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Two-coordinate Silver(I) Complexes of Trimesitylphosphine and Trimesitylarsine

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In pursuing our interest in metal complexes of sterically hindered phosphines [1], we are investigating the reactions of trimesitylphosphine, previously described as the bulkiest known phosphine [2, 3], with a variety of metal salts. Our recent X-ray structural study of $[\mathrm{HgP\ mesityl_3(NO_3)_2}]_2$ [4] (cone angle [1, 2] of 208° for P mesityl$_3$) and investigation of the facile metallation of trimesitylphosphine with palladium(II) and platinum(II) [5] firmly establish the extreme bulkiness of trimesitylphosphine. Earlier work had already demonstrated the high steric barrier to the formation of 1:2 adducts of mercury(II) [1, 6] and platinum(II) [7] with the less sterically hindered tri-*o*-tolylphosphine (range of cone angles of 183–198° [1]). Therefore, we have employed silver(I) hexafluorophosphate to obtain the first 1:2 adduct of a metal with trimesitylphosphine; the preparation and spectral characterization of $[\mathrm{Ag(P\ mesityl_3)_2}]\mathrm{PF_6}$(I) are described herein. The analogous complex $[\mathrm{Ag(As\ mesityl_3)_2}]\mathrm{PF_6}$(II) was also studied because the only previous report of a 1:2 adduct of trimesitylarsine [8] was unsubstantiated in our laboratory [5]. Previous reports of two-coordinate silver(I) complexes of phosphines and arsines are quite limited [9, 10] although the characterization of cationic $[\mathrm{Ag(t\text{-}Bu_3P)_2}]^+$ complexes was recently reported [11].

Reaction of 2 equivalents of trimesitylphosphine with 1 equivalent of $\mathrm{AgPF_6}$ in the dark in dichloromethane solution over a 15 hr period results in the formation of $[\mathrm{Ag(P\ mesityl_3)_2}]\mathrm{PF_6}$(I), obtained in 70% yield as a white crystalline solid, mp. 212 °C (dec). *Anal.* Calcd for $\mathrm{C_{54}H_{66}AgF_6P_3}$: C, 62.98; H, 6.46. Found: C, 62.36; H, 6.62 (Guelph Chemical Laboratories). Similarly, $[\mathrm{Ag(As\ mesityl_3)_2}]\mathrm{PF_6}$(II) was isolated as a white solid and recrystallized from benzene, mp. 227–231 °C (dec.). *Anal.* Calcd for $\mathrm{C_{54}H_{66}AgAs_2F_6P}$: C, 58.02; H, 5.95. Found: C, 58.24; H, 6.01. Metallic silver, which formed even when trimesitylarsine was deficient of a 1:2 molar ratio, was removed by filtration of the reaction mixture through a silica gel column. Both new complexes are very soluble in dichloromethane and light sensitive; compound(II) is more unstable towards storage at ambient temperature.

The cationic nature of the two new complexes is indicated by their molar conductances for 10^{-3} *M* nitromethane solutions; the values (Table I) are in reasonable agreement with those reported for 1:1 electrolytes and previous silver(I) complexes of this [10–12]. Infrared spectral data in the solid state show that the hexafluorophosphate ion shows its characteristic unperturbed bands, *i.e.*, strong and sharp infrared bands occur at 560 and 835 cm^{-1} [13]. Accordingly, the conductivity and infrared spectral data, together with the NMR data discussed below, are compatible with two-coordinate ionic structures in the solid state and in solution. The paucity of literature assignments for Ag–P and Ag–As stretching frequencies makes tenuous any such assignments for the present linear complexes. However, medium to strong bands near 120 cm^{-1} in the solid state Raman spectra of (I) and II), not observed for the free P mesityl$_3$ and As mesityl$_3$ ligands, are tentatively proposed as the symmetric Ag–P and Ag–As stretching frequencies (Table I). Other workers have previously assigned Ag–P stretching frequencies in the same region [11, 14].

The ^{1}H NMR spectra of the complexes at ambient temperature in $\mathrm{CDCl_3}$ solution show resonances (Table I) at positions slightly shifted from those observed for the free ligands, as expected for adduct formation [4, 5]. The much broader peak at 2.0 δ for (I) (peak width half-height = 18 Hz), than for (II) (4 Hz) is indicative of parital inequivalence of *ortho*-methyl groups due to the greater hindrance to mesityl rotation about the C–P bonds in the case of the P mesityl$_3$ complex. The ^{31}P NMR spectrum of (I) at ambient temperature consists of two sharp doublets arising from ^{109}Ag–^{31}P and ^{107}Ag–^{31}P spin–spin coupling (Table I) and a higher field septet due to the hexafluorophosphate anion. The latter multiplet was also observed at –144.75 δ [$^1J(^{31}\mathrm{P}–^{19}\mathrm{F})$ = 709 Hz] for (II), confirming the ionic nature of the complexes. The coordination chemical shift for (I) is 10.6 δ, considerably less than those reported for $[\mathrm{Ag(P}\ p\text{-}\mathrm{tolyl_3)_2}]^+$ (22.3 δ) [10] and $[\mathrm{Ag(PBu^t_3)_2}]^+$ (19.2 δ) [11], whereas the silver–phosphorus coupling constants are higher for (I) than for $[\mathrm{Ag(P}\ p\text{-}\mathrm{tolyl_3)_2}]^+$ [$^1J(^{107}\mathrm{Ag}–^{31}\mathrm{P})$ = 496 Hz] [10] and $[\mathrm{Ag(PBu^t_3)_2}]^+$ [$^1J(^{107}\mathrm{Ag}–^{31}\mathrm{P})$ = 437 Hz] [11]. Agreement with the estimated $^1J(^{107}\mathrm{Ag}–^{31}\mathrm{P})$ value of 452 Hz [10] for sp hybridized linear $\mathrm{L_2Ag^+}$ complexes is remarkably good considering the influence on coupling constant values for phosphines of such factors as their basicity, *trans*-influence, and the size

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TABLE I. Conductivity and Spectral Data.

Compound	Molar conductance[a] in CH_3NO_2	ν(Ag–P) or ν(Ag–As), cm^{-1} [b]	^1H NMR Data[c] δ, ppm	^{31}P NMR Data[d] δ, ppm	$^1J(^{109}Ag–^{31}P)$ Hz	$^1J(^{107}Ag–^{31}P)$ Hz
$[Ag(P\ mesityl_3)_2]PF_6$	84.6	130 ms	2.00 (6)			
			2.40 (3)	−28.45	591	513
			6.90 (2)	−144.75[e]		
$[Ag(As\ mesityl_3)_2]PF_6$	63.1	118 vs	2.03 (6)	−144.75[e]		
			2.30 (3)			
			6.92 (2)			

[a] In $ohm^{-1}\ cm^2\ mol^{-1}$ for 10^{-3} *M* solutions. [b] Solid state Raman bands. [c] In $CDCl_3$ solution at ambient temperature, with Me_4Si as internal standard. [d] In CH_2Cl_2/CD_2Cl_2 solution at ambient temperature, with negative shifts upfield from H_3PO_4 external standard. δ for P $mesityl_3$ in C_6H_6 = −39.00 ppm. [e] $^1J(^{31}P–^{19}F)$ = 709 Hz for ionic PF_6^-.

of their C–P–C bond angles. Further discussion of the interrelationship of the magnitude of the coordination chemical shift and coupling constants with these factors, as previously described for mercury(II) complexes of P *o*-$tolyl_3$, PCy_3 and PBu^t_3 [15], awaits further ^{31}P NMR and structural studies currently underway for these complexes. The extreme bulkiness of P $mesityl_3$ is nevertheless demonstrated in the present observation of silver–phosphorus spin–spin coupling at ambient temperature for (I), whereas silver (I) complexes of smaller tertiary phosphines undergo rapid ligand exchange [10, 15, 17]. ^{31}P NMR spectra of (I) at 183 K or with a two molar excess of free P $mesityl_3$ are very similar to that observed for (I) itself at ambient temperature (a separate singlet due to the free phosphine occurs at −36.99 δ in the excess P $mesityl_3$ case), indicating the lack of phosphine exchange. Preliminary results show however that the smaller phosphine PBu^n_3 (θ = 132°) [2] displaces P $mesityl_3$ from (I) via an associative mechanism; ^{31}P NMR exchange studies involving (I) and (II) will be reported later.

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