Simple Route to Trigonal and Dinuclear Diimine Substituted Silver(I) Phosphine Complexes

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The chemistry of Ag(I) phosphine complexes is complex [1–5]; this is understandable in view of the variable geometries for the d^{10} Ag(I) ion, its kinetic lability and the ease for disproportionation, polymerisation and ligand scrambling reactions [6–8]. Accordingly, most of the isolated Ag(I) phosphines, the trigonal complexes in particular, are susceptible to decomposition [9]. Reported here is the isolation of some stable mixed-ligand Ag(I) species via the substitution reaction of $[Ag(PPh_3)(NO_3)]_n$ with diimine ligands.

Experimental

General Procedures

All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. ^{31}P NMR spectra in $CDCl_3$ were recorded on a Joel 90Q instrument with H_3PO_4 as external reference. Infrared spectra were recorded with the Perkin-Elmer 1310 spectrometer. Conductivities were measured in 10^{-3} mol dm^{-3} solution using a CM-115 Kyoto electronic conductimeter with a cell constant of 1.049 cm^{-1}. $[Ag(PPh_3)(NO_3)]_n$ was prepared according to the literature [10]. Other reagents were supplied from commercial sources.

$[Ag(PPh_3)(phen)]BF_4$

Solid 1,10-phenanthroline (0.47 g; 2.38 mmol) was added to a solution of $Ag(PPh_3)(NO_3)$ (1.00 g; 2.32 mmol) in methanol (30 ml) and the mixture was stirred at room temperature (28 °C) for 1 h. The resultant milky suspension was filtered and to the filtrate was added an excess of aq. $NaBF_4$ solution. The white precipitate thus formed was filtered and recrystallised from acetone/water. The yields and melting points are listed in Table I.

NH_4PF_6 was used in the isolation of the PF_6^- salt. Preparation of $[Ag(PPh_3)(2,2'\text{-bipy})]X$ ($X = BF_4, PF_6$) follows a similar procedure.

$[Ag_2(PPh_3)_2(\mu\text{-bpe})](NO_3)_2$

An acetonitrile solution (20 ml) of $Ag(PPh_3)(NO_3)$ (0.51 g; 1.19 mmol) was filtered and cooled to 0 °C. To the cooled solution was added a solution of *trans*-1,2-bis(4-pyridyl)ethylene (bpe) (0.11 g; 0.60 mmol) in CH_3CN (10 ml). The mixture was slowly warmed to 28 °C and stirring was continued for 1 h. The white precipitate was isolated by filtration and washed well with CH_3CN.

The preparation of $[Ag_2(PPh_3)_2(\mu\text{-}4,4'\text{-bipy})](NO_3)_2$ follows a similar procedure.

Results and Discussion

$[Ag(PPh_3)(NO_3)]_n$ can be conveniently synthesised from $AgNO_3$ with free PPh_3 [10]. Lability of the nitrato group enables the complex to undergo facile substitution with diimines at ambient temperature. Displacement with chelating α-diimines such as 1,10-phenanthroline (phen) and 2,2'-bipyridyl (2,2'-bipy) yields the trigonal $[Ag(PPh_3)(N\text{-}N)]X$ (N-N = phen, 2,2'-bipy; $X = BF_4, PF_6$). With bridging bifunctional N-heterocycles such as 4,4'-bipyridyl (4,4'-bipy) and *trans*-1,2-bis(4-pyridyl)ethylene (bpe), sparingly soluble dimeric $[Ag_2(PPh_3)_2(\mu\text{-}N\text{-}N)](NO_3)_2$(N-N = 4,4'-bipy, bpe) are the result with Ag(I) linearly coordinated. All the complexes are stable with respect to air oxidation but decompose readily to silver metal upon UV irradiation. The molar conductances for the analytically pure cationic mononuclear and dinuclear complexes are in good agreement with those reported for 1:1 and 2:1 electrolytes respectively [11] (Table I). The substrate $[Ag(PPh_3)(NO_3)]_n$, on the other hand, shows limited conductance ($\Lambda_M = 5.25$ ohm^{-1} cm^2 M^{-1}) in nitrobenzene solution. Kinetic lability of the Ag–P bond, coupled with the poor solubility of the dimers, precludes a reliable NMR analysis on the products. $[Ag(PPh_3)(2,2'\text{-bipy})]BF_4$ is the only complex that displays a Ag–P coupling (δ $^{31}P = 18.91$ ppm; $J(^{107}Ag-^{31}P) = 640$ Hz) in its NMR spectrum at 25 °C. The presence of the uncoordinated anions, BF_4^-, PF_6^- and NO_3^-, is clearly indicated in the infrared spectral data. The analogous reaction of $[Ag(PPh_3)(NO_3)]_n$ with excess pyridine (py) does not yield the expected mixed-ligand product $[Ag(PPh_3)(py)_x]NO_3$. Instead, ligand scrambling occurs resulting in the isolation of the well-known $[Ag(PPh_3)_3]NO_3$ [1, 9, 12].

We are currently exploring the use of $[Ag(PPh_3)(NO_3)]_n$ as a substrate for the synthesis of other complexes with ligating nitrogen heterocycles. Kinetic stability of these diimine phosphine Ag(I) derivatives in comparison with other known systems [13, 14] will be of particular interest.

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TABLE I. Analytical and Conductance Data

Complexes	Melting point (°C); yield (%)	Elemental analyses (%)	Λ_M (ohm^{-1} cm^2 mol^{-1})[a]
$[Ag(PPh_3)(2,2'\text{-bipy})]X$			
(i) $X = BF_4$	201–202; 75	C, 54.91(54.81) H, 3.72(3.75) N, 4.27(4.57)	31.00[a]
(ii) $X = PF_6$	244–245; 82	C, 50.09(50.07) H, 3.29(3.43) N, 3.86(4.17)	35.30[a]
$[Ag(PPh_3)(phen)]X$			
(i) $X = BF_4$	249–250; 72	C, 56.42(56.54) H, 3.51(3.61) N, 3.93(4.39)	36.24[a]
(ii) $X = PF_6$	245–246; 75	C, 51.47(51.79) H, 3.12(3.31) N, 3.88(4.02)	29.11[a]
$[Ag_2(PPh_3)_2(\mu\text{-}4,4'\text{-bipy})](NO_3)_2$	262–266; 33	C, 53.66(54.12) H, 3.46(3.72) N, 5.92(5.49)	58.53[b] 148.62[c]
$[Ag_2(PPh_3)_2(\mu\text{-bpe})](NO_3)_2$	219–224; 31	C, 54.87(55.07) H, 3.60(3.82) N, 5.21(5.35)	84.37[b]

[a]Nitrobenzene. [b]Dimethylsulphoxide. [c]Methanol.

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References

1 S. M. Socol and J. G. Verkade, *Inorg. Chem., 23,* 3487 (1984).
2 M. Khan, C. Oldham and D. G. Tuck, *Can. J. Chem., 59,* 2714 (1981).
3 R. Ketari and A. Foucaud, *J. Org. Chem., 46,* 4498 (1981).
4 I. D. Salter, *J. Organomet. Chem., 295,* C17 (1985).
5 D. V. Sanghani, P. J. Smith, D. W. Allen and B. F. Taylor, *Inorg. Chim. Acta, 59,* 203 (1982).
6 M. R. Churchill and B. G. DeBoer, *Inorg. Chem., 14,* 2502 (1975).
7 B. K. Teo and J. C. Calabrese, *J. Am. Chem. Soc., 97,* 1256 (1975).
8 R. G. Goel and P. Pilon, *Inorg. Chem., 17,* 2876 (1978).
9 E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc., 94,* 6386 (1972).
10 R. A. Stein and C. Knobler, *Inorg. Chem., 16,* 242 (1977).
11 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).
12 F. Klanberg, E. L. Muetterties and L. J. Guggenberger, *Inorg. Chem., 7,* 2272 (1968).
13 F. A. Cotton and D. M. L. Goodgame, *J. Chem. Soc.,* 5267 (1960).
14 S. Araki, K. Matsumoto, K. Tanaka and T. Tanaka, *J. Inorg. Nucl. Chem., 38,* 727 (1976).