text{area downfield peak}}{\text{area upfield peak}})$	$\frac{1}{T}$ (K^{-1})	$\ln(\frac{\text{area downfield peak}}{\text{area upfield peak}})$
3.92×10^{-3}	-1.41	3.77×10^{-3}	-1.75
3.70×10^{-3}	-0.97	3.63×10^{-3}	-1.32
3.50×10^{-3}	-0.59	3.51×10^{-3}	-1.19
3.38×10^{-3}	-0.15	3.36×10^{-3}	-0.49
	$r = 0.991$		$r = 0.975$
	$\Delta H = 5$ Kcal/mole		$\Delta H = 6$ Kcal/mole
	$\Delta S = 15$ cal/mole K		$\Delta S = 18$ cal/mole K

although a possible explanation comes from the examination of molecular models. CPK models indicated that the only way to arrange six of these five-membered ring monocyclic phosphites is as shown in Figure 9. In this arrangement, the Co(III) is capped above and below by two layers of three ring oxygens in each layer. The ion is also belted by two layers, each layer consisting of alternating ring and exocyclic oxygens. As seen in Figure 9, the two equatorial layers can be arranged so that the exocyclic groups nearly eclipse (B) each other or are staggered (A). It is probable that $[Co(\underline{41})_6](BF_4)_3$ (for which only one ^{59}Co peak is observed) adopts



A

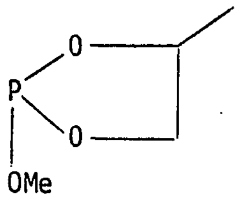
B

Figure 9. Possible rotameric configurations of a $[CoL_6]^{3+}$ ion where L is a monocyclic phosphite ester. P atoms coordinated to Co are not shown

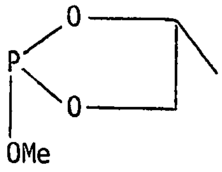
arrangement A wherein the bulky exocyclic groups are as far away from each other as possible. In [Co(39)$_6$](BF$_4$)$_3$ and [Co(40)$_6$](BF$_4$)$_3$ wherein the ligands are less sterically demanding, A and B can possibly exist in equilibrium. Nonbonded interactions between the four-atom and five-atom exocyclic chains on phosphorus and nearby ligand moieties in [Co(39)$_6$](BF$_4$)$_3$ and [Co(40)$_6$](BF$_4$)$_3$, respectively, may serve to slow down interconversion, which requires the rotation (perhaps simultaneous) of three Co-P bonds. Consistent with this model is the fact that the downfield peaks in the ^{59}Co NMR for [Co(39)$_6$](BF$_4$)$_3$ and [Co(40)$_6$](BF$_4$)$_3$ which probably correspond to the species wherein there is a greater amount ligand-ligand repulsions are favored at higher temperatures. In contrast, ^{59}Co NMR spectra of [Co(41)$_6$](BF$_4$)$_3$ and [Co(38)$_6$](BF$_4$)$_3$ (wherein rotamers A and B may be in rapid equilibrium due to the smaller size of the exocyclic group) obtained over the temperature range of -33°C to 70°C showed no noticeable differences in appearance.

When methyl groups are placed on anti positions on the ring in a 2-alkoxy-1,3,2-dioxaphospholane ($R_1 = R_4 = H$, $R_2 = R_3 = Me$ in Figure 6), it is seen that when R_5 is Me or Et the ^{59}Co NMR shift of the [CoL$_6$]$^{3+}$ complex is more than 100 ppm downfield of the corresponding commplexes in which the ring is unsubstituted. This is probably due to the slightly greater steric demands of the substituted ligand. When R_5 is changed to n-Pr in the ring-disubstituted ligands, a large downfield ^{59}Co shift is seen which shows that placing two methyl groups on the five-membered ring decreases the size of the exocyclic substituent which will induce a large downfield shift.

The 2-alkoxy-1,3,2-dioxaphospholane 48 can exist in two possible configurations 48a and 48b wherein the methoxy group can be either *cis* or *trans* to the ring methyl group. The cobalt(III) product obtained from



48a



48b

the reaction of a 2:1 mixture of the two isomers 48a:48b with $[Co(H_2O)_6](BF_4)_3$ showed one peak in the ^{59}Co NMR spectrum. Likewise, only one set of peaks was seen in the ^{13}C NMR spectrum of the Co(III) product (Table 17). It should be noted in this regard that only one type of methine and ring methyl carbon are also seen in the ^{13}C NMR of $[Co(\underline{51})_6]^{3+}$ where two might be expected, as is seen in the free ligand (Table 17).

The evidence tends to suggest that the Co(III) product obtained from this reaction is actually a mixture of Co(III) coordinated to various ratios of 48a and 48b. Reduction of the Co(III) complex with $NaBH_4$ in the presence of S_8 produced the two thiophosphates of 48a and 48b which were identified on the basis of their ^{31}P NMR shifts at 87.5 and 90.1 ppm, respectively, which matched the shifts of authentic samples. It must be remembered, however, that sulfuration of coordinated phosphites has not been shown to be stereospecific and in fact it probably is not in the case discussed on p. 89. In another experiment, a 2:1 mixture of 48a and 48b was added to a solution of $[Co(H_2O)_6](BF_4)_2$ in a 11:2 molar ratio. This resulted in the appearance of two peaks in the ^{31}P NMR at 166.5 and 169.0 ppm with the upfield peak being of slightly greater intensity due to the coordination of the two possible isomers to Co(I). It thus seems that both 48a and 48b do in fact coordinate to Co(III) upon the reaction of a mixture, but ^{59}Co NMR spectroscopy is not sensitive enough to distinguish compounds of the type $[Co(\underline{48a})_n(\underline{48b})_{6-n}]^{3+}$. It would not be unexpected that the steric and electronic properties of 48a and 48b are similar such that the effective ligand field of a mixed set of isomers is the same as a set of either isomer. Support for the assumption that the electronic properties of 48a and 48b are similar comes from the closeness of the selenium-phosphorus coupling constants in the corresponding selenophosphates of the two ligands (Table 17). It is not obvious why any sort of preference of Co(III) for either isomer should exist.

Evidence for the influence of electronic properties of phosphite ligands in determining the ligand field of $[Co(P(OR)_3)_6]^{3+}$ complexes can also be observed. The ^{59}Co chemical shifts of $[Co(P(OR)_3)_6]^{3+}$ complexes of ligands which are less basic tend to be upfield. It must be remembered that in addition to becoming less basic upon constraint, phosphites become less sterically demanding. It is seen that the ^{59}Co chemical shifts of $[Co(\underline{41})_6]^{3+}$ and $[Co(\underline{52})_6]^{3+}$ lie upfield of $[Co(\underline{9})_6]^{3+}$ although the ligands in the former two complexes presumably have larger cone angles. The upfield position of the ^{59}Co peaks in the case of the cyclic ligands must therefore be due to their lower σ basicity and presumably greater π acidity.

Remeasurement of δ^{59}Co of [Co(<u>72</u>)$_6$](BF$_4$)$_3$ and [Co(<u>71</u>)$_6$](BF$_4$)$_3$ again resulted in the chemical shift of the complex of the more basic ligand appearing upfield. Likewise, the relative ^{59}Co NMR chemical shifts of the Co(III) complexes of the isomeric phosphites <u>73</u> and <u>75</u> were the opposite as would be expected from basicity arguments. Caution must be taken in rationalizing the trends in ^{59}Co chemical shifts of these ligands. These six-membered ring phosphites can complex in various conformations of the six-membered ring, which will have differing steric demands and electronic characteristics.

Interestingly in this regard, it was found that reacting the unsubstituted monocyclic phosphite (<u>77</u>) with [Co(H$_2$O)$_6$](BF$_4$)$_2$ produced a cobalt(III) product which showed peaks in the ^{59}Co NMR at -520, -643, -765 and -886 ppm in an approximate intensity ratio of 2:4:3:1. The intensity ratios suggest that two types of ligand are complexed to cobalt. The ^{59}Co peaks were found not be temperature dependent. This result was found to be difficult to repeat. Three subsequent attempts to prepare [Co(<u>77</u>)$_6$](BF$_4$)$_3$ produced only a nontemperature dependent peak in the ^{59}Co NMR at -650 ppm of the Co(III) product obtained. One further attempt resulted in the reproduction of the initial spectrum. The ^{13}C NMR spectra of [Co(<u>77</u>)$_6$](BF$_4$)$_3$ samples which showed multiple peaks in the ^{59}Co NMR spectrum consisted of OCH$_2$ peaks at 72.1 and 69.6 ppm in an intensity ratio of 3 to 1, respectively, along with OCH$_3$ carbon at 56.8 ppm and C-<u>C</u>H$_2$-C carbon at 26.7 ppm. In a [Co(<u>77</u>)$_6$](BF$_4$)$_3$ sample which showed only one peak in the ^{59}Co NMR, the ^{13}C NMR showed three OCH_2 peaks of equal intensity at 66.3, 68.3 and 70.7 ppm along with OCH_3 carbon at 58.4 and a C-$\underline{C}H_2$-C carbon at 26.2 ppm It is possible that in the samples of $[Co(\underline{77})_6](BF_4)_3$ in which 3 OCH_2 peaks are seen in the ^{13}C NMR that more than one type of configurational isomer exists but ^{59}Co NMR spectroscopy cannot distinguish between them.

The cause of the appearance of multiple ^{59}Co NMR peaks in some preparations of $[Co(\underline{77})_6](BF_4)_3$ and the absence in others has not been determined. In order to gain a better understanding of the complexation of 2-methoxy-1,3,2-dioxaphospholanes to Co(III), CPK models of these complexes were made. In $[Co(\underline{72})_6]^{+3}$, CPK models show that placing the ligands in a boat conformation which preserves equatoriality of the ring methyls would lead to a less crowded structure in which the cobalt is pseudo-equatorially bound as opposed to having the ligands complex in a chair conformation wherein cobalt is axial. Conversely, it was found that for $[Co(\underline{71})_6]^{3+}$ a boat conformation for the ligand would force the Co into a sterically unfavorable pseudo-axial position. Both of these ions must adopt rotamer A (Figure 7) to avoid severe interligand steric interactions among the ring methyl groups around the equatorial plane in the belt of the complex (Figure 9). In $[Co(\underline{73})_6]^{3+}$, it was found that the ligands can complex in either a chair or twist boat conformation with the chair conformation perhaps being more favored. Models indicated that $\underline{75}$ could complex to Co(III) in either a chair, a boat or a twist boat conformation. Coordination of the ligands in the latter two conformations would force the cobalt into a pseudo-equatorial position. For $[Co(\underline{73})_6]^{3+}$

and $[Co(\underline{75})_6]^{3+}$, rotamer A (Figure 9) appears to be sterically more favorable and three isomers can be envisioned for this rotamer. In one, three ring methyls from the top set of ligands are directed over the top of the complex with three methyl groups from the bottom set pointing down and under the complex. In the second isomer, one set of ligands in the first isomer is rotated so that the ring methyl groups face the equatorial plane and in the third isomer both sets of methyl groups face this plane.

The above preferences do not apply to $[Co(\underline{77})_6]^{3+}$ in which the ligand is unsubstituted. Models show that the ligand can complex in a conformation in which the methoxy group is either axial or equatorial in a chair boat or twist boat conformation and could complex in either rotameric conformation (Figure 7). This wide range of possibilities with their varying steric and electronic characteristics could account for the multiple peaks in $[Co(\underline{77})_6]^{3+}$. The fact that only one methoxy carbon is seen in the ^{13}C NMR suggests that the ligands are bound such that the cobalt is either axial or equatorial with respect to the six-membered ring.

The two diphosphonite ligands $\underline{30}$ and $\underline{31}$ have been shown to have a very high ligand field on the basis of the fact that no d-d transition was seen in the visible range of the corresponding $[CoL_3]^{3+}$ complex (101). Since the d-d band is buried in the charge transfer region of the uv, the ligand field of these diphosphonites could not be quantified. ^{59}Co NMR spectroscopy shows that these ligands do indeed have an extremely strong ligand field. In fact, the ^{59}Co NMR chemical shift of $[Co(\underline{30})_3]^{3+}$ is the furthest upfield ever reported for a Co(III) complex. The diphosphonite

68 was also found to have a very high ligand field on the basis of the ^{59}Co NMR shift of $[Co(68)_3]^{3+}$. The π acceptor abilities of the diphosphonites 30 and 68 are somewhat less than the monodentate phosphite 17 and quite comparable in the respect to monodentate 9 as shown by CO stretches in $M(CO)_4(P)_2$ complexes (Table 19). It would seem that chelation provides for considerably better orbital overlap and hence a higher ligand field for the small (and therefore sterically sensitive) Co(III) ion. Such increased overlap could arise from the greatly reduced ligand-ligand repulsion in the octahedron which is engendered by the strainless connection of pairs of phosphorus atoms by aromatic rings or ethylene groups.

The tris-bisphosphine complex $[Co(32)_3]^{3+}$ has a weaker ligand field than the complexes of the monodentate phosphites, however, as evidenced by the position of the $T_{1g} \longleftarrow A_{1g}$ transition and the position of the ^{59}Co NMR chemical shift. These results can be explained both in terms of steric and electronic effects. Electronically, the electron withdrawing OR groups on the diphosphonite ligands should make them better π acceptors than the diphosphine 32. The better π acceptor ability of the diphosphonites 30, 31 and 68 as compared to the diphosphine 32 is shown by the relative positions of the CO stretches of $M(CO)_4(P)_2$ complexes (Table 19). Sterically, molecular models show $[Co(30)_6]^{3+}$, $[Co(31)_6]^{3+}$ and $[Co(68)_3]^{3+}$ to be rather uncrowded structures while the lability of $[Co(32)_3]^{3+}$ has been attributed to crowding twelve methyl groups around a small Co(III) ion (103).

Table 19. CO stretching frequencies in $M(CO)_4(P)_2$ complexes

Compound	Solvent	CO Stretching Frequency, cm^{-1}
$Cr(CO)_4(\underline{32})^a$	Hexane	2009m, 1921m, 1900s, 1894vs
$Mo(CO)_4(\underline{32})^a$	Hexane	2020m, 1929m, 1909s, 1903vs
$W(CO)_4(\underline{32})^a$	Hexane	2017m, 1922m, 1902s, 1897vs
$Cr(CO)_4(\underline{68})^b$	Not specified	2025m, 1935s, 1912vs
$Mo(CO)_4(\underline{68})^b$	Not specified	2033m, 1941s, 1916vs
$Cr(CO)_4(\underline{31})^c$	Cyclohexane	2028m, 1945m, 1918s
$Mo(CO)_4(\underline{31})^c$	Cyclohexane	2018m, 1948m, 1926s
$W(CO)_4(\underline{31})^c$	Cyclohexane	2028m, 1944m, 1921s
$\underline{cis}$-$Cr(CO)_4(\underline{9})_2{}^d$	Hexadecane	2026, 1947, 1939, 1914
$\underline{cis}$-$W(CO)_4(\underline{9})_2{}^d$	Hexadecane	2035, 1947, 1939, 1914
$Cr(CO)_4(\underline{17})_2{}^e$	Halocarbon oil	2035vw, 1957sh, 1918vs
$Mo(CO)_4(\underline{17})_2{}^e$	Halocarbon oil	2038vw, 1960sh, 1927vs
$W(CO)_4(\underline{17})_2{}^e$	Halocarbon oil	2040vw, 1955sh, 1913vs

---

[a] J. A. Connor, J. P. Day, E. M. Jones and G. K. McEwen, J. Chem. Soc. Dalton, 347 (1973).

[b] Reference 123.

[c] Reference 128.

[d] R. Mathieu, M. Lenzi and R. Poilblanc, Inorg. Chem. 9, 2030 (1970).

[e] J. G. Verkade, R. E. McCarley, D. G. Hendricker and R. W. King, Inorg. Chem. 4, 228 (1965).

A ^{59}Co NMR spectrum of the Co(III) product obtained from the simultaneous addition of 10 molar equivalents of 9 and 17 to an acetone/2,2-dimethoxypropane solution of $[Co(H_2O)_6](BF_4)_2$ shows peaks at -1026, -872, -854, -719, -696 and -530 ppm (Figure 10, Table 20). By running reactions at extreme ratios of 9 and 17, seven approximately equally-spaced resonances with two being split into two peaks were observed. The peaks were assigned as $[Co(\underline{9})_x(\underline{17})_{6-x}]^{3+}$ in order of

Table 20. ^{59}Co NMR chemical shifts of $[Co(\underline{17})_x(\underline{9})_{6-x}](BF_3)_3$

Compound	δ^{59}Co (ppm)
$[Co(\underline{17})_6](BF_4)_3$	-1308
$[Co(\underline{17})_5(\underline{9})](BF_4)_3$	-1175
cis/trans-$[Co(\underline{17})_4(\underline{9})_2](BF_4)_3$	-1026
mer-$[Co(\underline{17})_3(\underline{9})_3](BF_4)_3$	-872
fac-$[Co(\underline{17})_3(\underline{9})_3](BF_4)_3$	-857
trans-$[Co(\underline{17})_2(\underline{9})_4](BF_4)_3$	-719
cis-$[Co(\underline{17})_2(\underline{9})_4](BF_4)_3$	-696
$[Co(\underline{17})(\underline{9})_5](BF_4)_3$	-530
$[Co(\underline{9})_6](BF_4)_3$	-345

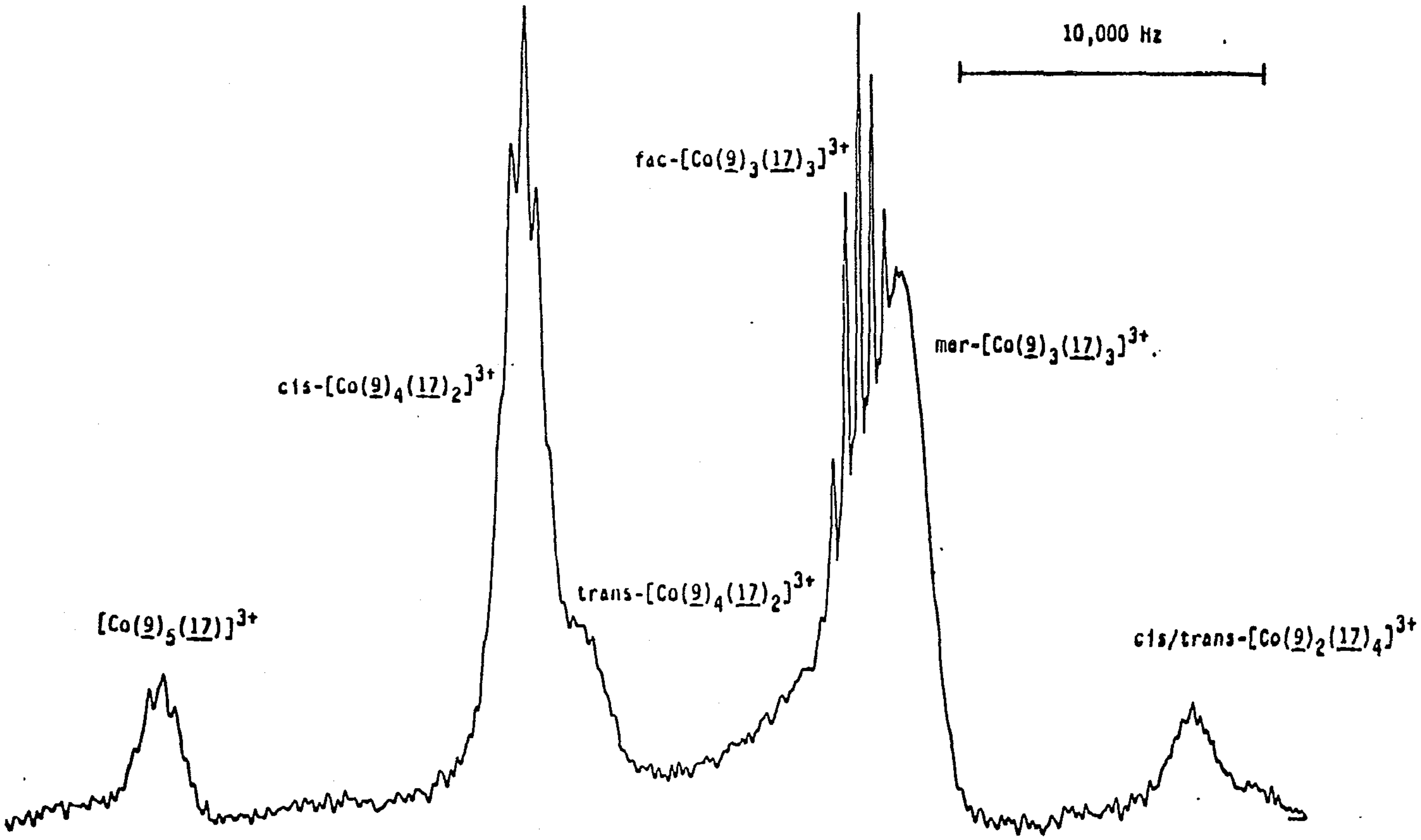


Figure 10. ^{59}Co NMR spectrum of the Co(III) product obtained upon simultaneously reacting 10 equivalents of $\underline{9}$ and of $\underline{17}$ to one equivalent of $[\mathrm{Co(H_2O)_6}](\mathrm{BF_4})_2$

increasing x. This is not unreasonable in view of the fact that samples which were shown to have a higher proportion of 9 by ^1H NMR showed a higher proportion of the downfield ^{59}Co NMR peaks. In a similar type of system, it was found that $\delta^{93}Nb$ for a mixed set of hexahaloniobates can be predicted to a good approximation by equation 21 below (142).

$$\delta_{calcd} = \frac{n}{6}\, \delta_{NbCl_6^-} + \frac{6-n}{6}\, \delta_{NbBr_6^-} \qquad (21)$$

In previous work, it was suggested that the ^{59}Co NMR shifts in compounds of the type $[CoA_xB_{6-x}]$ are additive (143,144). Substantial deviations from the "Rule of Additivity of Ligand Effects" on ^{59}Co NMR shifts were later found (145). These deviations were especially significant if interaction between coordinated ligands could occur as in the case of NO_3^- complexes. Assignments of cis-trans and fac-mer isomers were made on the basis of the point charge model of Yamasaki et al to determine the relative electric field gradients (EFG) at the centers of $[CoA_xB_{6-x}]$ complexes (146). This model predicts that $[CoA_6]$ and fac-$[CoA_3B_3]$ complexes will have an EFG of 0, $[CoA_5B]$ and cis-$[CoA_4B_2]$ complexes will have an EFG of 2 units, mer-$[CoA_3B_3]$ will have an EFG of 3 units while a trans-$[CoA_2B_4]$ commplex will have an EFG of 4 units. This type of model has been previously used to account for the ^{93}Nb NMR linewidths in mixed $[NbCl_xBr_{6-x}]^-$ species (147). It has also been found that for the series $Mo(CO)_{6-n}(9)_n$, the sharpest lines are seen in the ^{95}Mo NMR spectrum where n = 0 and 6 or for the fac isomer where n = 3 (148). In the $Co[(9)_x(17)_{6-x}]^{3+}$ system, well-resolved couplings were only seen where x = 0 and 6 and for one of the isomers where n = 3, which is assigned as the fac isomer. The cis and trans isomers were assigned on the basis of the general rule that the ^{59}Co NMR signals of trans isomers are upfield of the corresponding cis isomers (144) in addition to the electric field gradient arguments above (146).

The Co(I) complexes which were formed in reactions 12 and 14 are transparent in the ^{59}Co NMR region due to the large electric field gradients at the ^{59}Co nucleus of these complexes. The $[CoL_3]^+$ complexes where L is a bidentate phosphonite are of interest since in these complexes only two of the three ligands can be bidentate. The ^{31}P NMR spectrum of $[Co(\underline{68})_3]BF_4$ consisted of a resonance at 215 ppm due to bound ligand as well as a peak at 189 ppm due to uncoordinated phosphorus. The peak assignments were made on the basis of intensities. This shows that any exchange between coordinated and uncoordinated ligand is slow on the ^{31}P NMR time scale. The ^{1}H NMR of this complex was very complex and could not be readily interpreted even when observed at 300 MHz. On the basis of ^{1}H NMR spectroscopy $[Co(\underline{30})_3]BF_4$ was also found to be nonexchanging. The OCH_3 resonance of this complex consisted of a broad multiplet along with a sharp doublet (^{3}JPH = 11.8 Hz) in an intensity ratio of 5 to 1 (101).

Relaxation Effects in Octahedral Cobalt(III) Complexes

For nuclei of $I > 1$, relaxation can occur via interaction between the electric quadrupole moment and asymmetries in the electric charge distribution. This interaction, called quadrupolar interaction, is the dominant relaxation mechanism for nuclei of $I > 1$ (109,149).

For the case of rapid molecular tumbling and axial symmetry of the molecular electric field, theory gives

$$R_{1q} = R_{2q} = \frac{3}{40} \frac{2I + 3}{I^2(2I - 1)} \left(\frac{e^2Qq}{\hbar}\right)^2 \tau_c \qquad (22)$$

where R_{1q} and R_{2q} are the rates of spin-lattice and spin-spin relaxation due to quadrupole interactions, respectively, and τ_c is the molecular correlation time. The $(\frac{e^2Qq}{\hbar})$ term, which is referred to as the quadrupole coupling constant, consists of the nuclear quadrupole moment Q, the electric field gradient q, and the fundamental constants e and h. For species which are highly symmetrical, such as $[NMe_4]^+$, the electric field gradient is small, the rate of quadrupolar relaxation is slowed and hence T_1 and T_2 become longer, since in systems where quadrupolar relaxation is the dominant mechanism of relaxation, $T_1^{-1} = T_2^{-1} = R_{1q} = R_{2q}$.

Experimental evidence indicates that it is improper to treat the B atoms in tetrahedral AB_4 molecules and octahedral AB_6 molecules as point charges. For example, an effective electric field gradient of eq = -0.15 x 10^{15} esu was estimated for TcO_4^- in aqueous solution (150). The broadening of the inner lines of the ten line ^{17}O NMR multiplet of this ion is due to scalar interaction with an atom undergoing quadrupolar relaxation (151). Furthermore, the T_1 values of ^{59}Co measured for a series of octahedral complexes at 8.08 MHz in aqueous solution are 0.103 sec in $K_3Co(CN)_6$, 5.0 x 10^{-2} sec in $[Co(NH_3)_6]Br_3$ and 9.0 x 10^{-3} sec in $[Co(en)_3]Cl_3$. These values indicate that there is a finite electric field gradient at cobalt in these complexes (152). The electric field gradient seen in a presumably octahedral complex is thought to be caused by asymmetric vibrations (152,153). In ionic octahedral Co(III) complexes, it has also been shown that T_1 of ^{59}Co can also be decreased by increasing ionic association (154,155).

The effect of the symmetry of the ligands on the shape of the ^{31}P NMR spectra of tetrahedral $[CuL_4]^+$ complexes where L is a phosphite has also been noted. Natural abundance copper consists of two isotopes (Table 21) which, like ^{59}Co, are both quadrupolar. Wroblewski prepared complexes where L is the levoratory enantiomer of <u>70</u> or of racemic <u>73</u>. He noted that he could observe phosphorus-copper coupling in the ^{31}P NMR of

Table 21. NMR properties of ^{63}Cu and ^{65}Cu

Isotope	Natural Abundance %	Spin	Magnetogyric ratio $\gamma/10^7$ rad T^{-1} sec	Quadrupole Moment $Q/10^{-28}$ m^2
^{63}Cu	67.09	3/2	7.0904	-0.16
^{65}Cu	30.91	3/2	7.5958	-0.15

$[Co(\underline{70})_4]^+$ (δ = 124.5, $^1J^{31}P^{63/65}Cu$ = 1230 Hz), but the ^{31}P NMR where L was the less symmetric ligand $\underline{73}$ consisted of a broad resonance at 125.5 ppm ($W_{1/2}$ = 1108 Hz) (100).

The T_1 values of ^{59}Co in six $[Co(P(OR)_3)_6](BF_4)_3$ complexes were measured to see what effect the symmetry of the ligands might have on this parameter. In two of these complexes, ($[(Co(\underline{9})_6](BF_4)_3$ and $[Co(\underline{17})]_6(BF_4)_3$), the ligand possesses C_3 symmetry while in the other four complexes investigated, ($[Co(\underline{27})_6](BF_4)_3$, $[Co(\underline{38})_6](BF_4)_3$, $[Co(\underline{75})_6](BF_4)_3$ and $[Co(\underline{41})_6](BF_4)_3$), the ligands do not possess C_3 symmetry. It is seen in Table 22 that the complexes of the more symmetric ligands have T_1 values which are longer by an order of magnitude than the complexes of the less symmetric monocyclic phosphites. This result shows that asymmetries in the ligands in these $[Co(P(OR)_3)_6]^{3+}$ complexes do have an effect on the electric field gradient at ^{59}Co. Even in $[Co(\underline{17})_6](BF_4)_3$, where the ligands are constrained to C_{3v} symmetry, the 4-fold symmetry of the octahedron is broken. These results indicate that in Co(III) complexes, the ligands cannot be considered point charges and that the symmetry of these ligands can have profound consequences on the electric field gradient at ^{59}Co.

As the temperature of an acetonitrile solution of $[Co(\underline{17})_6]^{3+}$ is raised from 240K to 343K, the T_1 of ^{59}Co increases by a factor of 7.3. This is due to a decrease in molecular correlation time. As seen in equation 22, the rate of quadrupolar relaxation is proportional to the molecular correlation time. As the temperature is raised in solution, the time between molecular collisions will shorten and any asymmetries in the

Table 22. T_1 of ^{59}Co in $[Co(P)_6]^{3+}$ complexes and ^{59}Co NMR linewidths[a]

Compound	Temp, K	$T_1(^{59}Co)$, s	$\frac{1}{\pi T_1(^{59}Co)}$, Hz	$W_{1/2}(^{59}Co)$, Hz
$[Co(\underline{17})_6](BF_4)_3$	240	1.0×10^{-3}	---	---
$[Co(\underline{17})_6](BF_4)_3$	275	2.8×10^{-3}	---	---
$[Co(\underline{17})_6](BF_4)_3$	298	3.6×10^{-3}	8.8×10^{1}	8.0×10^{1}
$[Co(\underline{17})_6](BF_4)_3$	343	7.3×10^{-3}	---	---
$[Co(\underline{9})_6](BF_4)_3$	275	1.4×10^{-3}	2.3×10^{2}	1.7×10^{2}
$[Co(\underline{38})_6](BF_4)_3$	275	1.5×10^{-4}	2.1×10^{3}	2.8×10^{3}
$[Co(\underline{41})_6](BF_4)_3$	275	2.3×10^{-4}	1.4×10^{3}	2.3×10^{3}
$[Co(\underline{27})_6](BF_4)_3$	275	1.9×10^{-4}	1.7×10^{3}	2.9×10^{3}
$[Co(\underline{75})_6](BF_4)_3$	275	7.7×10^{-5}	4.1×10^{3}	*ca.* 5×10^{3}

[a] Measured in CD_3CN.

electron distribution will be smoothed out more efficiently. An increase in T_1 with increasing temperature has previously been noted in aqueous solutions of $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$ and $[Co(CN)_6]^{3-}$ (155).

Although $[CoL_6]^{3+}$ complexes where L is a phosphite have long been known, there exist no reports in the chemical literature of the ^{31}P NMR of these complexes although Yarbrough, in his Ph.D. dissertation, did report the ^{31}P NMR spectra of $[Co(\underline{9})_6](BF_4)_3$ and $[Co(\underline{17})_6](BF_4)_3$ (135). These spectra, which were measured in aqueous solution at 36.4 MHz, were extremely broad. It was found that these complexes were only sparingly soluble in H_2O, but were very soluble in CH_3CN. It was also thought that sensitivity could be improved by taking measurements at a higher field since in principle NMR sensitivity should increase quadratically with field strength (109). It was found that ^{31}P NMR spectra of $[Co(P)_6]^{3+}$ complexes could be readily observed in concentrated CH_3CN solutions at 121.5 MHz (Table 23).

A treatment of the appearance of the NMR spectrum of spin 1/2 nuclei coupled to quadrupolar nuclei was put forth by Pople (156). According to this treatment, the shape of the spin 1/2 resonance is determined by the dimensionless parameter η shown below

$$\eta = 10\pi T_1 J \tag{23}$$

where T_1 is the spin-lattice relaxation time of the quadrupolar nucleus and J is the scalar coupling constant.

For the spectra of nuclei of spin 1/2 coupled to a nucleus of spin 1, if $\eta^2 = 10^3$, the spectra should consist of a three line pattern of intensity ratio 2:3:2. The ^1H NMR spectrum of $^{14}NH_3$ measured by Ogg and Ray was of this form (157). As η is decreased, the theoretical spectrum broadens and eventually becomes a narrow peak as η approaches 1.

For the limiting case of a $[Co(P)_6]^{3+}$ molecule in which the phosphorus ligands are point charges (electric field gradient at ^{59}Co is 0), the ^{31}P NMR will be an octet of intensity ratio 1,7,21,35,35,21,7,1. Conversely, when the electric field gradient at ^{59}Co is very large, as in a trigonal-bipyramidal $[Co(P)_5]^+$ complex, the disturbance of the ^{59}Co nucleus is so rapid that the transitions of the ^{31}P nucleus cannot be

Table 23. ^{31}P NMR data for $[Co(P)_6]^{3+}$ complexes[a]

	$\delta^{31}P$[b]	$W_{1/2}$, Hz
$[Co(\underline{9})_6](BF_4)_3$	110.5	*ca.* 3000[c]
$[Co(\underline{17})_6](BF_4)_3$[d]	113.1	80[e]
$[Co(\underline{30})_3](BF_4)_3$	173.5	937
$[Co(\underline{32})_3](BF_4)_3$[f]	45.2	*ca.* 1300
$[Co(\underline{27})_6](BF_4)_3$[g]	131.4	*ca.* 1700
$[Co(\underline{38})_6](BF_4)_3$[g]	136.2	*ca.* 2100
$[Co(\underline{39})_6](BF_4)_3$	130.4	*ca.* 1700
$[Co(\underline{40})_6](BF_4)_3$	130.8	*ca.* 1700
$[Co(\underline{41})_6](BF_4)_3$[g]	121.2	225
$[Co(\underline{42})_6](BF_4)_3$	122.8	*ca.* 2000
$[Co(\underline{48})_6](BF_4)_3$	132.9	886
$[Co(\underline{50})_6](BF_4)_3$	126.5	*ca.* 2000
$[Co(\underline{51})_6](BF_4)_3$	128.2	814
$[Co(\underline{52})_6](BF_4)_3$	120.4	312
$[Co(\underline{68})_3](BF_4)_3$	189.1	*ca.* 1700
$[Co(\underline{71})_6](BF_4)_3$	101.0	*ca.* 2100
$[Co(\underline{72})_6](BF_4)_3$	101.9	*ca.* 2000
$[Co(\underline{73})_6](BF_4)_3$	104.5	*ca.* 2000
$[Co(\underline{74})_6](BF_4)_3$	100.8	554
$[Co(\underline{75})_6](BF_4)_3$	107.5	*ca.* 2000

[a] Measured in CH_3CN at 298K unless otherwise indicated.

[b] In ppm downfield from 85% H_3PO_4.

[c] Broad plateau approximately 3000 Hz wide at half height.

[d] Measured at 70°C.

[e] $^1J_{Co-P}$ = 411 Hz.

[f] Measured in DMSO.

[g] Measured at 2°C.

associated with a particular state of the ^{59}Co nucleus. For example, the ^{31}P{H} linewidth of [Co(17)$_5$]BF$_4$ (42 Hz in CH$_3$CN at 25°K) is much narrower than that of [Co(P)$_6$]$^{3+}$ complexes (Table 23).

The shape of the ^{31}P NMR resonance of [Co(17)$_6$]$^{3+}$ in acetonitrile, measured at ambient temperature is that of a broad plateau. Raising the temperature and hence the T$_1$ on ^{59}Co results in the eight-line pattern shown in Figure 11. From the theory of Pople, the appearance of a spin ½ nucleus coupled to a nucleus of spin 7/2 where the amount of quadrupolar broadening is less than the magnitude of the spin-spin coupling will be as an eight-line pattern of intensity ration 1.00,0.538,0.582,0.700,0.700, 0.582,0.538,1.00 as drawn in Figure 12. This pattern has also been observed in the ^{15}N spectrum of [Co(NH$_3$)$_6$]$^{3+}$ (158) and the ^{13}C NMR spectrum of [Co(CN)$_6$]$^{3-}$ (154).

The experimental spectrum obtained here and the two aforementioned spectra verify the theory of Pople for spin 1/2 nuclei coupled to spin 7/2 nuclei. This type of analysis has also been used to explain the spectrum of other spin-1/2 nuclei coupled to a quadrupolar nucleus (S = 3/2 (BF$_3$ and ClO$_3$F) (159), S = 5/2 (IF$_7$) (160-162), S = 9/2 (NbF$_6^-$) (163).

The ^{31}P NMR spectra of the [Co(P)$_6$](BF$_4$)$_3$ complexes where L is an unsymmetrical ligand consist of very broad lines as shown in Table 23. The appearance of these spectra as broad gaussian peaks as opposed to the broad plateau seen in the room temperature ^{31}P NMR of [Co(9)$_6$](BF$_4$)$_3$ and [Co(17)$_6$](BF$_4$)$_3$ is undoubtedly due to the smaller value of T$_1$ on cobalt in these complexes. In three complexes, the linewidths are relatively narrow. For example, the linewidth of the ^{31}P NMR of [Co(41)$_6$](BF$_4$)$_3$ in

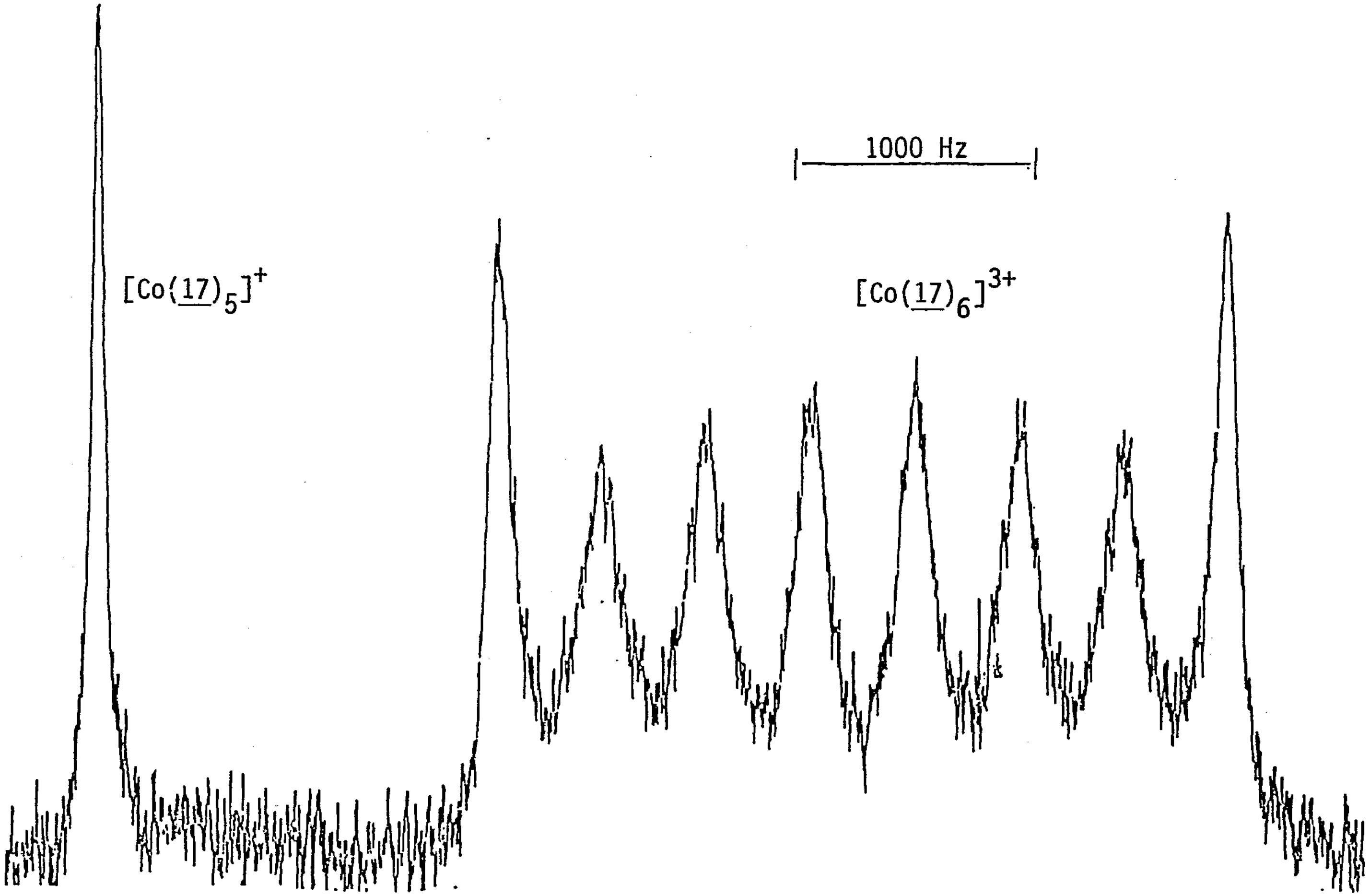


Figure 11. ^{31}P NMR spectrum (121.5 MHz) of $[\mathrm{Co}(\underline{17})_6](\mathrm{BF}_4)_3$ and $[\mathrm{Co}(\underline{17})_5]\mathrm{BF}_4$ at 70° in $\mathrm{CD}_3\mathrm{CN}$

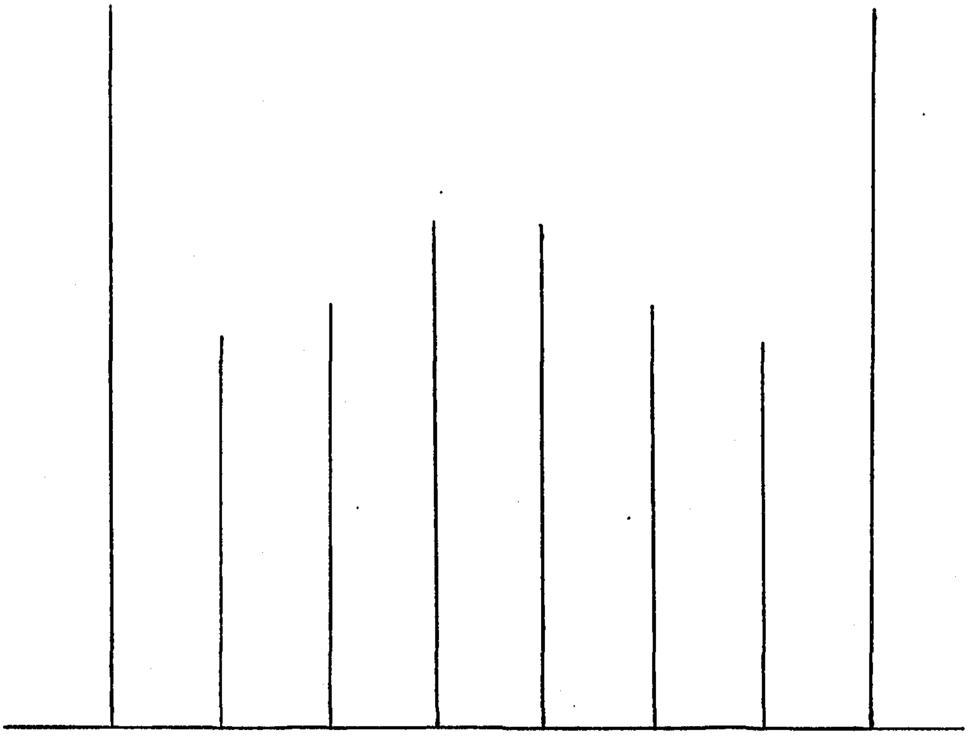


Figure 12. Calculated I NMR of hypothetical SI_6 molecule where I has spin 1/2, S has spin 7/2 and the quadrupolar broadening of I is less than the J coupling

CH_3CN at 275K is 225 Hz while the linewidth of $[Co(\underline{38})_6](BF_4)_3$ measured under the same conditions is ca. 2100 although the shape of this peak is somewhat flattened at the top. The reason for the smaller linewidth in $[Co(\underline{41})_6](BF_4)_3$ is due either to a smaller T_1 of cobalt in this complex or reduced cobalt-phosphorus coupling. Measurement of the T_1 of ^{59}Co of these complexes shows the former explanation not to be valid (Table 22). The increase in ligand-ligand repulsion in $[Co(\underline{41})_6](BF_4)_3$ compared to $[Co(\underline{38})_6](BF_4)_3$, which was previously seen to affect the ligand field of this complex, probably results in an increase in the cobalt-phosphorus bond length which will decrease the cobalt-phosphorus coupling. Previously, a correlation was found between $^1J^{195}Pt\text{-}^{31}P$ and platinum-phosphorus bond length for platinum complexes of trialkylphosphines (164). The decrease in platinum-phosphorus coupling with increasing bond length was attributed to either a reduction in covalency of the Pt-P bond or to a reduced contribution of the platinum 6s-orbital (164). The ^{59}Co NMR chemical shifts of $[Co(\underline{52})_6](BF_4)_3$ and $[Co(\underline{74})_6](BF_4)_3$ are also downfield of complexes where the exocyclic phosphorus substituent on the ligand is smaller (Table 17). Likewise, the ^{31}P NMR spectra of these two complexes are sharp compared to complexes where the exocyclic group is smaller.

The phosphorus-cobalt couplings in $[Co(\underline{38})_6](BF_4)_3$ and $[Co(\underline{41})_6](BF_4)_3$ are not directly observable. It has been suggested that for Co(III) complexes of amino acids, the linewidth in the ^{15}N ($I = 1/2$) and ^{59}Co NMR are related by the following equation (165)

$$W_{1/2}(^{15}N) = 21\ J^2/W_{1/2}(^{59}Co) \tag{24}$$

This equation was derived on the assumptions that the linewidths observed in the ^{59}Co NMR are due exclusively to quadrupolar interaction and that the linewidths observed in the ^{15}N NMR are determined by scalar interaction (166). The first assumption made here is probably not valid in view of the fact that T_2 of ^{59}Co calculated from the linewidth at one-half height was found to be shorter than T_1 in $[Co(NH_3)_6]Br_3$ due to unresolved scalar interaction between ^{14}N and ^{59}Co (152). It was noted that decoupling of ^{14}N decreased the width of ^{59}Co resonance (152). It will be shown that scalar interaction will not affect T_1 values but will affect T_2 relaxation times and hence NMR lineshapes (vide infra). If one assumes that quadrupolar relaxation dominates T_1, then the linewidth of the ^{59}Co NMR spectrum which would be observed if no other relaxation mechanisms contribute to T_2 would be $1/\pi T_1(^{59}Co)$. It was found, however, that the linewidths observed in $[Co(\underline{27})_6](BF_3)_3$, $[Co(\underline{38})_6](BF_4)_3$, $[Co(\underline{41})_6](BF_4)_3$ and $[Co(\underline{75})_6](BF_4)_3$ were significantly larger than $1/\pi T_1(^{59}Co)$ which indicates that another relaxation mechanism(s) in addition to quadrupolar interaction contribute to the ^{59}Co NMR linewidth. Since ^{31}P and ^{15}N are both of spin 1/2, equation 23 can be written in analogy to equation 22

$$W_{1/2}(^{31}P) = 21\ J^2/W_{1/2}(^{59}Co) \tag{23}$$

By using the measured linewidth of the ^{31}P NMR signal and estimating $W_{1/2}(^{59}Co)$ as $1/\pi T_1(^{59}Co)$, values of $^1J_{CoP}$ of 470 and 120 Hz can be calculated from equation 23 for $[Co(\underline{38})_6](BF_4)_3$ and $[Co(\underline{41})_6](BF_4)_3$, respectively. Although these calculated coupling constants cannot be verified, the value for $[Co(\underline{38})_6](BF_4)_3$, compares favorably with the couplings in Co(III) complexes where cobalt-phosphorus coupling is resolved (Table 24). It would seem reasonable to conclude that the anomalously narrow linewidth in the ^{31}P NMR of $[Co(\underline{41})_6](BF_4)_3$ is probably due to reduced cobalt-phosphorus coupling.

Couplings to phosphorus should increase with increasing positive charge on phosphorus. The higher P-H and ^{77}Se-P couplings in the protonated and selenated forms, respectively, of bicyclic ligands as opposed to monocyclic phosphites have been explained in this manner (6,7). Similarly, metal atom couplings to bicyclic phosphites are higher than for acyclic phosphites as shown in Table 25. The couplings of phosphorus to Co(III) in $Co[P(OR)_3]_6^{3+}$ complexes show the opposite trend in that $J^{59}Co$-^{31}P values for $[Co(\underline{17})_6](BF_4)_3$ and $[Co(\underline{69})_6](BF_4)_3$ are smaller than for $[Co(\underline{9})_6](BF_4)_3$ (Table 24). This result can be explained in terms of excitation energies. As seen in equation 4, couplings to phosphorus should decrease with increasing excitation energy. In the couplings to ^1H and ^{77}Se, excitation energies were assumed constant and were not considered (6,7). Pt(0) complexes are of d^{10} configuration so the excitation energy is not a low energy d-d transition and is probably relatively constant. In $Mo(CO)_5L$ and $W(CO)_5L$ complexes, the magnitude of the ligand field is mainly determined by the carbonyls and is therefore relatively constant. The ligand field in $[Co(\underline{9})_6]^{3+}$ is considerably weaker than in $[Co(\underline{17})_6]^{3+}$ which suggests that the singlet-triplet excitation term is dominant in determining the cobalt-phosphorus couplings in these complexes.

Table 24. Phosphorus-cobalt coupling constants

Compound	$^1J_{^{59}Co-^{31}P}$, Hz
$[Co(\underline{9})_6](BF_4)_3$	453±2, 443±6[a]
$[Co(\underline{17})_6](BF_4)_3$	411±2
$[Co(\underline{18})_6](BF_4)_3$	411±2, 412±6[a]
$[Co(\underline{69})_6](BF_4)_3$	399±2, 404±6[b]
$[Co(\underline{30})_3](BF_4)_3$	371±6[b]
$[Co(\underline{31})_3](BF_4)_3$	375±6[b]
$[Co(\underline{68})_3](BF_4)_3$	370±10
$K[Co(PF_3)_4]$	1222±24[c]

[a] Reference 95. Value obtained from ^{59}Co NMR spectrum which was measured at 21.35 MHz.

[b] R. Weiss, unpublished results. Department of Chemistry, Iowa State University, Ames, Iowa, 1978, under the direction of Dr. John Verkade. Value obtained from ^{59}Co NMR spectrum which was measured at 21.35 MHz.

[c] E.A.C. Lucken, K. Noack and D. F. Williams, J. Chem. Soc. (A), 148 (1967).

Table 25. One-bond coupling to phosphorus in some acyclic and bicyclic phosphite ester systems

Compound	Coupling, Hz
$[HP(OMe)_3]^+$	JPH = 826[a]
$[HP(OCH_2)_3CCH_3]^+$	JPH = 899[a]
$SeP(OMe)_3$	$J^{77}Se\text{-}P$ = 954[b]
$SeP(OCH_2)_3CCH_3$	$J^{77}Se\text{-}P$ = 1053[b]
$Pt[P(OEt)_3]_4$	$J^{195}Pt\text{-}P$ = 5386[c]
$Pt[P(OCH_2)_3CC_2H_5]_4$	$J^{195}Pt\text{-}P$ = 5836[c]
$W(CO)_5P(OMe)_3$	$J^{183}W\text{-}P$ = 393[d]
$W(CO)_5P(OCH_2)_3CCH_3$	$J^{183}W\text{-}P$ = 398[d]
$Mo(CO)_5P(OMe)_3$	$J^{95}Mo\text{-}P$ = 217±2[e]
$Mo(CO)_5P(OCH_2)_3CC_2H_5$	$J^{95}Mo\text{-}P$ = 227±2[e]

[a] Reference 6.

[b] Reference 7.

[c] S. N. Sze, P. S. Pregosin, Helv. Chim. Acta 60, 1371 (1977).

[d] Y. Gultneh, Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1981.

[e] Reference 148.

Phosphorus-cobalt couplings in $[Co(\underline{30})_3](BF_4)_3$ and $[Co(\underline{31})_3](BF_4)_3$ were observed by Weiss in the ^{59}Co NMR measured at 21.35 MHz (167). These complexes which have the highest ligand field of the $[Co(P)_6]^{3+}$ complexes examined showed the smallest couplings which again suggests that excitation energies are the dominant factor in determining the relative couplings in $[Co(P)_6]^{3+}$ complexes. Likewise, the cobalt-phosphorus coupling in $[Co(\underline{68})_3](BF_4)_3$, a complex of very high ligand field (Table 17), was also found to be relatively small (Table 24). When the ^{59}Co NMR of $[Co(\underline{30})_3](BF_4)_3$ and $[Co(\underline{31})_3](BF_4)_3$ were remeasured at 70.85 MHz, cobalt-phosphorus couplings could not be completely resolved. It is not known at this time whether this is due to a field dependence in relaxation rates or differences in measurement techniques. Field dependence in ^{59}Co NMR linewidths was previously observed only in cases in which hydrogen bonding interactions with the solvent occurred (168,169).

The spin-lattice relaxation times of phosphorus listed in Table 26 tend to be shorter than previously measured values in phosphine, phosphinito and phosphito complexes of Pd(II), Pt(II) and Ru(II) which ranged from 3.0-19.0 sec (170,171). The shorter T_1 values observed in $[Co(P(OR)_3)_6]^{3+}$ complexes are probably due to dipolar interaction between the ^{59}Co and ^{31}P nuclei, both of which have large magnetogyric ratios, although it must be remembered that strict comparisons of T_1 values measured in different solvents and at different temperatures should be made with caution (170). The increase in T_1 of ^{31}P with increasing temperature in $[Co(\underline{17})_6](BF_4)_3$ also suggests the dominance of relaxation

Table 26. T_1 and T_2 values of ^{31}P in $[Co(P)_6]^{3+}$ compounds[a]

Compound	Temp, K	$T_1(^{31}P)$, s	$T_2(^{31}P)$, s[b]
$[Co(\underline{17})_6](BF_4)_3$	240	1.1	---[c]
$[Co(\underline{17})_6](BF_4)_3$	298	2.1	---[c]
$[Co(\underline{17})_6](BF_4)_3$	343	4.4	1.9×10^{-3}
$[Co(\underline{9})_6](BF_4)_3$	275	4.2	---[c]
$[Co(\underline{38})_6](BF_4)_3$	275	0.9	1.4×10^{-4}[d]
$[Co(\underline{41})_6](BF_4)_3$	275	2.6	1.4×10^{-3}
$[Co(\underline{75})_6](BF_4)_3$	275	1.6	2.5×10^{-4}

[a] Measured in CD_3CN solution.

[b] Estimated by measuring peakwidth at 1/2 height.

[c] Peak had the shape of a broad plateau so T_2 could not be estimated from peakwidth.

[d] Peak was slightly flattened at top so T_2 is possibly somewhat longer than estimated.

by a dipolar as opposed to spin-rotation mode of relaxation since the rate of relaxation due to spin-rotation increases with temperature (109).

The very wide lines observed in the ^{31}P NMR of the $[Co(P(OR)_3)_6]^{3+}$ complexes are due to scalar interaction between cobalt and phosphorus. Scalar interaction can occur between two nuclei of spin I and S (where $I = 1/2$ and $S \geq 1/2$). The interaction of spin I with S (assuming that for a quadrupolar nucleus, for which $S > 1/2$, T_1 is quite short) provides a mechanism of relaxation for I.

It has been shown that the relaxation rate of I by scalar interaction is of the form

$$R^{I}_{1S} = \frac{8\pi^2 J^2}{3} S(S+1) \frac{T_1^S}{1 + (\omega_I - \omega_S)^2 (T_1{}^S)^2} \tag{24}$$

and

$$R^{I}_{2S} = \frac{4\pi^2 J^2}{3} S(S+1) \{T_1^S + \frac{T_1^S}{1 + (\omega_I - \omega_S)^2 (T_1^S)^2}\} \tag{25}$$

where S is the spin on nucleus S, ω_I and ω_S are the larmor frequencies of I and S and T_S is the relaxation time on nucleus S (149). From examination of equations 24 and 25, it is seen that scalar interaction will effect T_1 only when $\omega_I \approx \omega_S$ since the expression for R^{I}_{1S} approaches 0 when the difference between these two numbers becomes large. Scalar interaction affecting T_1 is very rare since the difference in Larmor frequencies between two nuclei is almost always very large as is the case with ^{59}Co and ^{31}P. It is thus seen that scalar interaction between cobalt and phosphorus will effect T_2 on phosphorus (and hence the shape of the ^{31}P NMR resonance) but will not effect T_1.

PART III. CRYSTAL AND MOLECULAR STRUCTURE OF $P(O\text{-}2,6\text{-}C_6H_3Me_2)_3$

INTRODUCTION

The amount of structural data for phosphite esters is quite limited since most of these compounds are liquids at room temperature. Only three reports of crystal structure determinations of $P(OR)_3$ compounds have appeared in the literature, those being of 79 (172), 80 (173) and 81 (174). No structural determinations of triarylphosphites have appeared although a substantial number of them are solids at room temperature. In studying the coordination properties of phosphorus ligands to silver(I) (Section I), it was found that 24 was a solid which could be readily crystallized from hexanes. It was also shown that $[Ag(24)_2]^+$ could not be isolated and was appreciably dissocated in solution. This result was rather surprising in view of the fact that $[Ag(5)_2]PF_6$ had previously been isolated in the solid state (18) and the cone angle for 5 reported by Tolman (212°) (9) is greater than that which he reports for 24 (190°) (9). In order to help alleviate the lack of structural data for triarylphosphites and also to help make a better comparison of the steric requirements of 5 and 24, x-ray structural data for 24 were obtained.

EXPERIMENTAL

The structure of 24 was solved by Iowa State University Instrument Services.

A crystal of 24 was grown by recrystallization from hexanes and was cut, mounted and sealed in a glass capillary to prevent hydrolysis by atmospheric moisture.

Data were taken using a Syntex P2_1 automated four-circle diffractometer operating with graphite monochromated Cu Kα radiation ($\lambda = 1.54/8$ Å) at ambient temperature. Preliminary examination of the crystal showed it to be trigonal with $a = 14.518(5)$, $b = 14.518(5)$ and $c = 6.353(1)$ with 2 atoms of 24 per unit cell. A density of 1.14 g/cc was calculated based on a cell volume at 1159.6 Å^3.

A variable ω-scan technique was employed to measure 1717 reflection intensities of 24 within a 2θ sphere of 114.1° ($\sin\theta/\lambda = 0.544$ Å^{-1}). Of these reflections, 414 were judged to be observed after correction for Lorentz polarization and background effects ($F_0 > 3\sigma(F_0)$). Systematic absences (h, h, $-2h$, ℓ absent if $\ell = 2n$) identified the space group as P3_1/c. Lattice constants were obtained by a least squares refinement of the precise $\pm 2\theta[|2\theta|>25^0)$ measurements of 12 strong independent reflections.

The programs MULTAN (175) and ALLS (55) were used to locate all of the nonhydrogen atoms. Two cycles of isotropic refinement of these positions by full matrix least squares techniques led to a conventional R factor of 0.094 and a weighted R factor of 0.112. On the final cycle of refinement, the shift/error ratios ranged from 0.73 to 3.78. The large amount of thermal motion prevented anisotropic refinement. The intermolecular bond distances (Table 27) and angles (Table 28) and final atomic positional and thermal parameters (Table A3) appear as indicated.

Table 27. Interatomic distances (Å) and their standard deviations (in parentheses) for 24

P-O	1.649(8)
O-C_1	1.419(16)
C_1-C_2	1.482(19)
C_1-C_6	1.352(20)
C_2-C_3	1.419(21)
C_3-C_4	1.433(24)
C_4-C_5	1.312(23)
C_5-C_6	1.443(21)
C_6-C_8	1.528(23)
C_2-C_7	1.435(23)
C_6-C_8	1.528(23)

Table 28. Bond angles (deg) and their standard deviations (in parentheses) for 24

O-P-O	97.4(4)
$P-O-C_1$	116.6(8)
$O-C_1-C_2$	112.8(14)
$O-C_1-C_6$	120.5(12)
$C_2-C_1-C_6$	126.3(13)
$C_1-C_2-C_3$	112.8(13)
$C_1-C_2-C_7$	122.6(12)
$C_2-C_3-C_4$	120.8(15)
$C_3-C_2-C_7$	124.7(13)
$C_3-C_4-C_5$	122.1(15)
$C_1-C_6-C_5$	115.7(13)
$C_1-C_6-C_8$	118.1(13)
$C_5-C_6-C_8$	126.1(14)
$C_4-C_6-C_5$	122.2(15)

RESULTS AND DISCUSSION

A computer drawing of 24 is shown in Figure 13. The phosphorus lies on a three-fold special position. The dihedral angle between the plane formed by the phosphorus atom, the oxygen atom and C_1 and the plane of all of the carbon atoms in the C_1-bearing ring is 73.6° (Table 29). In the sterically hindered phosphine 5, the average dihedral between each phenyl ring and the plane defined by the P-C bond and the idealized three-fold axis of the PC_3 unit is only 44.1° (176).

The O-P-O angle in 24, 97.4°, is somewhat less than that previously reported for phosphite esters (Table 30). Conversely, the average C-P-C angle in 5 (109.7°) is greater than that previously seen in simple acyclic phosphines. This was ascribed to the large steric demands of the mesityl group (173). The lack of expansion of the O-P-O angle in 24 shows the smaller steric requirement of a O-2,6-$C_6H_3Me_2$ phosphorus substituent compared to a mesityl group. The smaller O-P-O angle in 24 compared to the other phosphite esters in Table 30 is also in accord with Bent's rule which states that more electronegative groups prefer hybrid orbitals with less s character (177). In this case, the phenoxy groups on phosphorus in 24 are more electronegative than the alkoxy groups on phosphorus in the previous structures of phosphites. There is not a great deal of steric crowding in 24. The distance between C_7 and C_8 on adjacent phenyl rings is 4.42 Å while the sum of the covalent radii of two methyl groups is estimated to be 4.0 Å (178).

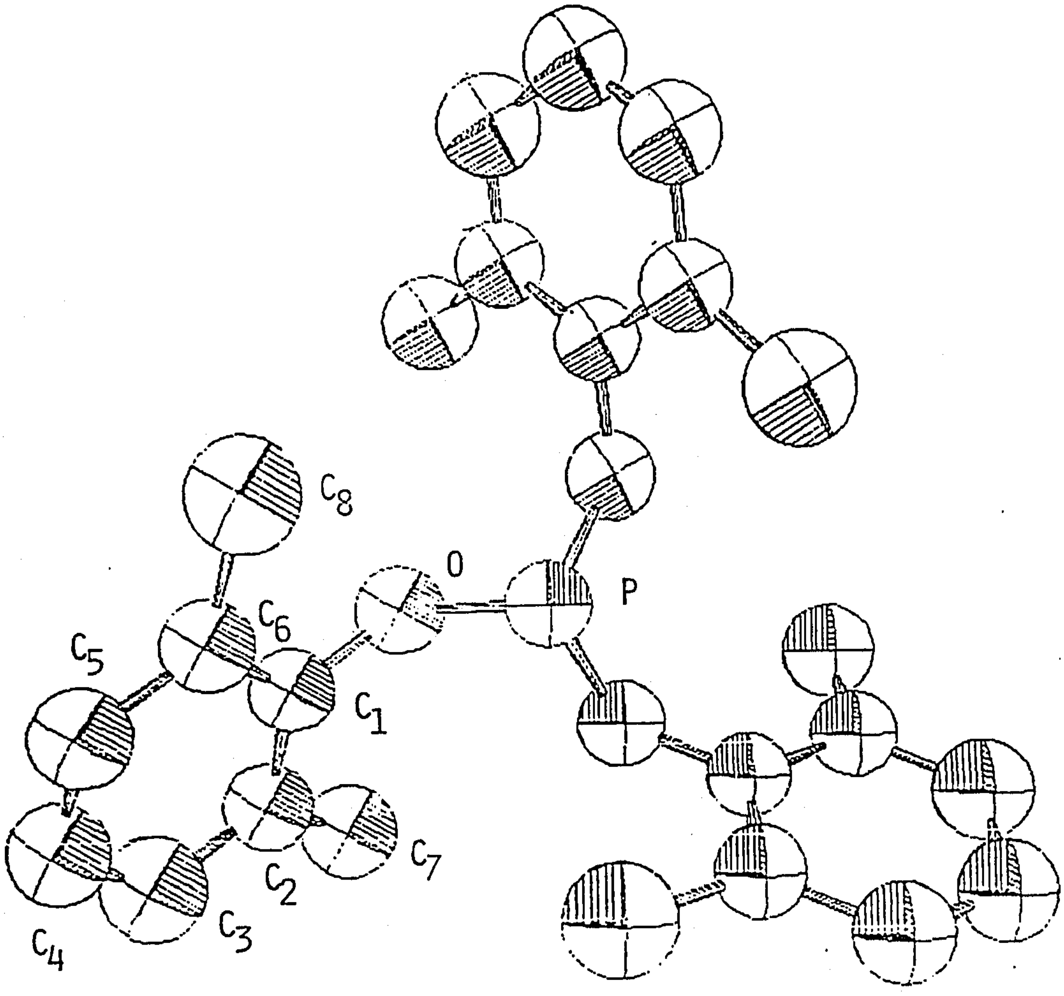


Figure 13. ORTEP drawing of 24

Table 29. Least-squares planes in 24

Atom	dev, Å	Atom	dev, Å
	Plane 1: C_1,O,P $0.5324X + 0.6718Y - 0.5150Z = 5.045$		
	Plane 2: C_1, C_2, C_3, C_4, C_5, C_6 $0.1290X + 0.7871Y + 0.6032Z = 4.866$		
C_1	0.026	C_4	0.005
C_2	-0.024	C_5	-0.010
C_3	0.010	C_6	-0.006
	Plane 3: C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8 $0.1088X + 0.7932Y + 0.5992Z = 4.641$		
C_1	0.068	C_5	0.023
C_2	-0.001	C_6	-0.003
C_3	0.004	C_7	-0.035
C_4	-0.011	C_8	-0.045
	Plane 4: Symmetry related C_8 atoms $0.000X + 0.000Y + 1.000Z = 4.57$		
P	-1.39		
	Plane 5: Symmetry related C_1 atoms $0.000X + 0.000Y + 1.000Z = 2.92$		
P	0.248		
	Plane 6: Symmetry related O atoms $0.000X + 0.000Y + 1.000Z = 2.357$		
P	0.8195		

Planes	Angle, deg	Planes	Angle, deg
1,2	73.34	2,3	1.23
1,3	73.61		

Table 30. Structural data for phosphite esters

Compound	POC(°)	OPO(°)	P-O(Å)	O-C(Å)
24	116.6(8)	97.4(4)	1.649(8)	1.419(16)
79[a]	119.2(12)	100.7(22)	1.617(7)	1.441(10)
80[b]	117.5(4)	101.1(3)	1.615(5)	1.447(8)
81[c]	117.5(4)[d]	100.8(4)[e]	1.631(6)[f]	1.424(15)[f]

[a] Reference 172.

[b] Reference 173.

[c] Reference 174.

[d] This angle refers to the unstrained exocyclic POC linkage.

[e] This is the average of the two relatively unstrained $O_{exo}PO_{endo}$ linkages.

[f] This bond refers to the exocyclic oxygen.

The P-O bond length in 24 is somewhat longer than in the previously structured phosphites (Table 30). It is possible that the electron-withdrawing O-2,6-$C_6H_4Me_2$ group is responsible in a manner which is presently obscure. It is also seen that the C-O bond length in 24 is shorter than the previously structured phosphites which is probably due to the fact that the C-O bond in 24 involves an aryl carbon, while the bonds in the other three phosphites involve alkyl carbons.

The structural data obtained here indicate that the Tolman cone angle model tends to underestimate the relative steric demands of 24 compared to 5. As seen in Figure 13 the P-O-C angle is oriented such that the plane of the three symmetry related C_1 atom lies only 0.25 Å below the phosphorus (Table 29). This has the effect of alleviating crowding compared to a conformation in which the phenyl rings are more coplanar. However, the observed conformation increases the steric bulk of the ligand. Assuming a metal-phosphorus distance of 2.28 Å, a C-H distance of 1.0 Å and a van der Waals radius of 1.0 Å for hydrogen, a crude estimate of the cone angle of 24, 212°, can be calculated from a coplanar arrangement of the M-P-C-H bonds. When the cone angle of 24 was calculated by Tolman (190°), the substituents on phosphorus were folded back to give a minimum cone which explains the large deviation between the two cone angle calculations.

The distance from the phosphorus atom to the plane formed by the three C_8 atoms lying above the phosphorus is approximately 1.39 Å. If 24 complexes with the same conformation it shows in the solid state in any linear complex of the type 24-M-24, the ligands must be in a staggered configuration as is seen in the solid state structure of $[Ag(5)_2]PF_6$ (18). It has previously been found that the conformation of complexed 5 is similar to that of the free ligand (18,179).

The distance between the plane formed by the methyl carbons oriented toward silver in $[Ag(5)_2]PF_6$ and phosphorus is only 1.01 Å. For symmetrical phosphorus ligands which have a cone angle greater than 180°, a "reach" parameter can be defined as the distance from the phosphorus to the plane formed by the three carbons lying furthest above the phosphorus. The instability of $[Ag(\underline{24})_2]^+$ may be due in part to the interligand repulsion caused by the larger reach of 24 (1.39 Å) compared to 5 (1.01 Å).

It has been noted that no reports appear in the chemical literature of complexes which contain more than two coordinated 4 ligands (180). It would be of interest to investigate the coordination properties of 24 toward transition metals. Perhaps it will be found that only one or two 24 ligands will coordinate to a transition metal complex which can be isolated in the solid state.

It must be remembered that because of the large amount of thermal motion in the structure of 24, all the bond distances and angles discussed are tentative. A better refinement can probably be made by taking x-ray data at a lower temperature.

REFERENCES

1. C. A. Tolman Chem. Rev. 1977, 77, 344.

2. F. A. Cotton Inorg. Chem. 1964, 3, 702.

3. J. C. Green, P. I. King and J.H.D. Eland Chem. Commun. 1970, 1121.

4. C. A. Tolman J. Am. Chem. Soc. 1970, 92, 2953.

5. S. L. Manatt, G. L. Juvinall, R. I. Wagner and D. D. Elleman J. Am. Chem. Soc. 1966, 88, 2689.

6. L. J. Vande Griend, J. G. Verkade, J.F.M. Pennings and H. M. Buck J. Am. Chem. Soc. 1977, 99, 2459.

7. R. D. Kroshefsky, R. Weiss and J. G. Verkade Inorg. Chem. 1979, 18, 469.

8. L. M. Ounapu, J. A. Mosbo, J. M. Risley and B. Storhoft J. Organomet. Chem. 1980, 194, 337, and references therein.

9. C. A. Tolman J. Am. Chem. Soc. 1970, 92, 2956.

10. C. A. Tolman, W. C. Seidel and L. W. Gosser J. Am. Chem. Soc. 1974, 96, 53.

11. E. L. Muetterties and C. W. Alegranti J. Am. Chem. Soc. 1972, 94, 6386.

12. D. A. Couch and S. D. Robinson Inorg. Chim. Acta 1971, 9, 39.

13. F. A. Cotton and D.M.L. Goodgame J. Chem. Soc. 1960, 5267.

14. J. G. Verkade and T. S. Piper Inorg. Chem. 1962, 1, 453.

15. K. J. Coskran, T. J. Huttemann and J. G. Verkade, Advances in Chemistry Series, A.C.S Publication, 1966, 62, 590.

16. J. M. Jenkins, T. J. Huttemann and J. G. Verkade, Advances in Chemistry Series, A.C.S. Publication, 1966, 62, 604.

17. R. G. Goel and P. Pilon Inorg. Chem. 1978, 17, 2876.

18. E. C. Alyea, G. Ferguson and A. Somogyvari Inorg. Chem. 1982, 21, 1369.

19. J. A. Pople and D. P. Santry Mol. Phys. 1964, 8, 1.

20. J. A. Pople and D. P. Santry Mol. Phys. 1965, 9, 311.

21. P. Diehl and R. W. Kunz, "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes", Springer-Verlag: Berlin, 1979.

22. G. A. Gray and T. A. Albright J. Am. Chem. Soc. 1977, 99, 3243, and references therein.

23. A. Pidcock in "Catalytic Aspects of Metal Phosphine Complexes", E. C. Alyea and D. Meek, Eds.; A.C.S. Symposium Series, 1982, 196, 1.

24. I. J. Colquhoun and W. McFarlane J. Chem. Soc., Chem. Commun. 1980, 145.

25. A. H. Cowley, R. E. Davis and K. Remadna Inorg. Chem. 1981, 20, 2146.

26. A. H. Cowley, R. E. Davis, M. Lattman and W. B. Jennings, J. Am. Chem. Soc. 1979, 101, 5090.

27. S. D. Worley, J. H. Hargis, L. Chang and W. B. Jennings Inorg. Chem. 1981, 20, 2146.

28. G. Kodama and R. W. Parry J. Inorg. Nucl. Chem. 1961, 17, 125.

29. C. E. Nordman Acta Crystallogr. 1960, 13, 535.

30. C. Rømming and J. Songstad Acta Chem. Scand., Ser. A 1978, A32, 688.

31. C. Rømming and J. Songstad Acta Chem. Scand., Ser. A 1979, A33, 187.

32. D. H. Brown, A. F. Cameron, R. J. Cross and M. McLaren, J. Chem. Soc., Dalton Trans. 1981, 1459.

33. C. Rømming and J. Songstad Acta Chem. Scand., Ser. A 1982, A36, 665.

34. C. Rømming, J. Iversen and J. Songstad Acta Chem. Scand. Ser. A 1980, A34, 333.

35. A. Torassoli, R. C. Haltiwanger and A. D. Norman Inorg. Nucl. Chem. Lett. 1980, 16, 27.

36. C. Rømming and J. Songstad Acta Chem. Scand., Ser. A 1980, A34, 631.

37. D. E. Schiff, J. W. Richardson, Jr., R. A. Jacobson, A. H. Cowley and J. G. Verkade, unpublished paper, Department of Chemistry, Iowa State University, Ames, Iowa, 1983.

38. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 4th ed., John Wiley and Sons: New York, 1980; p 49.

39. C. W. Heitsch and J. G. Verkade Inorg. Chem. 1962, 1, 392.

40. G. W. Waitkins and R. Shutt Inorg. Syn. 1946, 2, 186.

41. I. A. Nuretdinov and N. P. Grechkin Izv. Akad. Nauk SSSR Ser. Khim. 1964, 1883; Chem. Abstr. 1965, 62, 2747.

42. D. W. White, B. A. Karcher, R. A. Jacobson and J. G. Verkade J. Am. Chem. Soc. 1971, 101, 4921.

43. W. Gerrard, W. J. Green and R. J. Phillips J. Chem. Soc. 1954, 1148.

44. A. H. Ford-Moore and J. H. Williams J. Chem. Soc. 1947, 1465.

45. "Catalog Handbook of Fine Chemicals"; Aldrich Chemical Co.: Milwaukee, 1981; p 1150.

46. J. W. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones J. Chem. Soc. 1956, 78, 5715.

47. J. R. Cox and M. G. Newton J. Org. Chem. 1969, 34, 2600.

48. V. Mark and J. Van Wazer J. Org. Chem. 1964, 29, 1006.

49. H. N. Rydon and B. L. Tonge J. Chem. Soc. 1956, 3043.

50. D. W. White, R. D. Bertrand, G. K. McEwen and J. G. Verkade J. Am. Chem. Soc. 1970, 92, 7125.

51. D. B. Denney and S. L. Varga Phosphorus 1973, 2, 245.

52. P. Nicpon and D. W. Meek Inorg. Synth. 1967, 10, 157.

53. "Topics in Phosphorus Chemistry", M. Grayson and E. Griffith, Eds.; John Wiley and Sons: New York, 1967; Vol. 5.

54. R. A. Jacobson J. App. Crystallogr. 1976, 9, 115.

55. F. Takusagawa and R. A. Jacobson Acta Crystallogr. 1978, B39, 213.

56. R. L. Lapp and R. A. Jacobson "ALLS, A Generalized Crystallographic Least-Squares Program", Ames Laboratory, U.S. Department of Energy Report IS-4708, Iowa State University, Ames, Iowa, 1979.

57. D. T. Gromer and J. T. Weber "International Table for X-Ray Crystallography", Kynoch Press: Birmingham, England, 1974; Vol. II, Table 2,2A, p 71-92.

58. D. H. Templeton "International Tables for X-Ray Crystallography", Kynoch Press: Birmingham, England, 1962; Vol. III, Table 3.3.2c, pp 215-216.

59. L. J. Vande Griend, Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1975.

60. L. J. Vande Griend, D. W. White and J. G. Verkade *Phosphorus* 1973, 3, 5.

61. D. W. White and J. G. Verkade *Phosphorus* 1973, 3, 9.

62. L. J. Vande Griend and J. G. Verkade *J. Am. Chem. Soc.* 1975, 97, 5959.

63. M. J. Mays and P. A. Vergnano *J. Chem. Soc., Dalton Trans.* 1979, 1112.

64. R. V. Parish, O. Parry and C. A. McAuliffe *J. Chem. Soc., Dalton Trans.* 1981, 2098.

65. E. L. Muetterties and C. W. Alegranti *J. Am. Chem. Soc.* 1970, 92, 4114.

66. E. L. Meutterties, W. G. Peet, P. A. Wagner and C. A. Alegranti *Inorg. Chem.* 1970, 9, 2447.

67. K. N. Raymond and F. Basolo *Inorg. Chem.* 1966, 5, 949.

68. T.G.M.H. Dikhoff and R. G. Goel *Inorg. Chim. Acta* 1980, 44, L72.

69. A. P. Gaughan, Z. Dori and J. Ibers *Inorg. Chem.* 1974, 13, 1657.

70. A.A.G. Tomlinson, M. Bonamico, G. Dessy, V. Fares and L. Saramuzza *J. Chem. Soc., Dalton Trans.* 1972, 1671.

71. S. Buffagni, L. M. Vallarino and J. V. Quagliano *Inorg. Chem.* 1964, 3, 671.

72. L. M. Vallarino, W. E. Hill and J. V. Quagliano *Inorg. Chem.* 1965, 4, 1598.

73. W. Beck and K. Schloter *Z. Naturforsch.* 1978, 33B, 1214.

74. K. Isobe, K. Nanjo, Y. Nakamura and S. Kawaguchi *Chem. Lett.* 1979, 1193.

75. Y. Yamamoto, K. Aoki and H. Yamazaki *Inorg. Chim. Acta* 1982, 68, 75.

76. S. Brownstein *Can. J. Chem.* 1978, 56, 343.

77. H. Schmidbaur and K.-H. Räthlein *Chem. Ber.* 1973, 106, 2491.

78. B. E. Mann and A. Musco *J. Chem. Soc., Dalton Trans.* 1975, 1673.

79. C. B. Colburn, W. E. Hill, C. A. McAuliffe and R. V. Parish *J. Chem. Soc., Chem. Commun.* 1979, 218.

80. W. McFarlane and D. S. Rycroft *J. Mag. Res.* 1976, 24, 95.

81. A. W. Verstuyft, J. H. Nelson and L. W. Cary *Inorg. Chem.* 1976, 15, 732.

82. D. A. Redfield, J. H. Nelson and L. W. Cary *Inorg. Nucl. Chem. Lett.* 1974, 10, 727.

83. P.-P. Winkler and P. Peringer *Trans. Met. Chem.* 1982, 7, 313.

84. H. Schmidbaur, J. Adlkofer and K. Schwirton *Chem. Ber.* 1972, 105, 3382.

85. A. Kiffen, C. Masters and J. Visser *J. Chem. Soc., Dalton Trans.* 1975, 1311.

86. L. W. Gosser and G. W. Parshall *Inorg. Chem.* 1974, 13, 1947.

87. M. J. Nolte and G. Gafner *Acta Crystallogr.* 1974, B30, 738.

88. J. J. Guy, P. G. Jones and G. M. Sheldrick *Acta Crystallogr.* 1976, B32, 1937.

89. D.E.C. Corbridge, "Phosphorus, An Outline of Its Chemistry, Biochemistry, and Technology", Elsevier: Amsterdam, 1980.

90. R. B. King *Inorg. Chem.* 1963, 2, 936.

91. C. E. Jones and K. J. Coskran *Inorg. Chem.* 1971, 10, 55.

92. E. D. Morris and C. E. Nordman *Inorg. Chem.* 1969, 8, 1673.

93. W. G. Proctor and F. C. Yu *Phys. Rev.* 1951, 81, 20.

94. R. K. Harris and B. E. Mann, "NMR and the Periodic Table", Academic Press: London, 1978; Chapter 8.

95. R. Weiss and J. G. Verkade *Inorg. Chem.* 1979, 18, 529.

96. N. Juranić *Inorg. Chem.* 1980, 19, 1093.

97. R. Freeman, G. R. Murray and R. E. Richard *Proc. E. Soc. London Ser. A* 1977, 242, 455.

98. N. Juranić *Inorg. Chem.* 1983, 22, 521.

99. T. J. Huttemann, B. M. Foxman, C. R. Sperati and J. G. Verkade *Inorg. Chem.* 1965, 4, 950.

100. A. E. Wroblewski "Metal Complexes with Optically Active Phosphites as Ligands", unpublished results, Department of Chemistry, Iowa State University, Ames, Iowa, 1979, under the direction of Dr. John Verkade.

101. J. H. Meiners and J. G. Verkade *J. Coord. Chem.* 1977, 7, 131.

102. J. G. Verkade *Coord. Chem. Rev.* 1972, 9, 1.

103. T. Ohishi, K. Kashiwabara and J. Fujita *Chem. Lett.* 1981, 1371.

104. G. Albertin, G. Pelizzi and E. Bordignon *Inorg. Chem.* 1983, 22, 515.

105. D. W. Meek and S. A. Ehrhardt *Inorg. Chem.* 1965, 4, 584.

106. S. F. Pavkovic and D. W. Meek *Inorg. Chem.* 1965, 4, 20.

107. D. Rehder, H.-C. Bechthold, A. Kececi, H. Schmidt and M. Siewing *Z. Naturforsch.* 1982, 37B, 631, and references therein.

108. A. Kececi and D. Rehder *Z. Naturforsch.* 1981, 36B, 20.

109. E. D. Becker "High Resolution NMR. Theory and Chemical Applications", 2nd ed.; Academic Press: New York, 1980.

110. H. J. Lucas, F. W. Mitchell and C. N. Scully *J. Am. Chem. Soc.* 1950, 72, 5491.

111. D. Z. Denney, G. Y. Chen and D. B. Denney *J. Am. Chem. Soc.* 1969, 91, 6838.

112. R. Schmutzler *Chem. Ber.* 1963, 96, 2435.

113. J. P. Dutasta, A. C. Guimaraes, J. Martin and J. G. Robert *Tetrahedron Lett.* 1975, 1519.

114. N. Fritzowski, A. Lentz and J. Goubeau *Z. Anorg. Allg. Chem.* 1971, 386, 67.

115. K. Moedritzer, L. Maier and L.C.D. Groenweghe *J. Chem. Eng. Data* 1962, 7, 307.

116. K. Moedritzer and J. Van Wazer Inorg. Chem. 1964, 3, 139.

117. J. G. Verkade and L. T. Reynolds J. Org. Chem. 1960, 25, 663.

118. K. Bergesen, M. Bjorøy and T. Gramstad Acta Chem. Scand. 1972, 26, 2156.

119. H.-P. Abicht, unpublished results, Iowa State University, Ames, Iowa, 1981, under the direction of Dr. John Verkade.

120. P. C. Crofts, J.H.H. Markes and N. H. Rydon J. Chem. Soc. 1958, 4250.

121. A. E. Arbuzov and F. G. Valitova Izvest. Akad. Nauk SSSR, Otdel. Khim Nauk 1940, 529; Chem. Abstr. 1941, 35, 3990.

122. W. J. Vullo Ind. Eng. Chem. Prod. Res. Dev. 1966, 5, 347.

123. R. B. King and W. M. Rhee Inorg. Chem. 1978, 17, 2961.

124. J. G. Verkade, T. J. Huttemann, M. K. Fung and R. W. King Inorg. Chem. 1965, 4, 83.

125. M. Kainosho and A. Nakamura Tetrahedron 1960, 25, 4071.

126. J. A. Mosbo and J. G. Verkade J. Am. Chem. Soc. 1973, 95, 4659.

127. C. L. Bodkin and P. Simpson J. Chem. Soc. (B) 1971, 1136.

128. J. H. Meiners, M.S. Thesis, Iowa State University, Ames, Iowa, 1975.

129. J. Selbin, W. E. Bull and L. H. Holmes, Jr. J. Inorg. Nucl. Chem. 1961, 16, 219.

130. W. McFarlane and D. S. Rycroft J. Chem. Soc., Dalton Trans. 1973, 2162.

131. H. Clark and L. Manzer J. Organomet. Chem. 1973, 59, 411.

132. M. Haemers, R. Ottinger, D. Zimmerman and J. Reisse Tetrahedron 1973, 29, 3539.

133. R. A. Jacobson, B. A. Karcher, R. A. Montag, S. M. Socol, L. J. Vande Griend and J. G. Verkade Phosphorus and Sulfur 1981, 11, 27.

134. L. J. Vande Griend and J. G. Verkade Inorg. and Nucl. Chem. Lett. 1973, 9, 1137.

135. L. W. Yarbrough, Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1978.

136. D. W. White, Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1970.

137. F. A. Cotton, D. J. Darensbourg and W. H. Ilsley Inorg. Chem. 1981, 20, 578.

138. F. A. Cotton, D. J. Darensbourg, M. F. Fredrich, W. H. Ilsley and J. M. Troup Inorg. Chem. 1981, 20, 1869.

139. F. H. Westheimer Accounts Chem. Res. 1968, 1, 70.

140. C. A. Tolman, L. W. Yarbrough II and J. G. Verkade Inorg. Chem. 1977, 16, 479.

141. R. S. Drago, "Physical Methods in Chemistry", 1st ed.; W. B. Saunders: Philadelphia, 1977; Chapter 4.

142. R. G. Kidd and H. G. Spinney Inorg. Chem. 1973, 12, 1967.

143. F. Yajima, Y. Koike, A. Yamasaki and S. Fujiwara Bull. Chem. Soc. Japan 1974, 47, 1442.

144. Y. Nakashima, U. Sakaguchi and H. Yoneda Bull. Chem. Soc. Japan 1975, 48, 762.

145. N. Juranić, M. B. Celap, D. Vucelić, M. J. Malinar and P. N. Radivojsa Spectrochemica Acta 1979, 35A, 997.

146. A. Yamasaki, F. Yajima and S. Fujiwara Inorg. Chim. Acta 1968, 2, 39.

147. V. P. Tarasov, V. I. Privalov and Y. A. Baslaev Mol. Phys. 1978, 35, 1047.

148. G. T. Andrews, I. J. Colquhoun, W. McFarlane and S. O. Grim J. Chem. Soc., Dalton Trans. 1982, 2353.

149. T. C. Farrar and E. D. Becker "Pulse and Fourier Transform NMR", Academic Press: New York, 1971.

150. K. J. Franklin, C.J.L. Lock, B. G. Sayer and G. J. Schrobilgen J. Am. Chem. Soc. 1982, 104, 5303.

151. M. J. Buckingham, G. E. Hawkes, J. R. Thornback Inorg. Chim. Acta 1981, 56, L41.

152. D. M. Doddrell, M. R. Bendall, P. C. Healy, G. Smith, C.H.L. Kennard, C. L. Raston and A. H. White Aust. J. Chem. 1979, 32, 1219.

153. K. A. Valiev and M. M. Zaripov Sov. Phys. - JETP (Engl. Trans.) 1962, 14, 545.

154. V. P. Chacko and R. G. Bryant, Experimental NMR Conference, Asilonar, CA, April 1983; Abstr. B-41.

155. R. Adler and A. Loewenstein J. Mag. Res. 1971, 5, 248.

156. J. A. Pople Mol. Phys. 1958, 1, 168.

157. R. A. Ogg and J. D. Ray Disc. Faraday Soc. 1955, 19, 215.

158. Y. Akiro, M. Yoshie, Y. Yuzo and Y. Hiedo Denki Tsushin Digaku Gakuho 1977, 28, 107.

159. J. Bacon, R. J. Gillespie and J. W. Quail Can. J. Chem. 1963, 41, 3063.

160. N. Bartlett, S. Beaton, L. W. Reeves and E. J. Wells Can. J. Chem. 1964, 42, 2531.

161. E. L. Muetterties and K. J. Packer J. Am. Chem. Soc. 1964, 86, 293.

162. R. J. Gillespie and J. W. Quail Can. J. Chem. 1964, 42, 2671.

163. K. J. Packer and E. L. Mutterties J. Am. Chem. Soc. 1963, 85, 3035.

164. G. G. Mather, A. Pidcock and G.J.N.R. Rapsey, J. Chem. Soc., Dalton Trans. 2095 (1975).

165. N. Juranič, R. L. Lichter M. P. Celap, M.J. Malinar and P. N. Radivojsa Inorg. Chim. Acta 1982, 62, 131.

166. N. Juranič, private communication, University of Balgrade, Belgrade, Yugoslavia.

167. R. Weiss, unpublished results, Department of Chemistry, Iowa State University, Ames, Iowa, 1978, under the direction of Dr. John Verkade.

168. S.C.F. Au-Yeung and D. E. Eaton J. Mag. Res. 1983, 52, 351.

169. S.C.F. Au-Yeung and D. E. Eaton J. Mag. Res. 1983, 52, 366.

170. W. Bösch and P. S. Pregosin Helv. Chem. Acta 1979, 62, 838.

171. D. M. Appel, A.S.F. Boyd, I. W. Robertson, D. M. Roundhill and T. A. Stephenson Inorg. Chem. 1982, 21, 449.

172. L. E. Carpenter II, R. A. Jacobson and J. G. Verkade Phosphorus and Sulfur 1979, 6, 475.

173. D. S. Milbrath, J. P. Springer, J. C. Clardy and J. G. Verkade J. Am. Chem. Soc. 1976, 98, 5493.

174. M. G. Newton and B. S. Campbell J. Am. Chem. Soc. 1974, 96, 7790.

175. P. M. Main, M. M. Woolfson and G. Germain, MULTAIN: A Computer Program for the Automatic Determination of Crystal Structures, Department of Physics, University of York, York, England, 1971.

176. J. F. Blount, C. A. Maryanoff and K. Mislow Tetrahedron Lett. 1975, 913.

177. J. E. Huheey "Inorganic Chemistry: Principles of Structure and Reactivity", 2nd ed.; Harper and Row: New York, 1978.

178. L. Pauling "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

179. E. C. Alyea, S. A. Dias, G. Ferguson and M. Parvez Inorg. Chim. Acta 1979, 37, 45.

180. R. G. Goel and A. C. Srivastava J. Organomet. Chem. 1981, 204, C13.

ACKNOWLEDGEMENTS

I would like to take the opportunity here to acknowledge some of the people whose help made the writing of this dissertation possible. I first would like to thank the many friends and family members whose moral support was invaluable during the last five years. I would next like to thank Mr. Tom Lyttle, Dr. Dee Huang and the Instrument Services group for making sure I was able to have the necessary NMR time. A special thanks in this regard goes to Dave Scott. Dave was never too busy to lend a hand. I would also like to thank the people of Chemistry Stores, the glassblowing shop and the machine shop for the fine service they have given all of us over the years. I would be remiss here if I failed to thank Mr. Art Bartels for keeping the lab and office area clean during the last five years.

It was an enjoyable experience working with and learning NMR theory from Serge Lacelle. It was also a pleasure working with Dr. Jacobson and the x-ray group. I would like to acknowledge the experimental assistance and advice given to me by the past and present members of our research group as well as the stimulating discussions on anything and everything. A special thanks in these regards also goes to Dr. Yeung Yu.

I would like to thank my undergraduate advisor, Dr. R. F. Howe, for introducing me to chemical research and for the constant encouragement he has given me throughout my undergraduate and graduate studies. I would also like to thank my major professor, Dr. John Verkade, for the direction

he has given the research described herein and also for the assistance in writing this dissertation.

I would lastly like to thank Dr. Martha Russell for making the teaching of freshman chemistry such an enjoyable experience.

APPENDIX: FINAL POSITIONAL AND THERMAL PARAMETERS FOR $[Ag(P(NMe_2)_3)_2]BPh_4$ AND $P(O\text{-}2,6\text{-}C_6H_3Me_2)_3$

Table A1. Final positional parameters and their estimated standard deviations (in parentheses)[a] for $[Ag(P(NMe_2)_3)_2]BPh_4$

Atom	X	Y	Z
$[Ag(P(NMe_2)_3)_2]^{+1}$			
Ag	0.15492(5)	0.35297(3)	0.25956(3)
P_1	0.2497(2)	0.3205(1)	0.3788(1)
P_2	0.0548(1)	0.4135(1)	0.1513(1)
N_{1A}	0.1698(5)	0.3312(3)	0.4345(3)
N_{1B}	0.2848(5)	0.2279(3)	0.3904(3)
N_{1C}	0.3574(5)	0.3819(4)	0.4110(3)
N_{2A}	0.9593(5)	0.4753(3)	0.1658(3)
N_{2B}	0.9990(5)	0.3529(3)	0.0861(3)
N_{2C}	0.1349(4)	0.4721(3)	0.1168(3)
C_1	0.0776(7)	0.2738(6)	0.4311(5)
C_2	0.1341(9)	0.4105(5)	0.4457(5)
C_3	0.3113(7)	0.1848(5)	0.3331(4)
C_4	0.3408(8)	0.1964(5)	0.4597(4)
C_5	0.4197(7)	0.4165(5)	0.3651(4)
C_6	0.4244(8)	0.3834(6)	0.4857(4)
C_7	0.8967(6)	0.4545(5)	0.2174(4)
C_8	0.9001(6)	0.5354(4)	0.1167(4)
C_9	0.9289(7)	0.3818(4)	0.0168(3)
C_{10}	0.9623(6)	0.2757(4)	0.1024(4)
C_{11}	0.1943(7)	0.5362(4)	0.1624(4)
C_{12}	0.2166(6)	0.4335(4)	0.0828(4)

---

[a] Positional parameters are listed in fractional unit cell coordinates.

Table A1. (Continued)

Atom	X	Y	Z
$B(C_6H_5)_4^{-1}$			
B	0.6210(6)	0.2569(4)	0.2185(4)
C_1	0.6055(5)	0.3362(3)	0.1717(3)
C_2	0.6328(5)	0.3405(3)	0.1087(3)
C_3	0.6149(6)	0.4071(4)	0.0673(3)
C_4	0.5693(6)	0.4725(4)	0.0888(4)
C_5	0.5410(6)	0.4709(4)	0.1501(4)
C_6	0.5587(6)	0.4043(4)	0.1904(3)
C_7	0.6571(5)	0.2780(4)	0.3019(3)
C_8	0.7248(6)	0.3428(5)	0.3306(4)
C_9	0.7593(7)	0.3590(5)	0.4009(4)
C_{10}	0.7272(8)	0.3100(7)	0.4471(4)
C_{11}	0.6622(8)	0.2460(6)	0.4219(4)
C_{12}	0.6285(6)	0.2299(4)	0.3507(4)
C_{13}	0.4961(6)	0.2092(4)	0.1949(3)
C_{14}	0.4865(7)	0.1303(4)	0.2066(4)
C_{15}	0.3791(8)	0.0900(5)	0.1862(4)
C_{16}	0.2790(8)	0.1279(5)	0.1528(4)
C_{17}	0.2823(7)	0.2062(5)	0.1404(4)
C_{18}	0.3897(6)	0.2454(4)	0.1607(4)
C_{19}	0.7249(6)	0.2036(4)	0.2042(3)
C_{20}	0.7044(7)	0.1503(4)	0.1496(4)
C_{21}	0.7933(10)	0.1067(5)	0.1380(5)
C_{22}	0.9077(10)	0.1146(6)	0.1805(6)
C_{23}	0.9319(7)	0.1665(6)	0.2339(5)
C_{24}	0.8422(6)	0.2096(4)	0.2459(3)

Table A1. (Continued)

Atom	X	Y	Z
H_2	0.6679	0.2904	0.0932
H_3	0.6362	0.4089	0.0203
H_4	0.5558	0.5227	0.0583
H_5	0.5060	0.5210	0.1656
H_6	0.5375	0.4028	0.2373
H_8	0.7483	0.3795	0.2953
H_9	0.8097	0.4082	0.4207
H_{10}	0.7530	0.3219	0.5008
H_{11}	0.6387	0.2091	0.4572
H_{12}	0.5782	0.1806	0.3309
H_{14}	0.5649	0.1017	0.2322
H_{15}	0.3748	0.0308	0.1955
H_{16}	0.1992	0.0984	0.1373
H_{17}	0.2043	0.2349	0.1148
H_{18}	0.3940	0.3049	0.1513
H_{20}	0.6179	0.1446	0.1177
H_{21}	0.7750	0.0669	0.0966
H_{22}	0.9746	0.0815	0.1712
H_{23}	0.0170	0.1727	0.2660
H_{24}	0.8603	0.2495	0.2873

Table A2. Thermal parameters and their estimated standard deviations[a,b] (in parentheses) for $[Ag(P(NMe_2)_3)_2]BPh_4$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
$[Ag(P(NMe_2)_3)_2]^{+1}$						
Ag	5.91(4)	6.62(4)	3.4(3)	-0.04(2)	0.39(2)	1.70(2)
P_1	4.40(8)	4.84(9)	3.09(7)	-0.02(7)	0.69(6)	0.99(6)
P_2	3.99(8)	4.17(8)	2.96(7)	-0.09(6)	0.74(6)	0.73(6)
N1A	5.8(3)	5.0(3)	4.6(3)	0.2(2)	1.9(2)	0.4(2)
N1B	6.1(3)	5.1(3)	4.2(3)	0.7(2)	1.1(2)	0.6(2)
N1C	5.9(3)	6.4(3)	4.9(3)	-1.4(3)	1.0(2)	0.9(2)
N2A	5.0(3)	5.8(3)	4.3(3)	-0.1(2)	1.9(2)	0.2(2)
N2B	5.2(3)	4.0(2)	4.1(3)	-0.6(2)	0.9(2)	0.7(2)
N2C	4.1(2)	4.3(2)	4.0(2)	-0.1(2)	1.2(2)	0.2(2)
C_1	6.3(4)	9.3(6)	8.4(5)	-2.4(4)	3.2(4)	-0.6(4)
C_2	10.9(6)	6.0(6)	9.3(6)	2.1(4)	4.6(5)	0.1(4)
C_3	7.4(5)	6.7(4)	7.4(5)	-0.1(4)	4.0(4)	-1.3(4)
C_4	9.4(6)	6.1(4)	5.4(4)	1.2(4)	0.5(4)	2.1(3)
C_5	6.1(4)	8.5(5)	7.4(5)	-1.6(4)	2.4(4)	2.5(4)
C_6	9.1(6)	10.6(6)	4.6(4)	-3.5(5)	0.0(4)	0.3(4)
C_7	5.5(4)	8.6(5)	5.2(4)	-1.6(3)	3.1(3)	-0.8(3)
C_8	5.9(4)	5.7(4)	5.8(4)	1.4(3)	1.9(3)	0.8(3)
C_9	6.4(4)	5.7(4)	3.5(3)	0.3(3)	0.0(3)	0.4(3)

---

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}\ell^2)/4 + (B_{12}a^*b^*hk + B_{13}a^*c^*h\ell + B_{23}b^*c^*k\ell)/2]$.

[b] Isotropic thermal parameters of the hydrogen atoms were fixed at values assigned by $B_H = (1.0 + B)Å^2$ (B is the isotropic thermal parameter on the bonded carbon) giving B_{11} values H_2, 4.65; H_3, 5.13; H_4, 5.29; H_5, 5.35; H_6, 5.40; H_8, 6.22; H_9, 6.81; H_{10}, 7.30; H_{11}, 7.13; H_{12}, 5.56; H_{14}, 5.78; H_{15}, 6.70; H_{16}, 7.26; H_{17}, 6.87; H_{20}, 6.26; H_{21}, 7.90; H_{22}, 7.21; H_{23}, 6.55; H_{24}, 5.25

Table A2. (Continued)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C_{10}	6.3(4)	3.9(3)	6.4(4)	-1.0(3)	2.4(3)	0.8(3)
C_{11}	6.4(4)	6.2(4)	5.9(4)	-2.2(3)	1.9(3)	-1.7(3)
C_{12}	4.6(3)	5.8(4)	6.5(4)	1.0(3)	2.6(3)	0.21(3)
$B(C_6H_5)^{-1}$						
B	4.0(3)	4.1(3)	3.6(3)	0.3(3)	0.9(3)	0.2(3)
C_1	3.3(3)	3.9(3)	3.5(3)	-0.1(2)	0.6(2)	0.1(2)
C_2	4.2(3)	4.2(3)	3.7(3)	0.1(2)	0.7(2)	0.2(2)
C_3	5.2(3)	4.9(4)	3.5(3)	-0.3(3)	0.7(2)	0.3(3)
C_4	5.4(4)	3.8(3)	4.8(4)	-0.4(3)	0.2(3)	0.8(3)
C_5	5.7(4)	3.9(3)	5.1(4)	0.3(3)	1.1(3)	-0.1(3)
C_6	4.9(3)	4.2(3)	4.7(3)	0.3(3)	1.3(3)	0.0(3)
C_7	3.7(3)	5.6(4)	3.8(3)	0.7(3)	1.1(2)	1.1(3)
C_8	4.9(3)	7.8(5)	4.0(3)	-0.9(3)	0.9(3)	-0.7(3)
C_9	5.5(4)	9.0(6)	5.0(4)	0.0(4)	0.1(3)	-1.3(4)
C_{10}	6.9(5)	11.3(7)	3.5(4)	2.3(5)	0.6(3)	0.1(4)
C_{11}	7.6(5)	9.5(6)	3.8(4)	2.2(5)	1.7(3)	1.9(4)
C_{12}	5.2(4)	6.6(4)	4.5(3)	1.3(3)	1.1(3)	1.5(3)
C_{13}	4.6(3)	4.5(3)	3.8(3)	0.2(3)	1.0(2)	0.7(2)
C_{14}	6.1(4)	4.7(4)	5.6(4)	-0.2(3)	1.2(3)	1.1(3)
C_{15}	7.0(5)	5.7(4)	6.2(4)	-1.4(4)	1.3(4)	0.6(3)
C_{16}	6.7(5)	7.5(5)	5.6(4)	-2.7(4)	1.4(4)	-0.1(4)
C_{17}	4.9(4)	8.2(5)	5.7(4)	-0.3(4)	0.6(3)	1.6(4)
C_{18}	4.2(3)	5.5(4)	5.3(3)	0.0(3)	0.9(3)	0.8(3)
C_{19}	4.7(3)	4.1(3)	4.4(3)	0.7(3)	1.3(3)	1.8(3)
C_{20}	7.0(4)	4.7(3)	5.4(4)	1.2(3)	2.3(3)	0.3(3)
C_{21}	10.0(6)	5.3(4)	8.6(6)	2.1(5)	4.5(5)	0.7(4)
C_{22}	9.6(7)	6.6(5)	10.3(7)	4.5(5)	6.4(6)	4.6(5)
C_{23}	5.5(4)	7.6(5)	7.8(5)	2.5(4)	3.0(4)	3.6(4)
C_{24}	5.1(4)	5.8(4)	5.1(4)	0.9(3)	1.8(3)	1.9(3)

Table A3. Final positional[a] and thermal parameters and their estimated standard deviations (in parentheses) for $P(O\text{-}2,6\text{-}C_6H_3Me_2)_3$

Atom	X	Y	Z	B_{iso}, Å^2
P	0.6667	0.3333	0.5000	5.8(1)
O	0.6696(6)	0.2363(6)	0.3710(16)	6.3(2)
C_1	0.7317(10)	0.1958(9)	0.4610(23)	5.6(3)
C_2	0.8284(10)	0.2232(10)	0.3367(25)	6.5(3)
C_3	0.8878(13)	0.1785(13)	0.4213(28)	8.6(4)
C_4	0.8498(13)	0.1093(13)	0.6002(28)	7.6(4)
C_5	0.7605(13)	0.0860(12)	0.6954(26)	7.4(4)
C_6	0.6946(10)	0.1286(11)	0.6269(24)	6.4(3)
C_7	0.8584(12)	0.2902(13)	0.1539(27)	8.1(4)
C_8	0.5867(15)	0.1016(16)	0.7190(32)	9.2(5)

[a] Positional parameters are listed infractional unit cell coordinates.