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Contribution from the Department of Chemistry and Ames Laboratory of the DOE,
Iowa State University, Ames, Iowa 50011

Ligation of Phosphorus Ligands to Silver(I). 1. Coordination of One to Four $P(NR_2)_3$ Ligands and the Structure of a Nonlinear Two-Coordinate Complex

S. M. SOCOL,[1a] R. A. JACOBSON,[1b] and J. G. VERKADE*[1a]

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The ligation properties of three aminophosphine ligands, $P(NMe_2)_3$ (**1**), $P(NMeCH_2)_3CMe$ (**2**), and $P(\overline{NCH_2CH_2})_3$ (**3**), toward Ag(I) have been investigated. Reaction of **1** with silver salts yields the isolable ionic complexes $[Ag(\mathbf{1})_2]BPh_4$ and $[Ag(\mathbf{1})_3]BPh_4$ and neutral complexes of the type $Ag(\mathbf{1})_2X$ (X = Cl, Br, I, CN). Reaction of excess **2** with $AgBF_4$ also resulted in the formation of an ionic three-coordinate complex. The substantial steric requirement of **1** and **2** appears to preclude the formation of stable four-coordinate complexes. In contrast, the smaller ligand **3** readily forms isolable four-coordinate complexes of the type $[Ag(\mathbf{3})_4]X$, where X = BF_4, Cl, I. Addition of three successive molar equivalents of **2** or **3** to solutions of $AgBF_4$ at -95 °C allowed observation of $[AgL_{2,3}]BF_4$ in their ^{31}P NMR spectra. Evidence is presented suggesting that the 1:1 complexes are better formulated as weak or nonconducting $[Ag(L)BF_4]$ species. On the other hand, addition of **1** to solutions of $AgBF_4$ at -95 °C allowed observation of $[Ag(\mathbf{1})_{1-4}]BF_4$ in the ^{31}P NMR spectra. Addition of a fourth equivalent of **1** or **2** to the corresponding three-coordinate cations gave NMR results consistent with ligand exchange as did addition of ligand to $[Ag(\mathbf{1})_2X]$ (X = Cl, CN, NO_3), but addition of a fourth equivalent of **3** to $[Ag(\mathbf{3})_3]BF_4$ gave $[Ag(\mathbf{3})_4]BF_4$. At room temperature these complexes appear to undergo rapid ligand exchange. X-ray crystallographic studies of $[Ag(\mathbf{1})_2]BPh_4$ reveal a monoclinic space group $P2_1/c$ with $a = 11.975$ (3) Å, $b = 17.325$ (3) Å, $c = 20.079$ (5) Å, and $\beta = 107.08$ (3)°. Both ligands were found to be in an approximate C_s configuration with a Ag-P distance of 2.394 (3) Å and P-Ag-P angle of 167°.

Introduction

Phosphorus ligands of the type PZ_3 (Z = Ar, OAr, R, OR) are well recognized for their ability to stabilize metal complexes in a variety of oxidation states and coordination geometries. In recent years such ligands have also assumed considerable importance in the formation of homogeneous and heterogeneous transition-metal catalyst systems. In NiL_4 complexes, steric factors have been ascribed a dominant role in accounting for the coordination properties of such PZ_3 ligands,[2,3] whereas in AgL_4^+ systems ligand basicity effects gain importance owing to the presence of a positive charge and a larger metal radius.[4] Aminophosphines have not been nearly so extensively investigated as have phosphines and phosphites. The series **1-3**

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

offers the interesting opportunity to study a set of ligands of the same general class possessing differing steric properties and basicity. Molecular models show **1** and **2** to be nearly the same size while the cone angle of **3** (108°) is reported to be significantly less than that of **1** (157°).[5]

A useful measure of phosphorus basicity in PZ_3 systems is the value of the $^{31}P-^{77}Se$ one-bond spin-spin coupling in the corresponding selenide.[6] It has now been quite well established that phosphite esters become substantially less Lewis basic upon constraint as measured by BH_3 adduct equilibrium,[7] photoelectron spectroscopic,[8,9] and CNDO/2[10] studies. Moreover, $^1J(^{31}P-^{77}Se)$ values for the corresponding selenophosphates correlate very well with the BH stretching frequencies in the analogous phosphite-borane adducts.[6] To the extent that such correlations can be expected to carry over to aminophosphines, $^1J(^{31}P-^{77}Se)$ values of the corresponding selenides constitute a useful comparison of basicities among the parent aminophosphines. These values for **1-3** (784, 854, and 851 Hz, respectively)[11] suggest that the order of basicity is $\mathbf{1} > \mathbf{2} \simeq \mathbf{3}$. The greater basicity of **1** compared to that of **2** is substantiated by the smaller ν(CO) values in metal carbonyl complexes[12] and the lower lone-pair ionization energy of **1**.[8,13]

During the course of this study the crystalline compound $[Ag(\mathbf{1})_2]BPh_4$ 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 2, 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 **1** in a monovalent metal complex with those in zerovalent iron complexes reported earlier.[14]

The preferred conformation of tris(dialkylamino)phosphines has been a topic of recent interest. Of the five conformations that have been proposed for these molecules (A-E in Figure 1), the two that have drawn theoretical support for being the most stable are structures C and D. Recent ab initio molecular orbital calculations on $P(NH_2)_3$ suggest that C represents the most stable conformation with only a slight energy difference between this structure and D.[15] The same conclusion was reached in an MNDO study of $P(NMe_2)_3$.[16] Unfortunately, $P(NH_2)_3$ exists only as its borane adduct[17] and most uncomplexed acyclic tris(dialkylamino)phosphines such as **1** are liquids at room temperature, which become glasses at low temperature. Recently, however, a number of structures have appeared of coordinated **1**[14,15] or of larger systems containing the PN_3 moiety.[18-24] In these structures the aminophosphines

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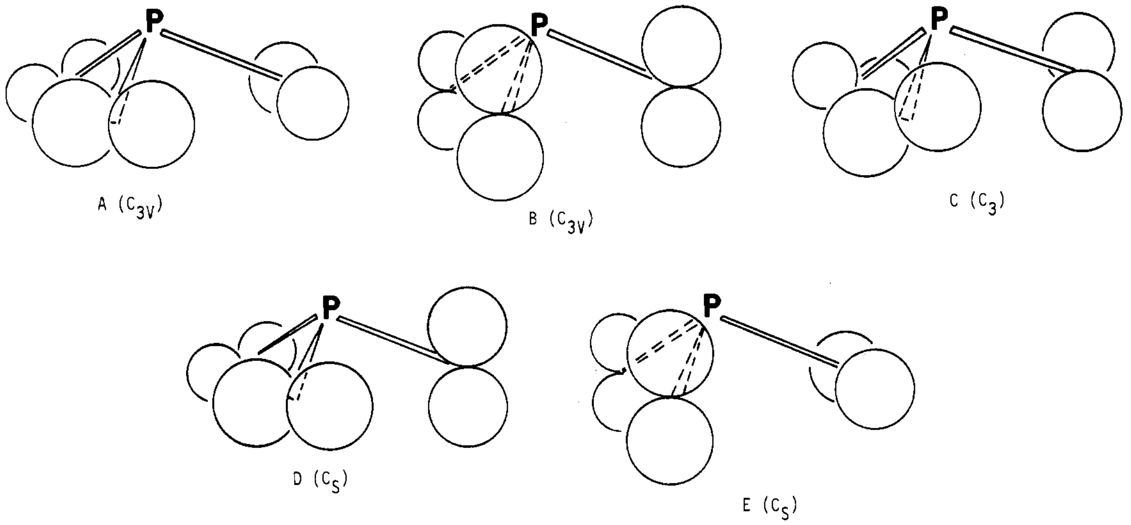

Figure 1. Some possible conformations of tris(dialkylamino)phosphines.

Table I. Conductance, ^{31}P NMR, and Melting Point Data

	molar conductance,[a] mhos cm^2 mol^{-1}	$\delta(^{31}P)$[b]	$^1J(^{107}Ag-^{31}P)$,[b] Hz	mp,[c] °C
$P(NMe_2)_3$ (1)		121.4[d]		
$[Ag(1)_2CN]$	0	124.3	437	68-69
$[Ag(1)_2I]$	0	119.3	507	85-88
$[Ag(1)_2Cl]$	0	121.2	535	82-83
$[Ag(1)_2NO_3]$	6.5	118.6	592	79-81
$[Ag(1)]BF_4$[e]	*f*	121.5	910	
$[Ag(1)_2]BPh_4$	59.8	115.4	610	115-116
$[Ag(1)_3]BPh_4$	54.1	122.1	393	125-126
$P(NMeCH_2)_3CMe$ (2)		83.8[d]		
$[Ag(2)BF_4]$[e]	*f*	90.2	811	
$[Ag(2)_2]BF_4$[e]		90.4	603	
$[Ag(2)_3]BPh_4$	45.1	101.1	394	155-158
$P(\overline{NCH_2C}H_2)_3$ (3)		131.3[d]		
$[Ag(3)BF_4]$	*f*	185.6	801	
$[Ag(3)_4]BF_4$	57.1	118.3	302	170
$[Ag(3)_4]Cl$		117.7	302	
$[Ag(3)_4]I$	2.6[g]	116.1	302	
$[Ag(3)_3I]$[e]		130.3	337	

[a] For 10^{-3} M solution at 25 °C in CH_2Cl_2. [b] Measured in 75/25 CH_2Cl_2/acetone-d_6 at −95 °C unless otherwise indicated. [c] All compounds melted with decomposition. [d] Measured at ambient temperature. [e] Compound was observed in solution but was not isolated. [f] See text. [g] Conductance was measured at −65 °C. Essentially zero conductance was measured at 25 °C.

adopt conformations closely resembling either C or D. For example, the ligand in $Fe(1)(CO)_4$ adopts conformation C[14] as does one of the ligands in *trans*-$Fe(1)_2(CO)_3$.[15] 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.[25] Support for this postulate comes from structural data of $OP(NR_2)_3$ molecules. As expected, the nitrogens are more planar in $OP[N(CH_2CH_2)_2O]_3$ than in $SeP[N(CH_2CH_2)_2O]_3$, wherein the phosphorus is less electronegative.[21] 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.[24]

Experimental Section

Materials. All solvents were reagent grade and were dried over molecular sieves (4A). For the conductivity measurements, CH_2Cl_2 was distilled from P_4O_{10}. Alfa Products was the source of $AgBF_4$, and **1** (85%) was obtained from Aldrich Chemical Co. and was distilled before use. Literature procedures were used to prepare **2**[6] and **3**.[26] *Because of a previous violent explosion in our laboratories, the purification of 3 by distillation was not attempted.*[11] The crude product was judged to be greater than 90% pure by ^{31}P NMR spectroscopy.

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 75/25 CH_2Cl_2/acetone-d_6 at −95 °C unless stated otherwise. Spectra of silver complexes that 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 with a Knaur vapor pressure osmometer at 37 °C. Conductance and ^{31}P NMR data are recorded in Table I.

Crystals of $[Ag(1)_2]BPh_4$ were grown by slow diffusion of Et_2O into a saturated solution of the complex in CH_2Cl_2. A crystal was cut to dimensions of approximately 0.2 × 0.2 × 0.2 mm and was mounted and sealed in a Lindemann capillary. The crystal was indexed in an automatic indexing procedure[27] using 12 independent reflections.

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Table II. Bond Distances (Å), Angles (deg), and Selected Intramolecular Contacts (Å) for $[Ag(1)_2]BPh_4$

	$Ag[P(NMe_2)_3]_2^+$		
Ag–P$_1$	2.395 (2)	N$_{2B}$–C$_9$	1.485 (8)
Ag–P$_2$	2.393 (2)	N$_{2B}$–C$_{10}$	1.475 (9)
P$_1$–N$_{1A}$	1.683 (7)	N$_{2C}$–C$_{11}$	1.482 (9)
P$_1$–N$_{1B}$	1.658 (6)	N$_{2C}$–C$_{12}$	1.504 (10)
P$_1$–N$_{1C}$	1.651 (6)	C$_1$···C$_3$	4.161 (12)
P$_2$–N$_{2A}$	1.655 (6)	C$_1$···C$_4$	3.316 (12)
P$_2$–N$_{2B}$	1.658 (5)	C$_2$···C$_5$	4.193 (13)
P$_2$–N$_{2C}$	1.681 (6)	C$_2$···C$_6$	3.363 (14)
N$_{1A}$–C$_1$	1.473 (11)	C$_3$···C$_5$	4.210 (12)
N$_{1A}$–C$_2$	1.475 (11)	C$_4$···C$_6$	3.386 (13)
N$_{1B}$–C$_3$	1.482 (11)	C$_7$···C$_{10}$	4.076 (11)
N$_{1B}$–C$_4$	1.462 (9)	C$_7$···C$_{11}$	4.252 (11)
N$_{1C}$–C$_5$	1.474 (12)	C$_8$···C$_9$	3.410 (10)
N$_{1C}$–C$_6$	1.479 (9)	C$_8$···C$_{11}$	3.369 (11)
N$_{2A}$–C$_7$	1.490 (11)	C$_9$···C$_{12}$	3.427 (11)
N$_{2A}$–C$_8$	1.465 (9)		
P$_2$–Ag–P$_1$	166.9 (1)	C$_3$–N$_{1B}$–C$_4$	114.1 (6)
Ag–P$_1$–N$_{1A}$	116.4 (2)	C$_3$–N$_{1B}$–P$_1$	118.8 (5)
Ag–P$_1$–N$_{1B}$	113.2 (2)	C$_4$–N$_{1B}$–P$_1$	121.5 (5)
Ag–P$_1$–N$_{1C}$	109.1 (2)	C$_5$–N$_{1C}$–C$_6$	113.8 (6)
N$_{1A}$–P$_1$–N$_{1B}$	100.6 (3)	C$_5$–N$_{1C}$–P$_1$	119.8 (5)
N$_{1A}$–P$_1$–N$_{1C}$	101.4 (3)	C$_6$–N$_{1C}$–P$_1$	122.6 (6)
N$_{1B}$–P$_1$–N$_{1C}$	115.6 (3)	C$_7$–N$_{2A}$–C$_8$	113.4 (6)
Ag–P$_2$–N$_{2A}$	108.2 (2)	C$_7$–N$_{2A}$–P$_2$	118.7 (5)
Ag–P$_2$–N$_{2B}$	114.8 (2)	C$_8$–N$_{2A}$–P$_2$	124.3 (5)
Ag–P$_2$–N$_{2C}$	116.5 (2)	C$_9$–N$_{2B}$–C$_{10}$	113.0 (5)
N$_{2A}$–P$_2$–N$_{2B}$	114.2 (3)	C$_9$–N$_{2B}$–P$_2$	120.9 (4)
N$_{2A}$–P$_2$–N$_{2C}$	100.9 (3)	C$_{10}$–N$_{2B}$–P$_2$	118.4 (5)
N$_{2B}$–P$_2$–N$_{2C}$	101.7 (3)	C$_{11}$–N$_{2C}$–C$_{12}$	110.9 (5)
C$_1$–N$_{1A}$–C$_2$	112.8 (7)	C$_{11}$–N$_{2C}$–P$_2$	115.2 (5)
C$_1$–N$_{1A}$–P$_1$	117.3 (5)	C$_{12}$–N$_{2C}$–P$_2$	116.4 (4)
C$_2$–N$_{1A}$–P$_1$	116.8 (6)		

$B(C_6H_5)_4^{-\,a}$

	min	max	av
B–C*	1.641	1.653	1.645
C–C	1.358	1.412	1.391
C*–B–C*	108.3	110.5	109.5
B–C*–C	121.9	123.9	122.6
C–C*–C	114.3	115.4	114.7
C*–C$_o$–C$_m$	121.8	123.3	122.9
C$_o$–C*–C$_o$	114.3	115.4	114.7
C$_m$–C$_p$–C$_m$	119.2	119.8	119.5
C$_o$–C$_m$–C$_p$	119.6	120.8	120.0

[a] C* refers to a carbon bonded to boron while C$_o$, C$_m$, C$_p$ refer to carbons on the ortho, meta, and para positions on the phenyl rings, respectively.

It was found to be monoclinic with a = 11.975 (3) Å, b = 17.325 (3) Å, c = 20.079 (5) Å, and β = 107.08 (3)° with four molecules of $[Ag(1)_2]BPh_4$ per unit cell. A density of 1.26 g/cm^3 was computed on the basis of 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 with an automated four-circle diffractometer, built in the Ames Laboratory, that was equipped with a scintillation counter and interfaced to a PDP-15 computer. By use of a procedure described previously,[28] data were collected with graphite-monochromated Mo Kα 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 ($F_0 > 3\sigma(F)$). Lattice constants were obtained by a least-squares refinement of $\pm 2\theta$ for 15 high-angle reflections.

Table III. Final Atomic Positional Parameters for $\{Ag[P(NMe_2)_3]_2\}B(C_6H_5)_4$

	x	y	z
		$Ag[P(NMe_2)_3]_2^+$	
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)
		$B(C_6H_5)_4^-$	
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)
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

The silver atom was positioned from a Patterson map. Electron density maps generated by the program ALLS[29] were used to locate the remaining non-hydrogen 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 weighted R factor of 8.9. Phenyl hydrogen positions were calculated by assuming a carbon–hydrogen bond length of 1.05 Å. Hydrogen atom temperature

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factors were set at 1.0 Å^2 greater than that of the corresponding carbon. The scattering factors[30] were modified for anomalous dispersion effects,[31] and hydrogens were included but not refined.

Bond distances and angles for $[Ag(\mathbf{1})_2]BPh_4$ and fractional coordinates are listed in Tables II and III, respectively. Thermal atom parameters and structure factors are collected in the supplementary material.

$[Ag(\mathbf{1})_2]BPh_4$. Into a solution of $AgBF_4$ (0.210 g, 1.10 mmol) in 30 mL of ethanol was injected **1** (0.360 g, 2.21 mmol). After the mixture was allowed to stir for 30 s, $NaBPh_4$ (10.04 g, 1.40 mmol) was added to precipitate the product, which was isolated in 50% yield after recrystallization by slow diffusion of Et_2O into a saturated solution of CH_2Cl_2. ^1H NMR (ppm, CD_2Cl_2, −45 °C): 2.61, virtual triplet, 36 H, NCH_3, $|^3J(PH) + {}^5J(PH)| = 11.4$ Hz; 6.8–7.2 m, 20 H, C_6H_5. ^{13}C NMR (ppm, CD_2Cl_2, −70 °C): 135.1, 125.7, 121.7, C_6H_5; 37.3, virtual triplet, CH_3, $|^2J(PH) + {}^4J(PH)| = 11.0$ Hz.

$[Ag(\mathbf{1})_3]BPh_4$. Into a solution of $AgBF_4$ (0.123 g, 0.634 mmol) in 30 mL of ethanol was injected **1** (0.692 g, 4.23 mmol). After the solution was allowed to stir for 30 s, $NaBPh_4$ (0.250 g, 0.731 mmol) was added to precipitate $[Ag(\mathbf{1})_3]BPh_4$. After the precipitate was washed with ethanol, a product yield of 72% was realized. ^1H NMR (ppm, $(CD_3)_2CO$): 2.57 d, 54 H, NCH_3, $^2J(PH) = 10.5$ Hz; 6.8–7.2 m, 20 H, C_6H_5. Attempted recrystallization of $[Ag(\mathbf{1})_3]BPh_4$ from Et_2O/CH_2Cl_2 resulted in the precipitation of a mixture of $[Ag(\mathbf{1})_2]BPh_4$ and $[Ag(\mathbf{1})_3]BPh_4$.

$[Ag(\mathbf{2})_3]BPh_4$. Into a solution of $AgBF_4$ (0.157 g, 0.807 mmol) in 20 mL of ethanol was injected **2** (0.573 g, 2.90 mmol). Addition of $NaBPh_4$ (0.320 g, 0.936 mmol) resulted in precipitation of $[Ag(\mathbf{2})_3]BPh_4$ in 72% yield after washing with ethanol. This compound could be recrystallized with much difficulty without loss of ligand from acetone/EtOH. ^1H NMR (ppm, $(CD_3)_2CO$): 0.90 s, 9 H, CCH_3; 2.63 d, 27 H, NCH_3, $^3J(PH) = 18.2$ Hz; 2.79 d, 18 H, CH_2, $^3J(PH) = 4.88$ Hz; 6.8–7.2 m, 20 H, C_6H_5.

$[Ag(\mathbf{1})_2X]$. Complexes where X = Cl, CN, I, or NO_3 were prepared by reacting 8.0 molar equiv or more of ligand with an ether suspension of the corresponding Ag(I) salt. As an example, $[Ag(\mathbf{1})_2Cl]$ was prepared by injecting **1** (3.50 g, 21.5 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 (ppm, $(CD_3)_2CO$): 2.62 d, $^2J(PH) = 10.2$ Hz. Anal. Calcd for $C_{12}H_{36}N_6P_2ClAg$: C, 30.68; N, 17.90. Found: C, 31.08; N, 17.88.

$[Ag(\mathbf{3})_4]BF_4$. Addition of approximately 14 molar equiv of **3** to a solution of $AgBF_4$ (0.155 g, 0.796 mmol) in 20 mL of EtOH resulted in the immediate precipitation of $[Ag(\mathbf{3})_4]BF_4$. This heat- and light-sensitive compound is insoluble in ethanol and acetone but is soluble in CH_2Cl_2. A 76% yield of product was obtained after recrystallization from CH_2Cl_2/Et_2O. ^1H NMR (ppm, $(CDCl_3)$: 2.16 d, $^3J(PH) = 11.7$ Hz. Anal. Calcd for $C_{24}H_{18}AgBF_4P_4N_{12}$: C, 35.00; H, 5.83; N, 20.04. Found: C, 35.07; H, 6.28; N, 18.66.

$[Ag(\mathbf{3})_4]X$. Approximately 10 molar equiv of **3** was injected into a suspension of AgI (0.417 g, 1.78 mmol) in 50 mL of Et_2O. The yellow color of the AgI disappeared within 2 min, and the solution became a cloudy white. The solution was stored at −65 °C 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_2O and hexanes. An attempt at recrystallization of $[Ag(\mathbf{3})_4]I$ from CH_2Cl_2/Et_2O in the presence of 1 molar equiv of free ligand did not improve the physical appearance of the compound. ^1H NMR (ppm, $CDCl_3$): 2.1 d, $^3J(PH) = 11.0$ Hz. $[Ag(\mathbf{3})]_4Cl$, which could only be isolated as an oil, was prepared by using essentially the same procedure. ^1H NMR (ppm, $CDCl_3$): 2.1 d, $^3J(PH) = 10.8$ Hz.

Results and Discussion

All of the complexes described here are white crystalline solids (except $[Ag(\mathbf{3})_4]X$ (X = Cl, I), which are an oil and a powder, respectively) that are stable to air and moisture but generally sensitive to photodecomposition within 2 h upon exposure to room lighting at ambient temperature. The compounds are, however, indefinitely stable at −70 °C.

Cationic Complexes. When **1** is added to $AgBF_4$ in a 2:1 molar ratio, $Ag(\mathbf{1})_2^+$ is formed, which can be isolated in 50% yield as a crystalline tetraphenylborate salt. In the presence of a sevenfold excess of **1**, a 72% yield of $[Ag(\mathbf{1})_3]BPh_4$ 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 low-temperature ^{31}P NMR spectroscopy (vide infra). Like **1**, **2** is capable of forming an isolable three-coordinate complex, $[Ag(\mathbf{2})_3]BPh_4$, in high yield (72%). In contrast to the analogous complex of **1**, however, $[Ag(\mathbf{2})_3]BPh_4$ can be recrystallized without loss of ligand. Although **3** is approximately as basic as **2**, it appears that its smaller size allows it to form the isolable four-coordinate $[Ag(\mathbf{3})_4]BF_4$ in high yield (76%).

At room temperature the ionic complexes studied here appear to undergo ligand exchange in solution that is rapid on the NMR time scale. This is also true for all other ionic complexes for which NMR studies are reported except $\{Ag[P(t\text{-}Bu)_3]_2\}^+$[32] and $\{Ag[P(C_6H_2\text{-}1,3,5(CH_3)_3]_2\}^+$,[33] wherein the ligands are probably too sterically encumbered to participate in the associative process that is believed to be involved in the exchange.[32] In the present instances, the room-temperature $^{31}P\{H\}$ NMR spectra consist of singlets while the $^{13}C\{H\}$ and ^1H NMR spectra appear as doublets owing to $^2J(PNC)$ and $^3J(PNCH)$ coupling, respectively. Below −45 °C the ^{13}C NMR doublet for $[Ag(\mathbf{1})_2]^+$ becomes a triplet, which is consistent with $|J(AX) - J(AX')|^2 < 8J(XX')\nu_{1/2}$,[34] where A = ^{13}C and X, X′ = ^{31}P in the intact two-coordinate complex. The ^1H spectrum measured in $Me_2CO\text{-}d_6$ also becomes a triplet at −45 °C (δ 2.61, $|^3J(PH) + {}^5J(PH)| = 11.4$ Hz) owing to the chemically equivalent protons on each ligand, which are magnetically inequivalent because of substantial three-bond coupling to a phosphorus that in turn is strongly coupled to the second phosphorus.

Phosphorus-31 NMR spectroscopy is an excellent tool with which to study the ligand properties of phosphines and phosphite esters toward Ag(I) since coordination numbers from 2 to 4 manifest themselves in solution by characteristic $^{107,109}Ag$–P one-bond spin–spin couplings at low temperature.[4] The $^{31}P\{H\}$ NMR spectra of the aminophosphine complexes discussed here also consist of two approximate doublets at −95 °C due to spin–spin coupling to ^{107}Ag and ^{109}Ag.[35] The magnitudes of silver–phosphorus couplings in Table I of the $[AgL_{2-4}]^+$ complexes, where L is an aminophosphine ligand, are greater than those reported for the corresponding $[Ag(PR_3)_{2-4}]^+$ complexes but are less than those for the corresponding $\{Ag[P(OR)_3]_{2-4}\}^+$ complexes.[4,32,33] The increase in $^1J(AgP)$ values with increasing electronegativity of the substituents on phosphorus parallels the trend seen previously in one-bond ^{31}P–^{13}C, ^{31}P–^1H, ^{31}P=^{77}Se, ^{31}P–^{183}W, and ^{31}P=^{17}O couplings.[36]

Evidence for $[Ag(\mathbf{1})_{1-3}]BF_4$ can be observed by $^{31}P\{H\}$ NMR spectroscopy at −95 °C. Upon successive addition of molar equivalents of **1** to a 0.3 M solution of $AgBF_4$ in $CH_2Cl_2/(CD_3)_2CO$ (75/25), progressively smaller $^1J(AgP)$ values are observed at the corresponding chemical shifts given in Table I for these species. A similar trend observed previously in

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(35) Natural-abundance silver consists of two isotopes having spin $^1/_2$, ^{107}Ag (51% abundance) and ^{109}Ag (49% abundance). Ratios of $^1J(^{109}Ag\text{–}P)/^1J(^{107}Ag\text{–}P)$ are equal to the $\mu(^{109}Ag)/\mu(^{107}Ag)$ ratio of 1.149.

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AgL_x^+ systems (x = 2–4, L = PR_3, $P(OR)_3$) was attributed to a decreasing percentage of s character in the silver hybridization.[4] Addition of a fourth equivalent of **1** caused collapse of the ^{31}P NMR doublets to a broad singlet at 122 ppm, suggesting that $[Ag(\mathbf{1})_3]^+$ undergoes ligand exchange by an S_N2 mechanism in the presence of free ligand. The same observation was made with the two-coordinate complex $\{Ag[P(t\text{-}Bu)_3]_2\}^+$ reported earlier by others.[32] Analogous experiments with **2** revealed that $[Ag(\mathbf{2})_2]BF_4$ disproportionates to a small extent to $[Ag(\mathbf{2})_3]BF_4$ and $[Ag(\mathbf{2})BF_4]$ (vide infra), which may explain the failure of attempts to isolate $[Ag(\mathbf{2})_2]BPh_4$. As with $[Ag(\mathbf{1})_3]BF_4$, addition of a fourth molar equivalent of **2** to a solution of $AgBF_4$ caused collapse of the ^{31}P NMR doublets to a broad singlet at 96 ppm, indicating that $[Ag(\mathbf{2})_3]^+$ also probably undergoes exchange by an S_N2 mechanism in the presence of free ligand. In contrast, $[Ag(\mathbf{3})BF_4]$ (vide infra) and $[Ag(\mathbf{3})_{2-4}]BF_4$ can be observed upon adding successive molar equivalents of **3** to a solution of $AgBF_4$. Unfortunately, silver–phosphorus couplings could only be resolved for $[Ag(\mathbf{3})BF_4]$ and $[Ag(\mathbf{3})_4BF_4$. The doublets in the ^{31}P NMR spectrum at 147 and 132 ppm are probably associated with $[Ag(\mathbf{3})_2]BF_4$ and $[Ag(\mathbf{3})_3]BF_4$, but the breadth of these peaks prevents their assignment on the basis of the Ag–P couplings. The larger downfield coordination chemical shift seen in $[Ag(\mathbf{3})BF_4]$ is unique among the complexes reported here.

The formulations of the 1:1 complexes in the aforementioned NMR experiments as $[Ag(L)BF_4]$ (L = **2**, **3**) and as $[AgL]BF_4$ in the case of L = **1** 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 **1**, **2**, or **3** precluded conductivity studies in this solvent. Because of decomposition, difficulties were encountered in maintaining completely clear solutions in acetone at 25 °C. However, measurements could be carried out in acetone at −22 °C. 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. With use of approximately 10^{-2} M $AgBF_4$ in acetone at −22 °C, the conductivity of the solution was found to decrease 26 and 39% upon addition of **2** or **3**, respectively, but it rose to the original value upon addition of a second equivalent in each case. This suggests that the complexes present in the NMR experiments at −95 °C in 25% Me_2CO in CH_2Cl_2 are nonconducting or weakly conducting $[Ag(L)BF_4]$ species. It is interesting in this respect that previous workers have reported complexes of the type $[R_3PAgClO_4]$ (where R is a bulky trialkylphosphine or a triarylphosphine), which are two-coordinate in methylene chloride solution and in the solid state owing to coordination of the anion.[37] With **1**, no decrease in conductivity was observed, which is indicative of $[Ag(\mathbf{1})]BF_4$, 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. Whether this is true at −95 °C in 25% Me_2CO in CH_2Cl_2 cannot be concluded with certainty. However, the anomalously large $^1J(^{107}Ag-^{31}P)$ coupling of 910 Hz for this complex would appear to support the presence of substantial $[Ag(\mathbf{1})]BF_4$ in equilibrium with $[Ag(\mathbf{1})BF_4]$ while the 811- and 801-Hz values for the corresponding complexes of **2** and **3** can be construed to indicate a larger fraction of two-coordinate $[Ag(L)BF_4]$ species which would have less s character in the Ag–P bond. Coordination of BF_4^- has been observed previously, as for example in the solid-state structures of $[Ni(en)_2(H_2O)(BF_4)]BF_4$[38] and $Cu(PPh_3)_3BF_4$.[39] In the former study, IR experiments were inconclusive regarding the coordination of BF_4^-. Attempts to use this technique to elucidate the role of the anion in $Ag(\mathbf{1})BF_4$ failed owing to decomposition of the complex in the IR cell while the spectrum was being taken.

Isolated three-coordinate complexes of the type AgL_3^+ are still rare. Previously a number of complexes of the type AgL_3X (where L = $P(C_6H_4\text{-}p\text{-}Me)_3$, $P(OEt)_3$ and X = halide, pseudohalide, B_3H_8, S_2PF_2, O_2CCF_3, NO_3, PF_6, ClO_4, $B_9H_{12}S$) were described.[4] Many of these complexes disproportionate according to reaction 1 with the extent of disproportionation

$$2L_3Ag^+X^- \rightleftharpoons L_4Ag^+X^- + L_2AgX \text{ (or } L_2Ag^+X^-) \quad (1)$$

varying with the coordinating ability of X. Analogous disproportionation products of $[Ag(\mathbf{1})_3]^+$ and $[Ag(\mathbf{2})_3]^+$ were not detected in their ^{31}P NMR spectra at −95 °C. This is not unexpected since $[Ag(\mathbf{1})_4]^+$ and $[Ag(\mathbf{2})_4]^+$ 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 $[Ag(\mathbf{1})_3]^+$ and $[Ag(\mathbf{2})_3]^+$ broaden upon adding ligand at −95 °C, the corresponding $[AgL_4]^+$ species could well be intermediates in an S_N2 associative ligand-exchange process. Reaction 1 cannot be ruled out as a pathway for ligand exchange at higher temperatures.

In competition reactions wherein 3 molar equiv of **1** or **3** is added to a solution of $[Ag(\mathbf{2})_3]^+$, complete displacement of **2** occurs to form the corresponding complexes of **1** and **3** as determined by low-temperature ^{31}P NMR spectroscopy. This suggests that Ag^+ prefers a more basic ligand (**1**) or a smaller one (**3**).

Neutral Complexes. Addition of an eightfold excess of **1** to ether suspensions of AgX (X = Cl, CN, I, NO_3) produces high yields of crystalline three-coordinate $[Ag(\mathbf{1})_2X]$ complexes. As was discussed earlier, **2** (like **1**) is capable of forming isolable three-coordinate $[Ag(\mathbf{2})_3]BPh_4$ in high yield. However, **2** does not react with AgX (X = Cl, CN, I, NO_3) under the same conditions as does **1**. The lower basicity of **2** may be responsible for the inability of this ligand to compete successfully with the lattice forces in AgX to form a complex.

The $[Ag(\mathbf{1})_2X]$ complexes (X = Cl, CN, NO_3) display a singlet $^{31}P\{^1H\}$ NMR resonance at room temperature. Slowing of dissociative ligand exchange at −95 °C causes this singlet to split into an approximate doublet of doublets owing to silver–phosphorus coupling. By contrast the ^1H NMR spectra show a doublet at room temperature and a singlet at −95 °C. The proton doublet is consistent with three-bond $^1H-^{31}P$ coupling and ligand dissociation in a rapid equilibrium while the low-temperature proton singlet could arise from opposite signs of approximately equal values for $^3J(PH)$ and $^5J(PH)$ in the virtually coupled $AA'X_{18}X'_{18}$ system.[34] Addition of excess ligand at −95 °C leads to collapse of the doublet of doublets in the ^{31}P NMR spectrum to a broad singlet. This strongly suggests that $[Ag(\mathbf{1})_2X]$ undergoes ligand exchange by an S_N2 mechanism in the presence of excess ligand. The decrease in silver–phosphorus coupling for $[Ag(\mathbf{1})_2X]$ in the order X = NO_3 > Cl > I > CN (Table I) parallels that seen previously with $AgL_{2,3}X$, where L = $P(C_6H_4\text{-}p\text{-}Me)_3$ and $P(OEt)_3$,[4] and with AgLX, where L = $P(t\text{-}Bu)_3$.[33] For $[Ag(\mathbf{1})_2NO_3]$, the small but measurable conductivity suggests that NO_3^- dissociates to a slight extent. In contrast, $\{Ag[P(t\text{-}Bu)_3]_2\}NO_3$ is a 1:1 electrolyte, which is an indication of the greater steric demands of the ligand in this case.[32] When X is the more strongly binding CN^- ion, however, both $[Ag(\mathbf{1})_2CN]$ and $[Ag(P(t\text{-}Bu)_3)CN]$[33] are nonconductors.

The possibility exists for $Ag(\mathbf{1})_2X$ to dimerize in solution and the solid state. Osmometric molecular weights of $Ag(\mathbf{1})_2CN$ measured in 1,2-dichloroethane (found 282, calculated

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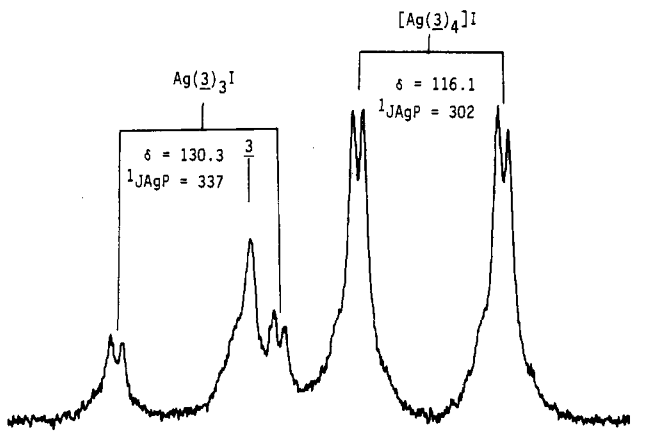

Figure 2. ^{31}P NMR spectrum of [Ag(3)$_4$]I at −88 °C in 75/25 CH_2Cl_2/Me_2CO-d_6. The Ag–P coupling constants refer to the ^{107}Ag nucleus.

459.9), Ag(1)$_2$I in THF (found 581, calculated 560.8), and Ag(1)$_2$Cl in THF (found 529, calculated 470) suggest that relatively little if any association occurs in solution.[40] We are reluctant, however, to draw any conclusion regarding the solution structure of these complexes at −95 °C since the osmometric data were taken in different solvents and at a temperature 132 °C higher than that at which the NMR studies were performed. The monomeric character of these complexes at −95 °C is implied, however, by the value of the ^{107}Ag–^{31}P coupling constants, which are greater than those we would expect (300–400 Hz) for four-coordinate dimeric complexes, and the fact that no four-bond silver–phosphorus coupling is observed analogously to the four-bond phosphorus–platinum coupling that is seen in halide-bridged L_2PtX_4 systems.[41]

In contrast to **1**, which can only form three-coordinate neutral complexes, the smaller ligand **3** forms four-coordinate complexes wherein the halide ion is displaced from the inner coordination sphere. At −95 °C [Ag(3)$_4$]Cl, which could only be isolated as an oil, shows no evidence for ligand dissociation in its ^{31}P NMR spectrum in spite of the coordination tendency of the chloride ion and a basicity of **3** similar to that of **2**. Iodide has previously been shown[4] to be a stronger ligand toward Ag$^+$ than Cl$^-$. In accord with this observation, Ag(3)$_4$I at −95 °C displays ^{31}P NMR peaks corresponding to equilibrium 2 as seen in Figure 2. An equilibrium constant of

$$[Ag(3)_4]^+ + I^- \rightleftharpoons [Ag(3)_3I] + 3 \qquad (2)$$

$K \simeq 0.2$ was calculated from ^{31}P NMR areas at −88 °C. At 25 °C virtually zero conductance is observed for a 10^{-3} M solution of Ag(3)$_4$I in methylene chloride, which is probably due to entropy effects that shift equilibrium 2 to the right. When the temperature of the solution is lowered to −65 °C, a small but measurable conductance is observed, even though solution conductances are expected to decrease with decreasing temperature owing to lower ionic mobility. The only other complex of the type [AgL$_4$]X, where X is a halide or pseudohalide, that has been isolated is [Ag(PMe$_3$)$_4$]Cl,[42] and it is unstable. Apparently **3** and PMe$_3$ are sufficiently basic and small to form such isolable species wherein halide is excluded from the primary coordination sphere. Previously it was concluded from ^{31}P NMR data that addition of L to the corresponding AgL$_3$X compounds, where L was P(OEt)$_3$ or P(C$_6$H$_4$-*p*-Me)$_3$, produced AgL$_4$$^+$ species in equilibrium with the reactants.[4]

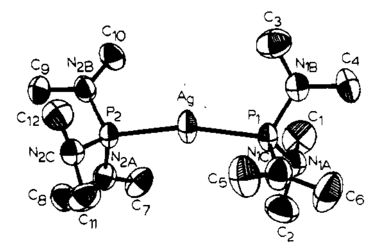

Figure 3. ORTEP drawing of the [Ag(1)$_2$]$^+$ cation.

Structure of [Ag(1)$_2$]BPh$_4$. Dicoordination is quite uncommon for metal complexes, and it is largely limited to a relatively few compounds of monovalent copper, silver, and gold and of divalent mercury.[43] The two-coordinate molecular structure reported here represents the second example in which Ag(I) is complexed to phosphorus ligands.

The solid-state structure of the cation in [Ag(1)$_2$]BPh$_4$ is shown in Figure 3. The P–Ag–P moiety is bent with an angle of 167°, and the silver–phosphorus distance is 2.394 (3) Å. The reason for nonlinearity of these atoms is not apparent. Though ligation of the tetraphenylborate anion has been observed in coordinatively unsaturated systems,[44,45] no close intermolecular contacts were found between the anion and the cation in the present case. In the structure of the two-coordinate complex {Ag[P(C$_6$H$_2$-2,4,6-Me$_3$)$_3$]$_2$}BF$_4$, the P–Ag–P angle is nearly linear (179.4°) with a silver–phosphorus bond distance of 2.461 (6) Å.[46] It is believed that the extremely large cone angle of P(C$_6$H$_2$-2,4,6-Me$_3$)$_3$ precludes bending of the P–Ag–P bond.[46] The shorter Ag–P bond distance in [Ag(1)$_2$]BPh$_4$ is ascribed at least in part to the smaller steric requirements of **1** compared to those of P(C$_6$H$_2$-2,4,6-Me$_3$)$_3$. Excellent support for an essentially two-coordinate structure in solution for [Ag(1)$_2$]BPh$_4$ comes from its solid-state CP/MAS ^{31}P NMR spectroscopic studies,[47] wherein parameters found for this complex ($\delta(^{31}P) = 115.2$, $J(^{107}Ag^{31}P) = 603$ Hz) are very close to the solution values (Table I).

Both of the ligands in [Ag(1)$_2$]BPh$_4$ are in the approximately C_s conformation D in Figure 1, similar to one of the ligands in *trans*-[(1)$_2$Fe(CO)$_3$], wherein the most pyramidal nitrogen directs its lone pair approximately anti to the Ag–P bond while the other Me$_2$N groups are twisted in opposite directions.[14] As was noted previously, a relationship exists between the sum of the bond angles around nitrogen ($\sum$N) and the nitrogen–phosphorus bond lengths.[14,15,18–22] For example, $\sum N_{2A}$ is 346.9° and the N_{1A}–P_1 distance is 1.683 Å while the more planar nitrogen N_{1C} ($\sum N_{1C}$ = 356.2°) is only 1.651 Å from P_1, presumably because of more s character in its bond to P_1.

Both ligands in [Ag(1)$_2$]BPh$_4$ exhibit one larger and two smaller N–P–N bond angles. In each ligand the larger N–P–N bond angles involve the two nitrogen atoms which are closest to trigonal-planar geometry. This large N–P–N angle could arise from the greater repulsion of the predominantly 2p nitrogen lone pairs which are pointed toward one other. Similar observations have been recorded in related aminophosphine derivatives.[14,15,18–22] Two of the carbons on each ligand (C_4, C_6, C_8, and C_9) participate in two rather short nonbonding carbon–carbon interactions (Table II). Moreover,

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(40) Substantial deviations from monomeric behavior occur in these complexes (−39% in the case of Ag(1)$_2$CN). Measurements by others made for Ag[P(*p*-tolyl)$_3$]$_n$X species were also as much as 40% low.

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these four carbons form the largest P–N–C angles. These large angles do not appear to be unambiguously associated with the short nonbonded C–C distances, however, since analysis of the structural data for $Fe(CO)_4(\mathbf{1})$ and *trans*-$Fe(CO)_3(\mathbf{1})_2$ reveals that similar nonbonded interactions do not involve large P–N–C angles. The cone angles of **1** (168°) and **2** (164°) calculated from the X-ray structural data of $[Ag(\mathbf{1})_2]BPh_4$ and $OP(NMeCH_2)_3CCH_3$,[48] respectively, are indeed of comparable size as was assumed at the onset from models. Interestingly the cone angle of **1** is larger in $[Ag(\mathbf{1})_2]BPh_4$ than when it is measured from space-filling models (157°). Since $[Ag(\mathbf{1})_2]BPh_4$ shows no evidence of ligand–ligand repulsion, the ligand cone angle might be expected to decrease in more crowded complexes.

From the structural data for $[Ag(\mathbf{1})_2]BPh_4$ it can be concluded that because of considerable similarities to structures of a variety of other PN_3 compounds, the ligand conformations observed are not determined by lattice effects. Our results also lend further credence to conclusions from theoretical work, which suggests that structures C and D in Figure 1 represent 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 they prefer (at least in the solid state) a conformation wherein one or more of the nitrogens assumes some pyramidal character.

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Registry No. **1**, 1608-26-0; **2**, 14418-26-9; **3**, 1194-53-2; $[Ag(\mathbf{1})_2]BPh_4$, 87883-94-1; $[Ag(\mathbf{1})_2I]$, 87883-95-2; $[Ag(\mathbf{1})_2Cl]$, 87883-96-3; $[Ag(\mathbf{1})_2NO_3]$, 87883-97-4; $[Ag(\mathbf{1})]BF_4$, 87883-99-6; $[Ag(\mathbf{1})_2CN]$, 87884-00-2; $[Ag(\mathbf{1})_3]BPh_4$, 87884-02-4; $[Ag(\mathbf{2})BF_4]$, 87884-03-5; $[Ag(\mathbf{2})_2]PF_4$, 87884-05-7; $[Ag(\mathbf{2})_3]BPh_4$, 87884-07-9; $[Ag(\mathbf{3})BF_4]$, 87884-08-0; $[Ag(\mathbf{3})_4]BF_4$, 87884-10-4; $[Ag(\mathbf{3})_4]Cl$, 87884-11-5; $[Ag(\mathbf{3})_4]I$, 87884-12-6; $[Ag(\mathbf{3})_3I]$, 87884-13-7.

Supplementary Material Available: Listings of thermal parameters and observed and calculated structure factors and a computer drawing of the unit cell (15 pages). Ordering information is given on any current masthead page.

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[48] These cone angles were calculated by assuming an M–P distance of 2.28 Å, a C–H bond length of 1.00 Å, a hydrogen van der Waals radius of 1.00 Å, and tetrahedral angles around carbon. The P–M–H angle was calculated for a coplanar arrangement of the M–P–C–H bonds for C_7, C_{10}, and C_{11} in the ligand of the silver complex. These angles were then doubled, and the average was taken to give 168°. A similar treatment of the structural data for the $P(NCH_3CH_2)_3CCH_3$ moiety in $OP(NCH_3CH_2)_3CCH_3$ (Clardy, J. C.; Kolpa, R. L.; Verkade, J. G. *Phorphous Relat. Group V Elem.* **1974**, *4*, 133) gave an average cone angle of 164°.

Contribution from the Lehrstuhl für Anorganische Chemie I der Ruhr-Universität Bochum, D-463 Bochum 1, West Germany,
and Anorganisch Chemisches Institut der Universität Heidelberg, D-6900 Heidelberg, West Germany

Preparation and Characterization of Binuclear (1,4,7-Triazacyclononane)molybdenum(III) Complexes. Crystal Structures of $[Mo^{III}_2(\mu\text{-}OH)_2Cl_2(C_6H_{15}N_3)_2]I_2$ and $[Mo^{III}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)(C_6H_{15}N_3)_2]I_3\cdot H_2O$

KARL WIEGHARDT,*[1a] MANFRED HAHN,[1a] WOLFGANG SWIRIDOFF,[1b] and JOHANNES WEISS*[1b]

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Binuclear complexes of molybdenum(III) have been prepared by hydrolysis of the mononuclear $LMoCl_3$ (**2**) in aqueous solution containing acetate or hydrogen carbonate ions: $[LMo(\mu\text{-}O_2CCH_3)(\mu\text{-}OH)_2)MoL]I_3\cdot H_2O$ (**3a**), $[LMo(\mu\text{-}OH)_2(\mu\text{-}CO_3)MoL]I_2\cdot H_2O$ (**4**) (L = 1,4,7-triazacyclononane). The reactions of the μ-carbonato complex with aqueous CH_3SO_3H, HCOOH, and HCl afford the complexes $[LMo(\mu\text{-}OH)_2(OH_2)_2MoL]I_4$ (**5**), $[LMo(\mu\text{-}OH)_2(\mu\text{-}O_2CH))MoL]I_3$ (**3b**), and $[LClMo(\mu\text{-}OH)_2MoClL]I_2$ (**6**), respectively. **5** is readily oxidized by $HClO_4$ or O_2 forming a Mo(V) dimer, $[Mo_2O_2(\mu\text{-}O)_2L_2]I_2$. Crystals of **3a** belong to the space group $P2_1/a$ with $a = 9.833$ (2) Å, $b = 19.261$ (8) Å, $c = 14.967$ (2) Å, $\beta = 100.00$ (2)°, $V = 2792$ (6) Å^3, and $Z = 4$. Crystals of **6** belong to the space group $C2/c$ with $a = 12.889$ (6) Å, $b = 14.219$ (4) Å, $c = 14.280$ (4) Å, $\beta = 116.70$ (3)°, $V = 2338$ (6) Å^3, and $Z = 4$. The structures refined to $R = 0.053$ and 0.057 for **3a** and **6**, respectively. The structure of **3a** consists of a binuclear cation of two distorted octahedra bridged by one acetate and two hydroxo ligands. The Mo–Mo distance is 2.471 (2) Å, and the formal bond order may be three ($\sigma^2\pi^2\delta^2$). The structure of **6** consists also of a binuclear cation of two distorted octahedra sharing an edge. The $Mo(\mu\text{-}OH)_2Mo$ ring is planar, the Mo–Mo distance being 2.501 (3) Å ($Mo\equiv Mo$, $\sigma^2\pi^2\delta^2$).

Introduction

An extensive range of binuclear Mo(V) compounds with the $Mo_2O_4^{2+}$ unit [bis(μ-oxo)bis(oxomolybdenum(V))] and O,N-donor ligands have been prepared in aqueous solution and have been characterized by X-ray analysis.[2] The short Mo–Mo distances (2.59–2.53 Å) and the observed diamagnetism indicate that a weak interaction (Mo–Mo single bond) exists between the two metal atoms.

Hydroxo-bridged binuclear diamagnetic complexes of molybdenum(III) containing O,N-donor ligands (e.g., edta) are known to a much lesser degree.[2a] Their preparation in aqueous solution was achieved via reduction of the corresponding Mo(V) dimers with strong reductants (e.g., zinc amalgam). Thus, bis(μ-hydroxo)(μ-acetato)(μ-ethylenediaminetetraacetato)dimolybdenum(III) has been fully characterized. The short Mo–Mo distance of 2.43 Å and its diamagnetism indicate the presence of a strong Mo–Mo interaction.[3] Paramagnetic,

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