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LETTER

Is $Rh(PMe_3)_3^+$ Formed upon Anion Exchange of $Rh(PMe_3)_4^+Cl^-$? Crystal and Molecular Structure of $Rh(PMe_3)_4^+BPh_4^-$ and $Ir(PMe_3)_4^+PF_6^-$

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Rhodium and iridium trimethylphosphine complexes serve as models [1] and as catalysts [2] for homogeneously catalyzed processes, by virtue of the high basicity and small size of this versatile ligand. Catalytic photochemical activation of hydrocarbons by $Rh(CO)(PMe_3)_2Cl$ [3] is thought to involve a 14e Rh(I) trimethylphosphine intermediate. Evidence for intermediacy of such a complex in C–H activation is provided by flash photolysis studies [4] and by studies of C–H reductive elimination [1b, 2a].

Whereas existence of stable 14e rhodium(I) complexes containing bulky phosphines [5] is perhaps not surprising, the isolation of stable $Rh(PMe_3)_3^+X^-$ ($X = BPh_4$, PF_6) reported by Wilkinson and coworkers [6] is, in our view, quite unexpected. Even more surprisingly, this complex is reported as being formed upon anion exchange of the 1:1 electrolyte $Rh(PMe_3)_4^+Cl^-$ (**1**), in an attempted preparation of $Rh(PMe_3)_4^+X^-$ [6]. Citations of this work appear in the literature [5e, 7] and it is pointed out as surprising in a recent review [8].

Because of our general interest in low valent electron-rich complexes of rhodium, we have repeated the reported procedure for the preparation of $Rh(PMe_3)_3^+BPh_4^-$ and have characterized the product by X-ray, showing that $Rh(PMe_3)_4^+BPh_4^-$ (**2**) is formed. We also report here the structure of the analogous $Ir(PMe_3)_4^+PF_6^-$ (**3**) [9], a highly reactive complex useful for the formation of various unusual adducts [9, 10].

Treatment of an aqueous solution of **1** under nitrogen with a slight excess of $NaBPh_4$ resulted in formation of a pale yellow powder, as reported [6]. The $^{31}P\{^1H\}$ NMR spectrum of this product in THF-d_8 at 25 °C shows a doublet at δ −8.58 (J(Rh–P) = 132 Hz) which is unexpected for a T-shaped ground state RhL_3 unit [5a, e, 11]**. Slow vapor diffusion of benzene into a pyridine solution of this complex during 3 days resulted in large orange plates exhibiting an unchanged $^{31}P\{^1H\}$ NMR spectrum. An X-ray structural study† unambiguously shows that $Rh(PMe_3)_4^+BPh_4^-$ (**2**) and not the *tris* complex was obtained (Fig. 1). (The preparation of $Rh(PMe_3)_4$-PF_6^- from a cationic Rh(I) indenyl complex was reported in ref. 12.) For comparison, we have also determined the structure of $Ir(PMe_3)_4^+PF_6^-$ (**3**) (Fig. 2), crystals of which were grown by vapor diffusion of pentane into a THF solution of the complex.

2 forms an interesting arrangement in which two cation–anion pairs entrap a benzene molecule. The distances of C5–Rh1 (3.53 Å) and C8–Rh2 (3.49 Å) are probably too large for an intermolecular 'agostic' Rh•••H interaction. No interaction is observed between the unsaturated rhodium center and the phenyl groups of the anion. The cation shows considerable distortion from planarity towards a tetrahedral arrangement, with P–P twist angles of 23.73 and 28.12° for Rh1 and Rh2, respectively. This is undoubtedly a result of steric crowding of the PMe_3 ligands. A comparison of the pseudo-*trans* P–Rh–P angles shows that this distortion in **2** (P–Rh1–P 158.96, 152.6°; P–Rh2–P 157.8, 162.02°) is smaller

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**The reported [6] $^{31}P\{^1H\}$ NMR spectra are: $Rh(PMe_3)_3^+$-BPh_4^- (in CD_3NO_2): δ −14.87 (br, d, J(Rh–P) = 110 Hz); $Rh(PMe_3)_3^+PF_6^-$ (in D_2O): δ −14.47 (br, s); −25 °C: δ −14.99 (d, J(Rh–P) = 132.5 Hz).

†Crystal data for **2**: $C_{78}H_{118}B_2P_4Rh_2$, monoclinic-b, $C2/c$ (No. 15), $a = 25.762(7)$, $b = 19.353(4)$, $c = 21.246(5)$ Å, $\beta = 131.26(1)°$, $T = 173$ K, $V = 7962.5$ Å^3, $Z = 4$, μ (Mo) = 6.05 cm^{-1}; Syntex R3, Mo Kα radiation; 8281 data collected using ω scan method, $4.2° \leqslant 2\theta \leqslant 52.0°$, 4826 unique reflections with $I \geqslant 3.0\sigma(I)$; solution by automated Patterson analysis (PHASE) and direct methods (MULTAN), refinement by full matrix least-squares technique, weights $[\sigma^2(I) + 0.0009I^2]^{-1/2}$, 408 parameters, all non-H atoms anisotropic, H atoms fixed, $R = 0.044$, $R_w = 0.052$.

For **3**: $C_{12}H_{36}IrP_4 \cdot PF_6$, orthorhombic, P_{nma} (No. 62), $a = 17.426(6)$, $b = 13.907(4)$, $c = 9.762(5)$ Å, $T = 90$ K, $V = 2121(2)$ Å^3, $Z = 4$, μ(Mo) = 65.37 cm^{-1}; Rigaku AFC5R diffractometer, 5051 data collected using ω scan method, $2° \leqslant 2\theta \leqslant 54.0°$, 1955 unique reflections with $F_o \geqslant 3\sigma(F_o)$; solution by automated Patterson analysis (SHELXS-86) and direct methods (SHELXS-86), refined by full matrix least-squares technique, weights $[\sigma^2(F)]$, 184 parameters, all non-H atoms anisotropic, H atoms from difference Fourier map refined, $R = 0.041$, $R_w = 0.034$.

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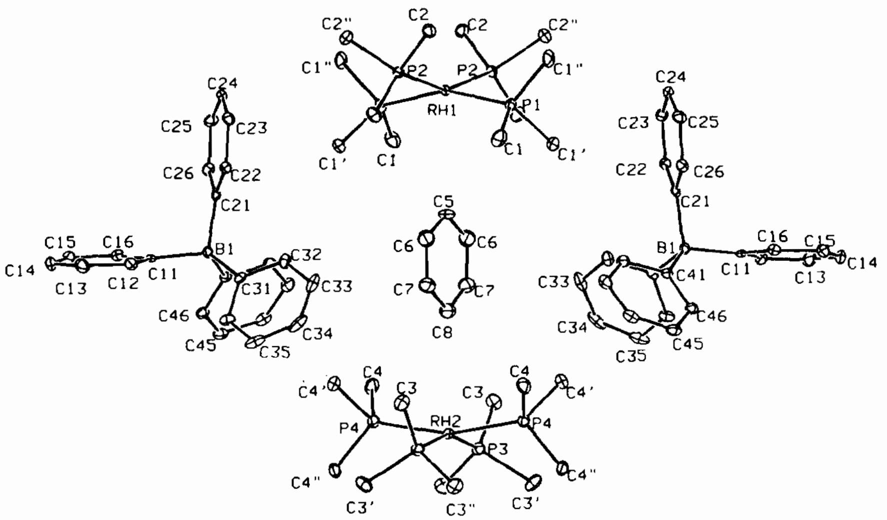

Fig. 1. Structure of 2 (hydrogen atoms omitted for clarity). Selected bond distances (Å): Rh(1)–P(1) 2.313(2); Rh(1)–P(2) 2.285(2); Rh(2)–P(3) 2.304(2); Rh(2)–P(4) 2.315(2). Selected bond angles (°): P(1)–Rh(1)–P(1a) 158.96(9); P(1)–Rh(1)–P(2) 92.48(6); P(1)–Rh(1)–P(2a) 92.48(6); P(2)–Rh(1)–P(2a) 152.6(1); P(3)–Rh(2)–P(3a) 157.8(1); P(3)–Rh(2)–P(4) 91.81(6); P(3)–Rh(2)–P(4a) 91.64(6); P(4)–Rh(2)–P(4a) 162.02(9).

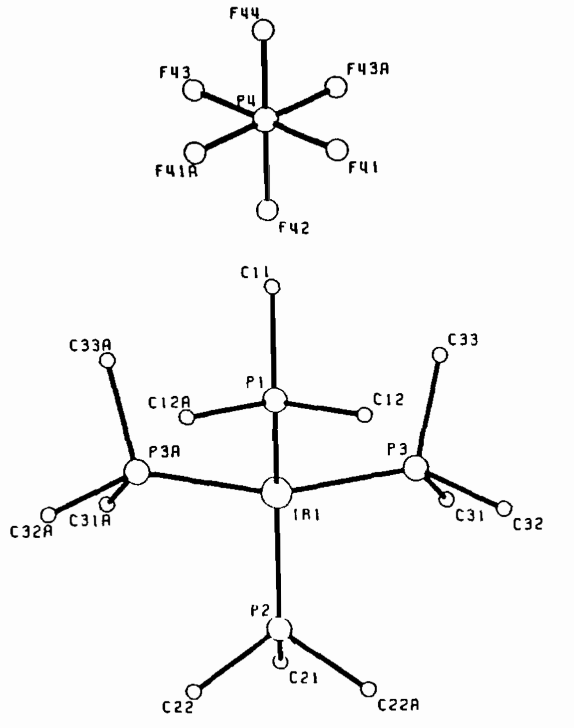

Fig. 2. Structure of 3 (hydrogen atoms omitted for clarity). Selected bond distances (Å); Ir(1)–P(1) 2.282(5); Ir(1)–P(2) 2.289(5); Ir(1)–P(3a) 2.290(5); Ir(1)–P(3) 2.290(4). Selected bond angles (°): P(1)–Ir(1)–P(2) 149.3(1); P(1)–Ir(1)–P(3) 93.2(2); P(2)–Ir(1)–P(3) 94.7(2); P(2a)–Ir(1)–P(3) 150.3(1).

than the one observed in 1 (P–Rh–P 151.46, 148.29°) or in $Rh(PMe_2Ph)_4{}^+BF_4{}^-$ (150.77, 150.01°) [13], both having similar pseudo-*trans* angles to those of the iridium analogues 3 (149.3°) and $Ir(PMePh_2)_4{}^+BF_4{}^-$ (150.5°) [14]. The uniqueness of 2 may be a result of the cage structure, which may also be responsible for the considerable difference between the two pseudo-*trans* angles in each one of the molecules of 2. All of the above rhodium and iridium complexes show very similar M–P distance (~2.3 Å) and also exhibit the same trend in M–P–C angles, the one involving the methyl on the transoid MP_2 plane being considerably larger (by as much as 12°) than the two other M–P–C angles of the same PR_3 group.

Conclusions

(i) Anion exchange of $Rh(PMe_3)_4{}^+Cl^-$ leads in our hands to $Rh(PMe_3)_4{}^+BPh_4{}^-$ and not to $Rh(PMe_3)_3{}^+BPh_4{}^-$ as previously reported.

(ii) $Rh(PMe_3)_4{}^+BPh_4{}^-$ in the currently reported (cage) arrangement is significantly less distorted than $Rh(PMe_3)_4{}^+Cl^-$, $Ir(PMe_3)_4{}^+PF_6{}^-$ and other $ML_4{}^+$ complexes.

(iii) $Ir(PMe_3)_4{}^+PF_6{}^-$, $Rh(PMe_3)_4{}^+Cl^-$ and $Rh(PMe_2Ph)_4{}^+BF_4{}^-$ are structurally very similar.

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