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Ligation of Phosphorus Ligands to Silver(I). 2. Electronic and Steric Effects in the Coordination of One to Four $P(OR)_3$ and PR_3 Ligands

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Syntheses for the isolable complexes $\{Ag[P(OPh)_3]_3\}BF_4$, $\{Ag[P(O\text{-}i\text{-}Pr)_3]_3\}BPh_4$, $\{Ag[P(O\text{-}i\text{-}Pr)_3]_4\}X$ (X = BF_4, BPh_4), $\{Ag[P(O\text{-}t\text{-}Bu)_3]_2\}BF_4$, $\{Ag[P(O\text{-}t\text{-}Bu)_3]X\}$ (X = Cl, I, CN), $\{Ag[P(O\text{-}t\text{-}Bu)_3]_2NO_3\}$ and $\{Ag[P(O\text{-}2,6\text{-}Me_2C_6H_3)_3]BF_4\}$ are described. ^{31}P NMR chemical shift and $^1J(^{107}Ag^{31}P)$ coupling constant data are reported for these and additional solution species of the type AgL_n^+ where n may vary from 1 to 4 for L = PEt_3, $PPhMe_2$, PPhMe, PPh_3, $P(OMe)_3$, $P(OEt)_3$, $P(O\text{-}t\text{-}Bu)_3$, $P(OCH_2CH_2Cl)_3$, $P(OCH_2CCl_3)_3$, $P(OCH_2)_3CEt$, $\overline{P(OCH_2)_2CHO}$, $P(OPh)_3$, $P(O\text{-}o\text{-}tol)_3$ and $P(O\text{-}2,6\text{-}Me_2C_6H_3)_3$. What appear to be linear correlations are observed for $^1J(AgP)$ vs. electronegativity of the atom bound to phosphorus in AgL_n^+ species for n = 1–4. It is concluded from the ^{31}P NMR data, the ligand-exchange characteristics of some of the complexes, and the results of ligand competition experiments that ligand electronic effects in addition to steric influences determine the coordination behavior of phosphorus ligands in these complexes. Comparison of the Ag(I) ligating properties of the very bulky ligands $P(O\text{-}t\text{-}Bu)_3$, $P(t\text{-}Bu)_3$, and $P(2,4,6\text{-}Me_3C_6H_2)_3$ reveals that steric effects appear to dominate. In contrast to $P(2,4,6\text{-}Me_3C_6H_2)_3$, which is expected to possess a larger cone angle than $P(O\text{-}2,6\text{-}Me_2C_6H_3)_3$, the former ligand allows isolation of an AgL_2^+ complex, which in the case of the latter ligand is observed only in solution and is in equilibrium with the monoligated species.

Introduction

An examination of the ligand properties of the aminophosphines **1**–**3** in part 1 of this series[1] revealed (inter alia) that (a) the coordination number limit of **1** and **2** for stable complexes of Ag(I) is 3, presumably because of the large cone angles for these ligands (168 and 164°, respectively[2]), (b) the

$P(NMe_2)_3$ **1** $P(NMeCH_2)_3CMe$ **2** $P(\overline{NCH_2CH_2})_3$ **3**

coordination number limit for the smaller ligand **3** (cone angle 108°, see ref 2) is 4 despite its lower basicity compared to $P(NMe_2)_3$, (c) the dominant form in solution of the 1:1 complexes of **2** and **3** to $AgBF_4$ is the nonconducting species $[AgLBF_4]$ wherein **2** and **3** are of comparable basicity, whereas the more basic **1** forms $[AgL]BF_4$, and (d) the ligands in $[Ag(\mathbf{2})_3]^+$ are completely displaced by **1** and **3**, suggesting that Ag^+ prefers the more basic **1** or the sterically smaller **3**. These observations are consistent with the idea that electronic as well as steric factors are important in the coordination of aminophosphines to Ag^+.

In a report by others, there was a suggestion that the apparently small differences in the affinity of Ag(I) for $P(C_6H_4\text{-}p\text{-}Me)_3$ and $P(OEt)_3$ as well as in the dissociation constants for $Ag[P(C_6H_4\text{-}p\text{-}Me)_3]_4^+$ and $Ag[P(OEt)_3]_4^+$ reflected a greater charge-neutralizing effect for a phosphine compared to a less basic phosphite, which approximately cancels its greater steric requirements.[3] Here, we present several lines of evidence that electronic effects can exceed steric influences in complexes of Ag(I) containing phosphorus ligands. In addition, the ligand $\overline{P(OCH_2)_2CHO}$ is shown from low-temperature solution NMR spectroscopy to form only a monoligated Ag(I) complex in solution despite its very small steric requirement, whereas $P(OCH_2)_3CEt$ and even larger phosphites such as $P(O\text{-}i\text{-}Pr)_3$ form isolable four-coordinate complexes. Several new two- and three-coordinate phosphite complexes are isolated for the first time including the interesting complex $[(2,6\text{-}Me_2C_6H_3O)_3PAgBF_4]$.

Table I. Conductances and Melting Points

	molar conductance,[a] Ω^{-1} cm^2 mol^{-1}	mp, °C
$[Ag(PPhMe_2)_4]BF_4$	115[b]	79-80
$[Ag(PPh_2Me)_4]BF_4$	126[b]	174-5
$[Ag(PPh_3)_4]BF_4$	107[b]	278-80
$\{Ag[P(OMe)_3]_4\}BF_4$	50.8	97-8
$\{Ag[P(OEt)_3]_4\}BF_4$	57.8	114-5
$\{Ag[P(OCH_2CH_2Cl)_3]_4\}BF_4$	49.5	66-7
$\{Ag[P(OCH_2)_3CEt]_4\}BF_4$	135[b]	dec >240
$\{Ag[P(O\text{-}i\text{-}Pr)_3]_4\}BF_4$	62.0	84-5
$\{Ag[P(O\text{-}i\text{-}Pr)_3]_4\}BPh_4$	139[b]	55-7
$\{Ag[P(O\text{-}i\text{-}Pr)_3]_3\}BPh_4$	139[b]	66-8
$\{Ag[P(OPh)_3]_3BF_4\}$	14.2[c]	95-8
$\{Ag[P(O\text{-}t\text{-}Bu)_3]_2\}BF_4$	63.0	91
$\{Ag[P(O\text{-}t\text{-}Bu)_3]_2NO_3\}$	7.3	137
$\{Ag[P(O\text{-}t\text{-}Bu)_3]Cl\}$	0	145-6
$\{Ag[P(O\text{-}t\text{-}Bu)_3]CN\}$	0	148
$\{Ag[P(O\text{-}2,6\text{-}Me_2C_6H_3)_3]BF_4\}$	7.3	215

[a] Measured on a ca. 10^{-3} M CH_2Cl_2 solution at 25 °C unless otherwise specified. [b] Measured on a ca. 10^{-3} M CH_3CN solution at 25 °C. [c] A conductance of 25.0 Ω^{-1} cm^2 mol^{-1} was measured in nitrobenzene at 25 °C wherein 1:1 electrolytes typically possess conductances between 20 and 30 Ω^{-1} cm^2 mol^{-1}.

Experimental Section

All solvents were reagent grade and were dried by using common techniques. All silver salts were from commercial sources and were used as received. The ligands $P(OMe)_3$, $P(OEt)_3$, $P(OCH_2CH_2Cl)_3$, $P(OPh)_3$, PPh_3, PEt_3, PMe_2Ph, $PMePh_2$, PF_3, and $P(O\text{-}o\text{-}tol)_3$ were purchased commercially and were purified by distillation or recrystallization with the exception of PF_3, which was used as received. Literature procedures were followed to prepare $\overline{P(OCH_2)_2CHO}$,[4] $P(OCH_2)_3CEt$,[5] $P(O\text{-}t\text{-}Bu)_3$,[6a] $MeO\overline{POCH_2CH_2O}$,[7] $MeO\overline{POCH_2CMe_2CH_2O}$,[8] $P(OCH_2CCl_3)_3$,[9] and $P(O\text{-}i\text{-}Pr)_3$.[10]

Melting points were measured on a Thomas Hoover capillary melting point apparatus and are uncorrected. Conductances were measured with an Industrial Instruments Inc. Model 16B7 conductivity bridge. ^1H (89.55 MHz) NMR spectra were recorded with a JEOL FX-90O spectrometer in the FT mode locked on the ^2H resonance of a deuterated solvent. ^{31}P NMR spectra were obtained with either

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Table II. ^{31}P NMR Chemical Shifts (ppm) and ^{107}Ag–^{31}P Spin–Spin Couplings (Hz) of AgL_nX^a

L	X	$\delta(^{31}P)$ of free L	$\delta(^{31}P)/^1J(AgP)$ of AgL_nX			
			$n = 1$	$n = 2$	$n = 3$	$n = 4$
PEt_3	BF_4	−20.0	10.3 712	8.9 482	1.9 304	7.7 218
P(*n*-Bu)$_3$	BF_4	−32.5	...^{b} 759^b	32.9^b 470^b	26.6^b 304^b	15.5^b 219^b
P(*p*-tol)$_3$	PF_6	1.1^c		13.4^c 496^c	10.6^c 321^c	5.6^c 224^c
$PPhMe_2$	BF_4	−47.0				−31.6 212
PPh_2Me	BF_4	−28.0				−16.0 230
PPh_3	BF_4	−7.4				7.5 222
P(*t*-Bu)$_3$	BF_4	60.8^d		80.0^d 444^d		
P(mesityl)$_3$	PF_6	−39.1^e		−25.8^e 513^e		
$P(OMe)_3$	BF_4	139.8				133.7 341
$P(OEt)_3$	ClO_4	139.8	125.4^f 1038^f	123^g 756^g	129^g 472^g	133^g 341^g
P(O-*i*-Pr)$_3$	BPh_4	140.6	123.0 1046	122.9 761	135.9 473	132.1 342
P(O-*t*-Bu)$_3$	BF_4	138.5	102.1 1118	102.7 747	113.8 469	
$P(OCH_2CH_2Cl)_3$	BF_4	138.9				131.1 346
$P(OCH_2CCl_3)_3$	BF_4	136.6	129.7 989	125.3 691	126.3 507	
$P(OCH_2)_3CEt$	BF_4	91.8				101.5 369
$P(OCH_2)_2CHO$	BF_4	106.1	118.0 1057			
$P(OPh)_3$	BF_4	127.5	120.0 992	116.8 667	115.7 505	116.5 345
P(O-*o*-tol)$_3$	BF_4	129.1	122.4 992	155.8 692	155.0 500	
P(O-2,6-$Me_2C_6H_3)_3$	BF_4	143.9	127.4 1063	120.6 700 ± 20		
$P(OEt)_3$	Cl	139.8		134.3^g 550^g	135.5^g 408^g	131^g 341^g
$P(OEt)_3$	NO_3	139.8		127.5^g 680^g	134.8^g 450^g	133.2^g 342^g
P(O-*t*-Bu)$_3$	Cl	138.5	114.4 888	118.4 614		
P(O-*t*-Bu)$_3$	I	138.5	106.0 719	113.4 570		
P(O-*t*-Bu)$_3$	CN	138.5	115.1 658			
P(O-*t*-Bu)$_3$	NO_3	138.5		121.1 717		

^{a} Measured in 75% CH_2Cl_2/25% acetone-d_6 at -95 °C unless otherwise indicated. Chemical shifts are in units of ppm downfield from 85% H_3PO_4. ^{b} Unpublished data of de Bie, M. J. A., quoted by: Diehl, P.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes"; Springer-Verlag: Berlin, 1979. ^{c} Measured in CH_2Cl_2 at -80 °C.[3] ^{d} Measured in CH_2Cl_2 at ambient temperature.[18] ^{e} Measured in CH_2Cl_2 at ambient temperature.[35] ^{f} Measured in this work on the BF_4^- salt. ^{g} Measured in 80/20 dichloromethane/toluene at −100 °C.[3]

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 and locked on the ^{2}H resonance of a deuterated solvent. The external reference was PCl_3 (219.4 ppm), and chemical shifts are reported with respect to 85% H_3PO_4. All ^{31}P NMR spectra were run in 75% CH_2Cl_2/25% acetone-d_6 at -95 °C unless otherwise indicated. Spectra of silver complexes obtained unlocked in 100% CH_2Cl_2 showed no significant difference in the values of ^1J(AgP) or $\delta(^{31}P)$. Conductance and ^{31}P NMR data are given in Tables I and II, respectively. Molecular weights were determined at 37 °C with a Knaur vapor pressure osmometer.

SeP(OR)$_3$. Selenophosphates were prepared by the procedure of Nicpon and Meek for the preparation of phosphine selenides.[11] A solution of phosphite (0.4 mmol) and KSeCN (0.4 mmol) was stirred in acetonitrile for 30 min. The selenophosphates were then extracted with benzene after removal of solvent. $SeP(OCH_2CCl_3)_3$ was further purified by sublimation at 100 °C (1 torr): SeP(O-*t*-Bu)$_3$ ^{31}P NMR ($(CD_3)_2CO$) δ 31.8, lit.[6b] δ 31.1; $SeP(OCH_2Cl_3)_3$ mp 77–79 °C, ^{1}H NMR ($CDCl_3$) δ 4.7 (d, ^3J(PH) = 8 Hz), ^{31}P NMR ($(CD_3)_2CO$) δ 71.7, low-resolution mass spectrum showing 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 ($CDCl_3$) δ 59.7, lit.[12] δ 58; SeP(O-2,6-$C_6H_3Me_2)_3$ ^{31}P NMR (CD_3CN) δ 51.0; SeP(O-*o*-tol)$_3$ ^{31}P NMR ($(CD_3)_2CO$) δ 55.0.

P(O-2,6-Me$_2$C$_6$H$_3$)$_3$. Although the preparation of this compound has previously been reported,[13] 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

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a solution of 2,6-dimethylphenol (41.3 g, 38.8 mmol) in 200 mL of Et_2O. The solution temperature was kept at 5 °C 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 °C (5 torr). Two recrystallizations from hexanes gave the product in 83% yield as white needles: mp 93–93.5 °C, (lit.[13] mp 83–4 °C); ^1H NMR ($CDCl_3$) δ. 2.2 (s, 2 H), 6.9 (m, 1 H, C_6H_3); ^{31}P NMR ($(CD_3)_2CO$) δ 143.9.

$\{Ag[P(OMe)_3]_4\}BF_4$. To a solution of $AgBF_4$ (0.302 g, 1.55 mmol) in 50 mL of acetone was injected $P(OMe)_3$ (3.20 g, 25.8 mmol). Addition of Et_2O resulted in the precipitation of the product, which was subsequently recrystallized by slow addition of Et_2O to an acetone solution to give a 74% yield of the complex: ^1H NMR ($(CD_3)_2CO$, 25 °C) δ 3.69 (d, $^3J(PH) = 11.7$ Hz). Anal. Calcd for $C_{12}H_{36}BF_4O_{12}P_4$: C, 20.85; H, 5.21. Found: C, 21.00; H, 5.41. Prepared in a similar manner in comparable yields were $[AgL_4]BF_4$ complexes where L = $P(OCH_2)_3CEt$, $P(OCH_2CH_2Cl)_3$, $P(OEt)_3$, and $P(O\text{-}i\text{-}Pr)_3$.

$[Ag(PPh_3)_4]BF_4$. This compound was prepared as described earlier for the perchlorate salt[14] with the modification that acetone was used as a solvent instead of EtOH. It was recrystallized in 81% yield from acetonitrile/ether. Prepared in a similar manner in comparable yields were analogous complexes where L = PMe_2Ph and $PMePh_2$, which were recrystallized from acetone/ether.

$\{Ag[P(OPh)_3]_3\}BF_4$. To a solution of $AgBF_4$ (0.173 g, 0.891 mmol) in 15 mL of acetone was injected $P(OPh)_3$ (2.18 g, 7.63 mmol). The solution was filtered, and the product was obtained in 74% yield after washing with Et_2O. This complex could be recrystallized by slow addition of ether to an acetone solution. Anal. Calcd for $C_{54}H_{45}AgBF_4O_9P_3$: C, 57.61; H, 4.00; P, 8.26. Found: C, 58.31; H, 4.25; P, 8.26.

$\{Ag[P(O\text{-}i\text{-}Pr)]_3\}BPh_4$. To a solution of $AgBF_4$ (0.219 g 1.12 mmol) in 20 mL of EtOH was added $P(O\text{-}i\text{-}Pr)_3$ (1.20 g, 5.76 mmol). The solution was allowed to stir for 2 min before $NaBPh_4$ (0.500 g, 1.46 mmol) was added. The product crystallized over a period of 2 h upon cooling to −20 °C. A 97% yield was obtained after washing with EtOH and drying on a vacuum line for $^1/_2$ h: ^1H NMR ($(CD_3)_2CO$) δ 6.5–7.5 (m, 20 H, C_6H_5), 4.7 (m, 9 H, CH), 1.3 (d, 54 H, CH_3, $^2J(HH) = 6.3$ Hz.

$\{Ag[P(O\text{-}t\text{-}Bu)_3]_2\}BF_4$. To a solution of $AgBF_4$ (0.340 g, 1.74 mmol) in 30 mL of Me_2CHOH was added $P(O\text{-}i\text{-}Pr)_3$ (3.45 g, 16.6 mmol). After the solution was allowed to stir for 2 min, $NaBPh_4$ (0.660 g, 1.93 mmol) was added to precipitate the product, which was subsequently recrystalled in 89% yield from acetone/ether: ^1H NMR ($(CD_3)_2CO$) δ 6.5–7.5 (m, 20 H, C_6H_5), 4.8 (m, 12 H, CH), 1.3 (d, 72 H, CH_3, $^2J(HH) = 6.3$ Hz).

$\{Ag[P(O\text{-}t\text{-}Bu)_3]_2\}BF$. To a solution of $AgBF_4$ (0.214 g, 1.10 mmol) in 20 mL of acetone was added $P(O\text{-}t\text{-}Bu)_3$ (1.50 g, 6.00 mmol). The solution was allowed to stir for 10 min. Addition of Et_2O (10 mL) and hexanes (50 mL) resulted in the precipitation of the complex in 67% yield: ^1H NMR ($(CD_3)_2CO$) δ 1.5 (s).

$\{Ag[P(O\text{-}t\text{-}Bu)_3]_2NO_3\}$. To a suspension of $AgNO_3$ (0.300 g, 1.76 mmol) in 20 mL of Et_2O was injected $P(O\text{-}t\text{-}Bu)_3$ (2.50 g, 10.0 mmol). The mixture was allowed to stir as the $AgNO_3$ reacted and dissolved. Cooling to −70 °C produced colorless needles that could be recrystallized from Et_2O in 59% yield; ^1H NMR ($CDCl_3$) δ 1.4 (s). Anal. Calcd for $C_{24}H_{54}AgO_9NP_2$: C, 42.99; H, 8.07. Found: C, 43.19; H, 8.39.

$\{Ag[P(O\text{-}t\text{-}Bu)_3]Cl\}$. To a suspension of AgCl (0.319 g, 2.22 mmol) in 50 mL of Et_2O was added $P(O\text{-}t\text{-}Bu)_3$ (2.23 g, 8.92 mmol). The AgCl went into solution over a period of 10 min. Hexanes were then added, and the solution was cooled to −70 °C overnight to precipitate the product. A yield of 69% was obtained after recrystallization from hexanes: ^1H NMR ($CDCl_3$) δ 1.4 (s). 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 was the analogous iodide complex, which could only be isolated as an oil in 55% yield upon attempted recrystallization from hexanes (^1H NMR ($CDCl_3$) δ 1.4 (s), and the analogous cyanide complex, which was recrystallized from hexane in 51% yield (^1H NMR ($CDCl_3$) δ 1.4 (s)).

$\{Ag[P(O\text{-}2,6\text{-}Me_2C_6H_3)_3]BF_4\}$. In 30 mL of CH_2Cl_2 containing ligand (0.450 g, 1.14 mmol) was suspended $AgBF_4$ (0.200 g, 1.02 mmol). The mixture was allowed to stir for 5 min during which time the $AgBF_4$ reacted and dissolved. 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 to a solution of 50% CH_2Cl_2/Et_2O: ^1H NMR (CD_3CN) δ 6.9 (m, 1 H, C_6H_3), 2.1 (s, 2 H, CH_3).

Results and Discussion

Isolated Complexes. The complexes described in the Experimental Section have not been previously reported. Additional experimental data for these compounds, except for $\{Ag[P(O\text{-}t\text{-}Bu)_3]I\}$ which is an oil, are collected in Table I. Of the four-coordinate AgL_4^+ compounds reported here, the complexes in which L = $P(OMe)_3$ have previously been isolated as the ClO_4^- [15] and BPh_4^- [16] salts, L = $P(OCH_2)_3CMe$ (herein $P(OCH_2)_3CEt$) as the ClO_4^- and NO_3^- salts,[17] and L = PPh_3 as the ClO_4^-, BrO_3^-, and NO_3^- [14] salts. In so far as possible we used BF_4 and BPh_4 anions for safety reasons. In a previous report[3] $\{Ag[P(OEt)_3]_4\}X$ (X = Cl, Br, I, SCN, NO_3, ClO_4) were isolated as oils.

The compounds $\{Ag[P(OPh)_3]_3\}BF_4$, $\{Ag[P(O\text{-}i\text{-}Pr)_3]_3\}BPh_4$, and $\{Ag[P(O\text{-}t\text{-}Bu)_3]_2\}BF_4$ appear to represent the first examples of isolated silver(I) complexes that are tri- and diligated by phosphite esters, respectively, wherein a normally poorly coordinating anion such as BF_4^- or BPh_4^- is also present. From the conductances listed in Table I for these complexes, it can be concluded that in CH_2Cl_2 solution $\{Ag[P(O\text{-}t\text{-}Bu)_3]_2\}BF_4$ appears to be two-coordinate with a completely dissociated BF_4^- ion. Substantially complete anion dissociation also occurs in the $[AgL_3]BPh_4$ complex where L = $P(O\text{-}i\text{-}Pr)_3$ since its conductance in CH_3CN is identical with the analogous $[AgL_4]BF_4$ complex where L is a phosphine (Table I). The low conductance of $\{Ag[P(OPh)_3]_3BF_4\}$ seems to be inductive in origin since $\{Ag[P(p\text{-}tol)_3]_{2,3}\}X$ (X = PF_6^-),[3] as well as $\{Ag[P(O\text{-}t\text{-}Bu)_3]_2BF_4\}$ (Table I), conduct substantially better. Not unexpectedly, the complexes $\{Ag[P(O\text{-}t\text{-}Bu)_3]X\}$ (X = Cl, CN) are nonconductors. The low conductance of $\{Ag[P(O\text{-}t\text{-}Bu)_3]_2NO_3\}$ is somewhat puzzling, however, since the coordination of a second phosphite ester ligand might be expected to completely displace a ligated NO_3^- ion that is weakly coordinating compared to I^- or CN^-. Thus, $\{Ag[P(t\text{-}Bu)_3]_2NO_3\}$ behaves as a 1:1 electrolyte.[18] As will be seen later, the ^{31}P NMR spectrum of $\{Ag[P(O\text{-}t\text{-}Bu)_3]_2NO_3\}$ complex is not consistent with dissociation of a phosphite ligand according to equilbrium 1.

$$\{Ag[P(O\text{-}t\text{-}Bu)_3]_2NO\} \rightleftharpoons \{Ag[P(O\text{-}t\text{-}Bu)_3]NO_3\} + P(O\text{-}t\text{-}Bu)_3 \quad (1)$$

^{31}P NMR Spectra. As seen in Table II, coordinated phosphine chemical shifts are generally downfield of the free ligand while they tend to be upfield in the case of phosphite esters. Although the ^{31}P NMR chemical shifts of the AgL_n^+ species are not diagnostic of the value of n, the magnitude of $^1J(AgP)$ under slow-exchange conditions has been shown[3,19,20] to be very helpful in this respect. In Figure 1 are plotted the electronegativities of the atoms bound to phosphorus in the ligands in AgL_n^+ against the $^1J(AgP)$ data in Table II for acyclic[21] phosphines and phosphites and also the data from our previous work with $P(NMe_2)_3$.[1] From this figure it is seen that the progression of $^1J(AgP)$ with electronegativity from PEt_3 to $P(NMe_2)_3$ to $P(OEt)_3$ is quite linear for n = 1–3.[21]

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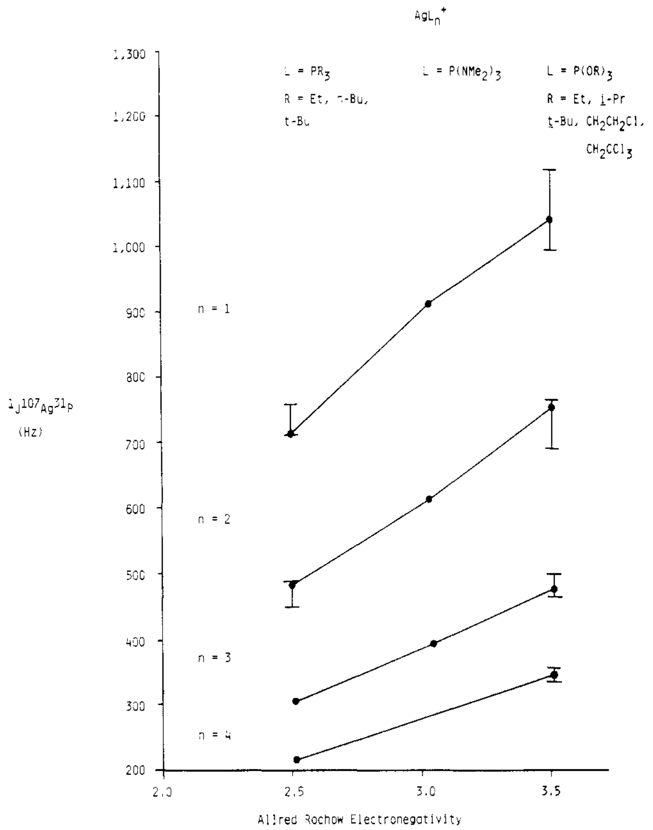

Figure 1. Plots of $^1J(^{107}Ag^{31}P)$ against Allred Rochow electronegativities of the atoms bound to phosphorus in AgL_n^+ species. Pauling electronegativities provide very similar results. Couplings (taken from Table II) correspond to the ligands indicated, and lines are drawn through points for L = PEt_3, $P(NMe_2)_3$, and $P(OEt)_3$ (see text).

It should be noted that the nearly linear slopes are drawn through points representing PEt_3 and $P(OEt)_3$ since those for the corresponding methyl analogues were not available for a possibly better comparison with $P(NMe_2)_3$. The results shown in Figure 1 parallel the linearity of $^1J(^{77}Se^{31}P)$ with phosphorus substituent electronegativity.[7] A second feature of Figure 1 is the gradual increase in slope with decreasing *n*. As *n* decreases for a given ligand, the increasing s character in the Ag(I) bonding hybrids is expected to augment Ag–P coupling.[1,3,19,20] Of secondary importance but concomitant with a decrease in *n* is a diminution in the effectiveness of the ligand in neutralizing the positive charge on the silver cation. Hence, the positive charge of silver in the Fermi contact term also increases in importance along with the increase in s character of the silver hybridization. The charge effect is expected to augment as the Lewis basicity of the ligand decreases from PR_3 to $P(NR_2)_3$ to $P(OR)_3$, thus perhaps accounting for the rising slopes in the same order. A third feature of interest in Figure 1 is that ^1J(AgP) for $Ag[P(NMe_2)_3]_4^+$ (ca. 280 Hz) can be predicted, on the assumption of persistance of the linearity of the relationship for *n* = 4. Evidence for this ion as an intermediate was presented earlier,[1] but ^1J(AgP) could not be detected for it. It may be noted in this connection, however, that ^1J(AgP) for $Ag[P(NCH_2CH_2)_3]_4^+$ was determined to be 302 Hz.[1]

The ^{31}P NMR assignments in Table II for species not isolated were made by comparison with data published in the literature cited in the table for analogous systems and with cited data obtained on isolated compounds containing ligands of the same type. The unisolated species were observed in the NMR solvent (Table II) by successive addition of molar equivalents of ligand.

Table III. Data for Steric and Ligation Characteristics of Phosphorus Ligands

ligand	cone angle,[a] deg	$\Sigma\chi$[b]	^1J-($^{77}Se^{31}P$),[c] Hz	solid[d]	soln[e]
$P(NCH_2CH_2)_3$	108		851[f]	4	4
$P(NMeCH_2)_3CMe$	164	6.5	854[f]	3	3
$P(NMe_2)_3$	157	5.7	784[f]	3	3
PEt_3	132	5.4	705[o]	...	4
P(*t*-Bu)$_3$	182	0.0	712[g]	2[h]	2[h]
PMe_2Ph	122	9.5	710[i]	4	4
$PMePh_2$	136	11.2	725[i]	4	4
PPh_3	145	12.9	735[i]	4	4
P(*p*-tol)$_3$	145	10.9	723[j]	4[k]	4[k]
P(mesityl)$_3$	212			2[l]	2[l]
$P(OCH_2)_2CHO$	<101		1099[m]	...	1
$P(OCH_2)_3CEt$	101	33.9[n]	1053[m]	4	4
$P(OMe)_3$	107	23.1	954[m]	4	4
$P(OEt)_3$	109	20.4	935[o]	4	4
$P(OCH_2CH_2Cl)_3$	110	27.9	955[o]	4	4
$P(OCH_2CCl_3)_3$	115	35.7	1018	...	3
P(O-*i*-Pr)$_3$	130	18.9	912[o]	4	4
P(O-*t*-Bu)$_3$	172		924	2	3
$P(OPh)_3$	127	29.1	1025	3	4
P(O-*o*-tol)$_3$	140	27.9	1022	...	3
P(O-2,6-$Me_2C_6H_3)_3$	190		1012	1	2

[a] Taken from: Tolman, C. A. *Chem. Rev.* 1977, *77*, 313. $P(OCH_2)_2CHO$ is assumed to be less than the values for $P(OCH_2)_3CEt$ (101°) and $P(NMeCH_2)_3CMe$, which is ca. 164° based on X-ray structural data of its oxide and BH_3 adduct: Clardy, J. C.; Kolpa, R. L.; Verkade, J. G. *Phosphorus Relat. Group V Elem.* 1974, *4*, 133. [b] Values calculated from data given in reference quoted in ref 2. [c] Values for the selenide derivatives. [d] Isolated compounds. [e] Observed in the ^{31}P NMR spectrum (see text). [f] White, D. W.; Karcher, B. A.; Jacobson, R. A.; Verkade, J. G. *J. Am. Chem. Soc.* 1979, *101*, 4921. [g] DuMont, W. W.; Kroth, H.-J. *J. Organomet. Chem.* 1976, *113*, L35. [h] Reference 18. [i] McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* 1973, 2162. [j] Pinnell, R. P.; Megerle, L. A.; Manatt, S. L.; Kroon, P. A. *J. Am. Chem. Soc.* 1973, *95*, 977. [k] Reference 3. [l] Reference 35. [m] Reference 7. [n] Calculated from data for $(OC)_3Ni[P(OCH_2)_3CMe]$ given in: Verkade, J. G.; McCarley, R. E.; Hendricker, D. G.; King, R. W. *Inorg. Chem.* 1965, *4*, 228. [o] Stec, W. J.; Okruszek, A.; Uznanski, B.; Michalski, J. *Phosphorus Relat. Group V Elem.* 1972, *2*, 97.

Electronic Effects. Several observations can be made that appear to be devoid of steric influences and hence can be attributed to electronic effects of the ligands. Successive addition of molar equivalents of $P(OCH_2)_2CHO$ to $AgBF_4$ results in the detection at −95 °C of an $AgLBF_4$ species only (Table II). Ratios of ligand to metal larger than 1 give rise to an additional ^{31}P NMR resonance corresponding to free ligand. For a phosphite ligand of such small cone angle (<101°, Table III) it seems odd that detectable coordination beyond one phosphite molecule of this type does not occur in contrast to all the other phosphites in Table II including the related cage $P(OCH_2)_3CEt$. A rationale for the anomalous behavior of $P(OCH_2)_2CHO$ is that the phosphorus is sufficiently electronegative by reason of its abnormally small OPO and POC bond angles[22] that its σ basicity is reduced and its π acidity is augmented to the point where it effectively behaves as a Lewis acid for Ag^+. Sufficient polarization of Ag^+ in this

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(21) Only data for acyclic ligands appear in Figure 1 since constraint of aminophosphines and phosphites results in abnormally large ^1J(SeP) couplings (see ref 7) and also, as seen herein, in larger than expected ^1J(AgP) couplings for the constrained phosphite ester complexes.

(22) Vande Griend, L. J.; Verkade, J. G.; Pennings, J. F. M.; Buck, H. M. *J. Am. Chem. Soc.* 1977, *99*, 2459.

manner could prevent additional ligands from coordinating to the metal. More evidence for the poor σ basicity and presumably strong π acidity of this ligand compared to $\mathrm{P(OMe)_3}$ and $\mathrm{P(OCH_2)_3CMe}$ is found in the energies of CO stretches in metal carbonyl complexes,[23] the values of $^1J(\mathrm{HP})$ and $^1J(^{77}\mathrm{Se}^{31}\mathrm{P})$ in the protonated and selenated ligands, respectively, the energies of the P=O stretches of the corresponding phosphates,[24] and the energies of the B—H stretch of their $\mathrm{BH_3}$ adducts.[25] No evidence of coordination of $\mathrm{PF_3}$ to Ag(I) could be seen in ^{31}P NMR spectra taken at −90 °C of a saturated solution of $\mathrm{PF_3}$ in acetone that was 0.1 M in $\mathrm{AgBF_4}$. This result is not unexpected in view of the fact that the $\sum\chi$ value of $\mathrm{PF_3}$ (56.3)[26] is significantly greater than for phosphorus ligands that coordinate to silver(I). The poor basicity of $\mathrm{PF_3}$ compared to phosphites and phosphines has also been demonstrated by the high value of $^1J(\mathrm{PH})$ for $\mathrm{HPF_3^+}$.[27]

A consideration of cone angles alone (Table III) leads to the conclusion that $\mathrm{P(OCH_2CCl_3)_3}$ (115°) should easily form a Ag(I) complex of coordination number greater than 3, since P(O-*i*-Pr)$_3$ (130°), $\mathrm{P(OPh)_3}$ (127°), and $\mathrm{PPh_3}$ (145°) all form four-coordinate $\mathrm{AgL_4^+}$ species. The low σ basicity of $\mathrm{P(OCH_2CCl_3)_3}$ owing to the inductive effects of the halogens appears to be responsible for this phenomenon as is also suggested by comparison of the $\sum\chi$ and $^1J(\mathrm{SeP})$ values for these ligands in Table II.

The isolable AgLX complexes where L = P(O-*t*-Bu)$_3$ and P(*t*-Bu)$_3$ and X = CN, Cl, or I also afford information regarding the role of ligand electronic effects. Again in contrast to the phosphine complexes that exhibit Ag–P coupling at room temperature, the phosphite complexes do not, although ligand exchange is slowed sufficiently to observe coupling at −95 °C. A dissociative mechanism may operate here, in which the anion donates strongly enough to permit more facile dissociation of the phosphite than the more strongly basic phosphine. Following dissociation, ligand exchange could also be effected by equilibrium 2. Indeed, addition of excess phosphine or

$$\mathrm{[AgLX] + L \rightleftharpoons [AgL_2X]\ or\ [AgL_2]^+ + X^-} \qquad (2)$$

phosphite at −95 °C leads to $\mathrm{AgL_2^+}$ plus free ligand in the case of the phosphine[18] whereas with the phosphite $\mathrm{[AgL_2X]}$ is formed with the chloride and the iodide.[28,29] With the iodide, ^{31}P NMR spectra taken between 180 and 200 K indicate that $\mathrm{AgL_2I}$ is favored with decreasing temperature. Since $\mathrm{AgL_3^+}$ for L = P(O-*t*-Bu)$_3$ can exist in solution (vide infra), it can be concluded that the phosphite is insufficiently basic compared to P(*t*-Bu)$_3$ to displace halogen from $\mathrm{[AgL_2X]}$.

Ligand competition reactions were performed as shown in equilbrium 3.[30] For all ligands in these experiments, the

$$\mathrm{AgL_4^+ + 4L' \rightleftharpoons AgL'_4 + 4L} \qquad (3)$$

stronger free ligand displaced all of the bound ligand and in several instances reverse reactions were carried out to verify that the equilibria favored binding of the stronger ligand. The reactions, which were followed by ^{31}P NMR, revealed the orders

$$\mathrm{PMe_2Ph > MeO\overline{PO(CH_2)_2O} \simeq MeO\overline{POCH_2CMe_2CH_2O}}$$
$$\mathrm{\simeq PEt_3 > P(OMe)_3 > P(OCH_2)_3CEt,\ \overline{P(OCH_2)_2CHO}}$$

and

$$\mathrm{P(O\text{-}\mathit{i}\text{-}Pr)_3 > P(OCH_2)_3CEt > P(OPh)_3}$$

With the cone angle,[31] ^{1}J(SeP),[31] and $\sum\chi$ data in Table III as criteria of relative steric requirements and basicities, respectively, dominant basicity influences in equilibrium 3 are seen in the relationships of the following ligand pairs:

$\mathrm{PMe_2Ph}$ > monocyclic phosphites
$\mathrm{PMe_2Ph > P(OMe)_3}$
$\mathrm{P(OMe)_3 > P(OCH_2)_3CEt}$
$\mathrm{PEt_3 > P(OMe)_3}$
$\mathrm{PMe_2Ph > P(OCH_2)_3CEt}$
all L > $\mathrm{\overline{P(OCH_2)_2CHO}}$
$\mathrm{PPh_3 > P(OCH_2)_3CEt}$
$\mathrm{PEt_3 > P(OCH_2)_3CEt}$
P(O-*i*-Pr)$_3$ > $\mathrm{P(OCH_2)_3CEt}$

It is noteworthy that the relationship found here between $\mathrm{P(OMe)_3}$ and $\mathrm{P(OCH_2)_3CEt}$ with respect to $\mathrm{AgL_4^+}$ was observed to be opposite for $\mathrm{NiL_4}$ wherein steric effects dominate.[32] Dominant steric influences can also be seen among the above ligation orders, and they will be discussed in the next section. Addition of a large excess of $\mathrm{P(OMe)_3}$ to $\mathrm{\{Ag[P(NMe_2)_3]_2\}BPh_4}$ does not result in the displacement of the more basic (though larger) $\mathrm{P(NMe_2)_3}$. Examination of the ^{31}P NMR of a solution containing equivalent amounts of $\mathrm{\{Ag[P(NMe_2)_3]_2\}BPh_4}$ and $\mathrm{P(OMe)_3}$ shows that the resonance for $\mathrm{P(OMe)_3}$ is a much broadened singlet at 130 ppm (10 ppm upfield of the shift of the free ligand) indicative of a weak interaction between $\mathrm{P(OMe)_3}$ and $\mathrm{Ag[P(NMe_2)_3]_2^+}$. Additional $\mathrm{P(OMe)_3}$ shifted the position of the resonance toward that of the free ligand.

Steric Effects. The low conductance of {Ag[P(O-*t*-Bu)$_3$]$_2$NO$_3$} in $\mathrm{CH_2Cl_2}$ contrasts that of {Ag[P(*t*-Bu)$_3$]$_2$}NO$_3$, which was previously reported to be a 1:1 electrolyte in the same solvent.[18] The higher conductance of the latter complex can be ascribed to the larger size of the phosphine ligands that blocks coordination of the $\mathrm{NO_3^-}$ ion. Earlier, poorly conducting complexes of the type $\mathrm{[AgL_2NO_3]}$ where L = P(C$_6$H$_4$-*p*-Me)$_3$,[3] $\mathrm{P(NMe_2)_3}$,[1] and $\mathrm{P(OMe)_3}$[16,33] were reported. The last complex was determined by X-ray crystallography to be dimeric with bridging nitrates in the solid state, but solution molecular weight and infrared data were ambiguous.[33] Dimeric behavior for complexes wherein L = $\mathrm{P(NMe_2)_3}$ or P(O-*t*-Bu)$_3$ is less likely owing to the large size of these ligands.

In solution, $\mathrm{P(OPh)_3}$ is seen in Table II to form an $\mathrm{AgL_4^+}$ species with $\mathrm{AgBF_4}$. The more sterically hindered P(O-*o*-tol)$_3$ and P(O-2,6-Me$_2$C$_6$H$_3$)$_3$, however, are limited to forming

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(23) Vande Griend, L. J. Ph.D. Thesis, Iowa State University, Ames, IA, 1975. For example $\nu_{\mathrm{CO}}E'$ for *trans*-Fe(CO)$_3$[$\mathrm{\overline{P(OCH_2)_2CHO}}$]$_2$ (1962 cm^{-1}) compares to that previously reported for *trans*-Fe(CO)$_3$[P(OCH$_2$)$_3$CCH$_3$]$_2$ (1933 cm^{-1}) (Verkade, J. G.; McCarley, R. E.; Hendricker, D. G.; King, R. W. *Inorg. Chem.* **1965**, *4*, 228) and for *trans*-Fe(CO)$_3$[P(OMe)$_3$]$_2$ (1923 and 1914 cm^{-1}) (Cotton, J. D.; Heaylwood, R. L. *Aust. J. Chem.* **1969**, *22*, 2673).

(24) Vande Griend, L. J.; White, D. W.; Verkade, J. G. *Phosphorus Relat. Group V Elem.* **1973**, *3*, 5.

(25) White, D. W.; Verkade, J. G. *Phosphorus Relat. Group V Elem.* **1973**, *3*, 9.

(26) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953.

(27) Vande Griend, L. J.; Verkade, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 5958.

(28) These unisolated compounds are formulated as nonconductors at low temperature on the basis of their ^{31}P NMR spectral parameters (Table II), which reveal chemical shifts different from those of the corresponding $\mathrm{[AgL_2]BF_4}$ species and lower Ag–P coupling constants that are expected from decreased silver charge and s character in the Ag–P bonds. Their monomeric behavior is inferred from the lack of four-bond Ag–P coupling, which might be expected in the case of an halide-bridged dimer as in $\mathrm{[L_2PtX_4]_2}$ (Kiffen, A.; Masters, C.; Visser, J. *J. Chem. Soc., Dalton Trans.* **1975**, 1311) and the room temperture molecular weights of the [AgLCl] (found 402, calculated 393) and [AgLCN] (found 305, calculated 384) in 1,2-dichloroethane.

(29) The ^{31}P NMR spectrum of $\mathrm{[AgL_2CN]}$ could not be frozen out down to 178 K.

(30) For the ligand $\mathrm{\overline{P(OCH_2)_2CHO}}$ the corresponding Ag(I) complex is $\mathrm{AgL^+}$ (see earlier discussion).

(31) The cone angles of the monocyclic phosphites $\mathrm{MeO\overline{POCH_2CH_2O}}$ and $\mathrm{MeO\overline{POCH_2CMe_2CH_2O}}$ are assumed to be less than 107°, which is the value for $\mathrm{P(OMe)_3}$ (see ref 2). The $^1J(\mathrm{SeP})$ values for the five- and six-membered selenophosphates are 1011[7] and 985 Hz, respectively: Vande Griend, L. J. Ph.D. Thesis, Iowa State University, 1975.

(32) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

(33) Meiners, J. H.; Clardy, J. C.; Verkade, J. G. *Inorg. Chem.* **1975**, *14*, 632.

silver(I) complexes in which the phosphites triligate and diligate, respectively. Since the basicities of these aryl phosphites are similar,[34] the steric effect clearly dominates here.

From the ligand-displacement orders observed in connection with equilibrium 3, the following relationships among ligand pairs are seen from the cone angle and ^1J(PSe) data in Table III to be dominated by steric effects:

$P(OMe)_3 > PPh_3$
$P(OCH_2)_3CEt > P(OPh)_3$
monocyclic phosphites $> P(OMe)_3$
monocyclic phosphites $> PPh_3$

Addition of 4 molar equiv of $P(OMe)_3$ to a solution of $\{Ag[P(O\text{-}t\text{-}Bu)_3]_2\}BF_4$ results in the quantitative formation of $\{Ag[P(OMe)_3]_4\}BF_4$. Since $P(OMe)_3$ appears from the ^1J(PSe) data in Table III to be less basic than $P(O\text{-}t\text{-}Bu)_3$, the smaller size of $P(OMe)_3$ seems to be the overriding factor in the displacement reaction.

Very Bulky Ligands. Although both $P(O\text{-}t\text{-}Bu)_3$ and $P(t\text{-}Bu)_3$ form isolable $[AgL_2]BF_4$ complexes if excess ligand is used in the preparation, $\{Ag[P(t\text{-}Bu)_3]_2\}BF_4$ displays Ag–P spin–spin coupling in its solution ^{31}P NMR spectra at room temperature.[18] However, NMR spectra of solutions containing an equimolar mixture of this complex and free ligand consist of a singlet at room temperature while at −90 °C separate signals due to free phosphine and the dicoordinate complex are observed.[18] In contrast, the analogous $P(O\text{-}t\text{-}Bu)_3$ complex does not display Ag–P coupling at room temperature although it is observed at −90 °C. Again in contrast to the $P(t\text{-}Bu)_3$ complex for which addition of excess ligand collapses the AgP coupling to a singlet at room temperature,[18] a 0.2 M solution of the $P(O\text{-}t\text{-}Bu)_3$ complex in the presence of 2 molar equiv of ligand consists of signals assignable to the corresponding $[AgL_3]BF_4$ complex plus free ligand. Earlier it was suggested that $\{Ag[P(t\text{-}Bu)_3]_2\}BF_4$ undergoes ligand exchange by an associative mechanism in the presence of excess ligand.[18] This is clearly the case for the analogous $P(O\text{-}t\text{-}Bu)_3$ complex since evidence for the formation of the $[AgL_3]^+$ species can be observed. A three-coordinate $P(t\text{-}Bu)_3$ complex appears to be less stable owing to the larger size of the ligands. The instability of AgL_3^+ is even more pronounced with the still larger $P(2,4,6\text{-}Me_3C_6H_2)_3$ since addition of excess ligand to the AgL_2^+ species resulted in no detectable change in the ^{31}P NMR spectrum.[35]

In an attempt to make a two-coordinate cationic silver complex of a phosphite ligand that would less readily exchange at room temperature, complexes of $P(O\text{-}2,6\text{-}Me_2C_6H_3)_3$ were examined. It was believed that the greater steric requirements of $P(O\text{-}2,6\text{-}Me_2C_6H_3)_3$ as opposed to $P(O\text{-}t\text{-}Bu)_3$ would destablize a three-coordinate cation and hence retard the intermolecular exchange of the two-coordinate cation. When 4 equiv of $P(O\text{-}2,6\text{-}Me_2C_6H_3)_3$ was added to a methylene chloride solution of $AgBF_4$, however, $\{Ag[P(O\text{-}2,6\text{-}Me_2C_6H_3)_3]BF_4\}$ precipitated from solution upon addition of hexanes. As expected, this complex showed a relatively low conductivity in CH_2Cl_2 (Table I), which suggests coordination of the BF_4 anion. The nature of the BF_4^- interaction with the metal in these complexes is presently not clear. The room-temperature and −95 °C ^{19}F NMR spectra of $\{Ag[P(O\text{-}2,6\text{-}Me_2C_6H_3)_3]BF_4\}$ in solution give data consistent with the presence of ionic BF_4^-.[36] An indication that the BF_4^- interaction changes from the solution to the solid state comes from a comparison of the ^{31}P NMR spectrum for this complex and $\{Ag[P(NMe_2)_3]_2\}BPh_4$ in the two states. The latter complex was shown to have very comparable $\delta(^{31}P)$ and ^1J(AgP) values in solution and in the solid.[1,37] The phosphite complex, however, shows significant changes in NMR parameters from the solution (Table II) to the solid state ($\delta(^{31}P)$ 112.6, ^1J(AgP) = 803 Hz[37]). The decrease in Ag–P coupling may arise from a stronger interaction of the BF_4^- ion with the silver in the solid state wherein solvation effects are absent. Complexes of the type $[R_3PAgOClO_3]$ are known.[38] Here, the ligands are bulky trialkyl- or triarylphosphines, and the silver is two-coordinate in the solid state.

Though poorly resolved, $\{Ag[P(O\text{-}2,6\text{-}Me_2C_6H_3)_3]BF_4\}$ in a solution of 5% acetone-d_6 in CH_2Cl_2 displays Ag–P coupling at 273 K, a unique phenomenon among silver phosphite complexes. Because of its low coordination number, silver(I) forms an Ag–P bond sufficiently strong to prevent exchange by prior dissociation at this temperature. It may be noted here that although $P(OPh)_3$ is a ligand of similar basicity, $\{Ag[P(OPh)_3]_3BF_4\}$ does undergo rapid ligand exchange at 273 K, probably owing to dilution of the Ag–P bonding interaction by the larger coordination number. For this complex, dissociation would also appear to be more facile from the neutral $[AgL_3BF_4]$ species than from the AgL_3^+ ion. At 250 K, the AgP coupling in $\{Ag(P\text{-}O\text{-}2,6\text{-}Me_2C_6H_3)_3BF_4\}$ is well resolved but collapses upon addition of ligand. At 194 K in a solution containing a 3.3 molar ratio of ligand to silver, peaks for free phosphite ligand, monoligated silver and diligated silver in area ratios of 1 to 1.3 to 1 are observed. The metal–phosphorus coupling in the monoligated species is resolved while in the diligated species the resolution of this coupling is poorer. We were unable to isolate the diligated species, in contrast to the report of the isolation of $\{Ag[P(mesityl)_3]_2\}PF_6$,[35,39] which, however, exhibits Ag–P coupling in solution at ambient temperature. The AgL_2^+ cation where L = $P(O\text{-}2,6\text{-}Me_2C_6H_3)_3$ is apparently more unstable with respect to ligand dissociation compared with the corresponding $P(mesityl)_3$ species, despite the fact that the phosphine ligand is larger as defined by the Tolman cone angle. Hence, if ligand exchange occurs by a dissociative mechanism, it can be concluded that the phosphite–metal interaction in the complex, which is diligated by phosphorus, is weaker owing to the poorer basicity of the ligand and/or the effectively larger steric bulk of the ligand.[40] Although it has been found that excess ligand does not affect the the ^{31}P NMR spectrum of $\{Ag[P(mesityl)_3]_2\}PF_6$, smaller phosphines do displace the ligand by an associative mechanism.[35] The complex $\{Ag[P(mesityl)_3]_2\}PF_6$ apparently does not exchange its own ligand associatively,[35] and the fact that $\{Ag[P(O\text{-}2,6\text{-}Me_2C_6H_3)_3]BF_4\}$ is observed along with the corresponding AgL_2BF_4 complex (but with no detectable AgL_3BF_4 species) in the presence of excess ligand strongly suggests that AgL_2BF_4 species can exchange by dissociation to $[AgLBF_4]$.

Acknowledgment. J.G.V. thanks the NSF for a grant in support of this research.

Registry No. $[Ag(PPhMe_2)_4]BF_4$, 92054-73-4; $[Ag(PPh_2Me)_4]BF_4$, 92054-74-5; $[Ag(PPh_3)_4]BF_4$, 92054-75-6; $\{Ag[P(OMe)_3]_4\}BF_4$, 72907-62-1; $\{Ag[P(OEt)_3]_4\}BF_4$, 92054-76-7; $\{Ag[P(OCH_2CH_2Cl)_3]_4\}BF_4$, 92054-78-9; $\{Ag[P(OCH_2)_3CEt]_4\}BF_4$, 92142-13-7; $\{Ag[P(O\text{-}i\text{-}Pr)_3]_4\}BF_4$, 92054-80-3; $\{Ag[P(O\text{-}i\text{-}Pr)_3]_4\}BPh_4$, 92054-81-4;

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(34) The decrease in ^1J(SeP) with increasing cone angle of these ligands seen in Table II can be attributed to an increase in basicity owing to the inductive effect of the methyl groups on the aromatic rings.

(35) (a) Alyea, E. C.; Dias, S. A.; Stevens, S. *Inorg. Chim. Acta* **1980**, *44*, L203. (b) Alyea, E. C., personal communication.

(36) Brownstein, S. *Can. J. Chem.* **1978**, *56*, 343.

(37) Socol, S.; Frye, J.; Verkade, J. G., to be submitted for publication.

(38) Dikhoff, T. G. M. H.; Goel, R. G. *Inorg. Chim. Acta* **1980**, *44*, L72.

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Direct Observation of the Ground-State Splitting in d^5 and d^7 Metallocenes by Inelastic Neutron Scattering

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The splitting of the two lowest orbitally degenerate Kramers doublets in d^5 and d^7 metallocenes has been determined by inelastic neutron scattering spectroscopy at 10 K. The separation is 515 $\pm$ 10 cm^{-1} in Fe(C$_5$D$_5$)$_2$X, where X = PF$_6^-$, AsF$_6^-$, or I$_3^-$, and 173 $\pm$ 5 cm^{-1} in cobaltocene. The orbital degeneracy of the ground state is lifted under the combined effect of nonaxial ligand field components and spin–orbit coupling. The analysis of the neutron data confirms that the dynamic Jahn–Teller effect has to be taken into account. The vibronic coupling is of comparable importance, resulting in a drastic reduction of the ground-state parameters calculated in an adiabatic model. Several molecular vibrations, particularly of cobaltocene, have been observed by inelastic neutron scattering and IR. By comparison with d^5, d^6, d^7, and d^8 metallocenes, an assignment of frequencies to the fundamental modes of vibration has been performed.

1. Introduction

The dicyclopentadienyl transition-metal complexes, particularly ferrocene, have been the subject of many experimental and theoretical studies since their discovery. Of special interest to the theoretical chemist has been the nature of the unusual chemical bonding of these highly symmetrical sandwich compounds.[2] A very simple electrostatic model[3,4] allows the rationalization of a remarkably large number of properties of the full series of stable metallocenes of the first transition series such as ground-state configurations, trends in the metal–carbon bond lengths, and thermodynamic stabilities.

Ferrocene, the most stable metallocene, is a diamagnetic, closed-shell d^6 system. The remaining members of the first transition series are paramagnetic, where the d^5 and d^7 metallocenes may have a quasi orbitally degenerate ground state. The latter are of particular interest since they may be subject to a Jahn–Teller distortion allowing a deeper insight into their electronic structure. In order to determine quantitative information about chemical bonding and dynamic Jahn–Teller effects in orbitally degenerate sandwich molecules, d^5 and d^7 metallocenes have been diluted in a large variety of diamagnetic host systems and have been studied by EPR.[5-9] The pronounced host lattice dependence of the **g** tensors can be explained almost entirely by changes in the low-symmetry components of the matrix potentials splitting the orbital degeneracy of the guest molecule by different amounts. With use of perturbation theory a strong dependence of the g tensor of the ground state on the first excited Kramers doublet can be shown. Thus the separation of the two lowest states can be estimated by EPR experiments.[5-9]

On the other hand, theoretical calculations by Ammeter and Swalen[6] suggest that the splitting between these two states is drastically reduced by the dynamic Jahn–Teller effect compared to the case for the simpler adiabatic model. This reduction is associated with the fact that the upper doublet is energetically much closer to the lowest excited vibrational levels and therefore undergoes a much stronger vibronic mixing effect than the lower doublet. Hence the vibronic coupling suppresses a substantial part of the static rhombic field.

Even though these energy splittings are too large for direct determination by EPR, the splitting of the two lowest Kramers doublets has been estimated to be about 200 cm^{-1} in cobaltocene and, depending on the host lattice, between 500 and 1000 cm^{-1} in the ferrocenium ion.[5-10] Infrared and Raman spectroscopy, which cover the spectral range of interest, suffer in their applicability from the selection rule $\Delta S = 0$.[11]

Inelastic neutron scattering (INS) is a powerful tool for the study of low-energy excitations in crystalline transition-metal and lanthanide compounds.[12-14] Splittings on the order of a few to several hundred wavenumbers are accessible by INS;

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