HOMOLEPTIC Rh(III)–DIPHOSPHINE AND Rh(III)–DIARSINE COMPLEXES

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Dedicated to Professor Sergio Roffia in recognition of his contributions to inorganic electrochemistry, on the occasion of his retirement.

The first examples of homoleptic diarsine and diphosphine coordination to Rh(III), *viz.* $[Rh(1,2-C_6H_4\{AsMe_2\}_2)_3](OTf)_2]^{3+}$ and $[Rh(Me_2PCH_2PMe_2)_3]^{3+}$, are reported, together with details of their characterisation by multinuclear NMR spectroscopy and mass spectrometry.
Keywords: Rhodium complexes; P ligands; As ligands; Phosphines; Arsines; Phosphanes; Arsanes; Multinuclear NMR spectroscopy.

We recently reported the first systematic study of a range of homoleptic Ru(II)–diphosphine and –diarsine complexes, $[Ru(L–L)_3](OTf)_2$ (OTf = triflate, $^-O_3SCF_3$. L–L = $Me_2PCH_2PMe_2$, dmpm; $Me_2PCH_2CH_2PMe_2$, dmpe; $Et_2PCH_2CH_2PEt_2$, depe; $1,2-C_6H_4(AsMe_2)_2$, diars), from the useful halide-free starting material, $[Ru(dmf)_6](OTf)_3$ [1,2]. Key features of these complexes are the large ligand field (*ca* 35 000 cm^{-1}) exerted at Ru(II) by these ligands, evidence for steric crowding in $[Ru(diars)_3]^{2+}$ (from X-ray crystallography) and $[Ru(dmpe)_3]^{2+}$ (from Ru K-edge EXAFS), and unusual electrochemistry. In particular, the Ru(II)/Ru(III) redox process is irreversible even in ultra-pure electrolytes[2], and occurs at potentials significantly more positive than would be predicted on the basis of Lever's well-known electrochemical ligand parameters, E_L [3]. Interestingly, in comparison, corresponding Fe(II) complexes show significantly less steric crowding and have Fe(II)/Fe(III) redox waves at potentials in good agreement with the ligand E_L parameters[4].

We wished to extend our studies to Rh(III) since, although homoleptic Co(III)–phosphine and Co(III)–arsine complexes have been studied[5,6], there is no good evidence in the literature for related homoleptic Rh(III) complexes, although the softer Rh(III) might be expected to have a higher affin-

ity for such donors. The only characterised example of homoleptic P(III) coordination at Rh(III) of which we are aware is $[Rh(R_2P–O\cdots HOPR_2)_3]$ (R_2 = $–OCH_2C(Me)_2CH_2O–$), made adventitiously on reaction of $[(2,4\text{-pentane-dionato})Rh(cyclooctene)_2]$ with $R_2P(O)H$ in hot benzene[7]. Interest in homoleptic Rh(III) and Ir(III) complexes of soft neutral donors is stimulated by the remarkable recent synthesis of $[Ir(CO)_6]^{3+}$ by carbonylation of IrF_6 in superacid media; the corresponding Rh(III) complex is unknown, and all attempts at its synthesis have so far yielded $[RhCl(CO)_5]^{2+}$ (refs[8,9]). Among related ''soft'' donors, it is worth noting that there are several examples of homoleptic Rh(III)–thioether coordination, involving both macrocyclic and non-macrocyclic ligands[10,11], and homoleptic seleno- and even telluroether coordination to Rh(III) has recently been described[12]. Interestingly, the Rh(III)–thioether macrocycle complexes show (quasi)reversible Rh(II)/Rh(III) and Rh(I)/Rh(II) couples, and some of the unusual Rh(II) species have been isolated. However, this has been shown to be a property unique to macrocyclic ligands; both capping and linear *non-macrocyclic* tridentate thioethers give Ru(II) complexes with only irreversible electrochemistry[10,12].

RESULTS AND DISCUSSION

Synthesis and Characterisation

Treatment of $[Rh(H_2O)_6]^{3+}$, made *in situ* by reaction of $RhCl_3 \cdot nH_2O$ with $AgNO_3$ in water, with excess diars in EtOH, followed by precipitation with NH_4PF_6, gave $[Rh(diars)_3](PF_6)_3$ (**1**) in moderate yield after recrystallisation (Scheme 1). Microanalytical data agreed with the formulation. The ^1H NMR spectrum showed two equally intense resonances for the $AsMe_2$ groups, as
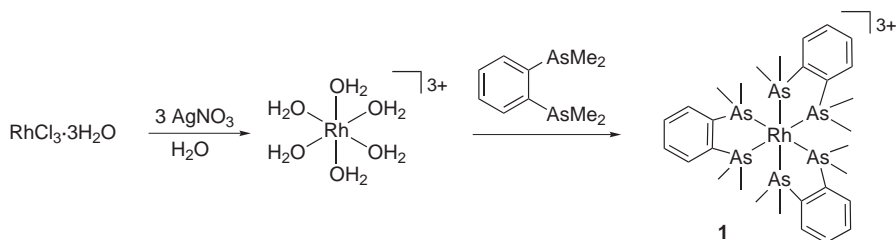
expected for a complex with this symmetry (for each $AsMe_2$, one methyl group is oriented towards a neighboring diars benzene ring, the other towards one of the two opposite triangular faces of the $RhAs_6$ octahedron consisting of one arsenic from each ligand). The aromatic region showed a

single AA′XX′ system, and the ^{13}C{^{1}H} NMR spectrum showed three aromatic C resonances, and two methyl resonances, as expected. The electrospray (positive ion) mass spectrum showed a cluster of peaks, with the correct isotope ratio, at 1251 a.m.u., for {[Rh(diars)$_3$](PF$_6$)$_2$}$^+$. In addition to bands characteristic of coordinated diars, the infrared spectrum showed a strong band due to the PF$_6^-$ ion at 842 cm^{-1}. Its presence was confirmed by the characteristic septet resonance in the ^{31}P{^{1}H} NMR spectrum, and doublet in the ^{19}F NMR spectrum.

It has so far proved difficult to grow crystals of **1** suitable for X-ray diffraction. Diffusion of diethyl ether into dilute acetonitrile solutions of **1** did afford single crystals, however, these diffracted poorly. We were unable to obtain a satisfactory solution of the data (R_1 = 0.2856, wR_2 = 0.4242), and therefore the structure is not discussed, but the identity of the crystals was confirmed as [Rh(diars)$_3$](PF$_6$)$_2$(NO$_3$). Evidently, nitrate ions are present as an impurity in **1**, although the microanalytical data agreed well with the formula [Rh(diars)$_3$](PF$_6$)$_3$, and the amount of nitrogen was below the detection limit (≈0.3%). This salt must therefore crystallise preferentially. The basic structural features of the [Rh(diars)$_3$]$^{3+}$ cation appear to be similar to [Co(diars)$_3$]$^{3+}$ (ref.[5]), and [Ru(diars)$_3$]$^{2+}$ (ref.[2]).

Preliminary electrochemical studies on a 1 mM solution of complex **1** in 0.1 M Et$_4$NBF$_4$ in acetonitrile revealed no oxidative electrochemistry on cycling from 0 V (*vs* SCE) to +2 V. On scanning negative, a totally irreversible reduction was observed at E_P^C = –0.5 V. This is evidently an EC process, since on scanning positive again, an irreversible oxidation at E_P^A +0.05 V is then observed. Therefore, as expected by analogy with non-macrocyclic thioether ligands, this homoleptic Rh(III)–arsine complex does not show reversible Rh(III)/Rh(II) behaviour.

The complex [Rh(dmpm)$_3$](PF$_6$)$_3$ (**2**) was similarly isolated, in 23% yield. It was less soluble than **1**, but NMR spectra could be recorded in DMSO-d_6. The ^{1}H NMR spectrum showed the expected pair of equally intense resonances for the –PMe$_2$ groups; coupling to P was not resolved in this solvent. The chemical shift of the methylene protons was consistent with chelating dmpm. The ^{13}C{^{1}H} NMR spectrum showed three resonances, also consistent with the symmetry of the molecule. Again, coupling to ^{31}P was not resolved. In addition to the resonance for PF$_6^-$, the ^{31}P{^{1}H} NMR spectrum showed a doublet resonance at –42.6 ppm. As expected for a diphosphine four-membered chelate, this is well upfield from values found for Rh complexes with bridging dmpm ligands. For example, the Rh(III) complex [{(η^5-C$_5$Me$_5$)RhCl$_2$}$_2$(μ-dmpm)] has δ(^{31}P) +20.3 ppm, and the Rh(I) dimer

trans,trans-$[Rh_2Cl_2(CO)_2(\mu\text{-dmpm})_2]$ has $\delta(^{31}P)$ –4 ppm ($^1J_{RhP}$ = 116 Hz). The small value of $^1J_{RhP}$ for **2**, 70 Hz, is consistent with Rh(III) with P-*trans*-P [13,14].

When $[Rh(H_2O)_6]^{3+}$ was treated with dmpe and the product was precipitated by the addition of NH_4PF_6, the crude product, isolated in 25% nominal yield, contained only some 50% of $[Rh(L–L)_3](PF_6)_3$ (**3**) by $^{31}P\{^1H\}$ NMR spectroscopy ($\delta(^{31}P)$ +33.3 ppm, $^1J_{RhP}$ = 79 Hz); the other resonances were a broad singlet at –28 ppm and a minor multiplet at +42 ppm. Repeated recrystallisations were required before a spectroscopically-satisfactory sample of **3** was isolated. Analytically, the purified product is a mixed nitrate-hexafluorophosphate salt. Once again, the crude product evidently contained nitrate ions, and the repeated recrystallisation from polar, aprotic solvents enriched the nitrate content, as during the recrystallisation of **1**. Attempts to isolate a pure product by ion-exchange chromatography are in progress. The identity of the cation of **3** is confirmed by the multinuclear NMR spectroscopic data. In particular, there are two equally-intense methyl resonances in the ^1H NMR spectrum, and two methyl carbon resonances in the $^{13}C\{^1H\}$ NMR spectrum. The ^{31}P chemical shift and $^1J_{RhP}$ are also consistent with the formulation; typical chemical shifts and $^1J_{RhP}$ for $[RhX_2(dmpe)_2]^+$ (X = halide; *cis* and *trans*), with P-*trans*-P, are *ca* +35–45 ppm and 80–85 Hz [13]. A correlation between Rh–P bond lengths in complexes $[RhX_2(Me_2P–R–PMe_2)_2]^+$ (R is $–CH_2CH_2–$ or $–(CH_2)_3–$), and their $^1J_{RhP}$, has been noted[13]. If this also holds good for **3**, the low value of $^1J_{RhP}$ may be an indication of steric crowding in the homoleptic complex compared with $[RhX_2(dmpe)_2]^+$, as might be expected by analogy with the isoelectronic Ru(II) system[2].

Attempts to examine the electrochemistry of the diphosphine complexes were unsuccessful. Both **2** and **3** were sparingly soluble in CH_3CN, but on the addition of supporting electrolyte (R_4N^+ salts with BF_4^-, ClO_4^- or OTf^- anions), they immediately re-precipitated.

Treatment of $[Rh(H_2O)_6]^{3+}$ with excess depe in EtOH, followed by precipitation with NH_4PF_6, gave a yellow precipitate, which was a complex mixture by $^{31}P\{^1H\}$ NMR spectroscopy. Similar reactions with aromatic diphosphines failed to yield homoleptic Rh(III) complexes.

This preliminary study has shown that it is possible to isolate a limited range of homoleptic Rh(III)–diphosphine and –diarsine complexes. In future work, we hope to investigate ligands more optimised for homoleptic coordination to Rh(III), such as $1,2\text{-}C_6H_4(EMe_2)_2$ (E = P and Sb) and $MeC(CH_2PMe_2)_3$, as well as alternative synthetic routes. Extensions to Ir(III) and Os(II) are also planned.

EXPERIMENTAL

General methods and instrumentation were as recently described[15,2], except that owing to the high fluorine content of the tris(hexafluorophosphate) salts, we were unable to carry out microanalyses in-house, and these were therefore obtained commercially in duplicate (Butterworth Laboratories Ltd.). Chemical shifts are given in ppm (δ-scale), coupling constants (J) in Hz. All reactions were carried out under an Ar atmosphere using standard Schlenk techniques. $RhCl_3 \cdot 3H_2O$ was obtained from Johnson–Matthey Ltd. The phosphine ligands were obtained from Strem Chemicals Ltd. All other chemicals were obtained from the Aldrich Chemical Company, and were used as received.

Tris(1,2-bis{dimethylarsino}benzene)rhodium(III) Hexafluorophosphate (**1**)

To a solution of $RhCl_3 \cdot 3H_2O$ (0.20 g, 0.79 mmol) in water (10 cm^3) was added $AgNO_3$ (0.40 g, 2.4 mmol), and the reaction mixture was refluxed for 2 h. The resulting yellow solution was filtered from the AgCl precipitate into a solution of the diarsine (0.68 g, 2.4 mmol) in MeOH (10 cm^3). The mixture was then refluxed for 24 h, then allowed to cool to room temperature. To the now plum-coloured solution was added solid NH_4PF_6 (0.45 g, 2.8 mmol). A pale cream-coloured precipitate appeared, which was filtered off, washed with water and diethyl ether, and dried. The crude product was recrystallised from acetone/diethyl ether as a white solid, filtered off and dried *in vacuo*. Yield 0.36 g (34%). ^{1}H NMR (400 MHz, acetone-d_6): 7.55, 7.22 m's, 12 H, AA'XX', $|J_{AX} + J_{AX'}|$ = 7.4 (C_6H_4); 1.80 s, 18 H (MeAs); 1.40 s, 18 H (MeAs). ^{13}C{^{1}H} NMR (101 MHz, acetone-d_6): 136, 134, 131 (C_6H_4); 20, 17.5 (Me_2As). ^{19}F NMR (376 MHz, acetone-d_6): –103 d, J_{PF} = 708 (PF_6^-). ^{31}P{^{1}H} NMR (162 MHz, acetone-d_6): –143.0 septet, J_{PF} = 708 (PF_6^-). IR (Nujol): 842 (s), PF_6^-. UV-VIS (MeCN, E_{max}/10^{-3} cm^{-1} (log ε)): 40.0 (3.10). MS (ES$^+$): 1251 [M – PF_6]$^+$. For $C_{30}H_{48}As_6F_{18}P_3Rh$ (1396.1) calculated: 25.81% C, 3.47% H, 0% N; found: 25.48% C, 3.42% H, <0.3% N.

Tris(bis{dimethylphosphino}methane)rhodium(III) Hexafluorophosphate (**2**)

This was prepared exactly as for **1**, using $RhCl_3 \cdot 3H_2O$ (0.36 g, 1.3 mmol). The yellow crude product was washed with acetone, whereupon it became off-white, then diethyl ether, and was dried *in vacuo*. It proved too insoluble to recrystallise. Yield 0.28 g (23%). ^{1}H NMR (400 MHz, DMSO-d_6): 4.04 br m, 6 H (PCH_2P); 2.09 br s, 18 H (PMe); 1.99 br m, 18 H (PMe). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): 40.9 br s (PCH_2P); 17.4 br s (PMe); 16.1 br s (PMe). ^{19}F NMR (376 MHz, DMSO-d_6): –103 d, J_{PF} = 708 (PF_6^-). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6): –42.6 d, J_{RhP} = 70 (dmpm); –143.5 septet, J_{PF} = 708 (PF_6^-). IR (Nujol): 842 (s), PF_6^-. UV-VIS (MeCN, E_{max}/10^{-3} cm^{-1} (log ε)): 40.3 (3.52). For $C_{15}H_{42}F_{18}P_9Rh$ (946.2) calculated: 19.04% C, 4.47% H, 0% N; found: 19.10% C, 4.10% H, <0.3% N.

Tris(1,2-bis{dimethylphosphino}ethane)rhodium(III) Hexafluorophosphate (**3**)

To a solution of $RhCl_3 \cdot 3H_2O$ (0.10 g, 0.37 mmol) in water (5 cm^3) was added $AgNO_3$ (0.20 g, 1.2 mmol), and the reaction mixture was refluxed for 2 h. The resulting yellow solution was filtered from the AgCl precipitate into a solution of the diphosphine (0.20 g, 1.3 mmol) in MeOH (5 cm^3). The mixture was refluxed for 24 h, then allowed to cool to room temperature. The resulting yellow precipitate was filtered off, washed repeatedly with acetone, then diethyl ether, and dried *in vacuo*. Examination by ^{31}P{^{1}H} NMR spectroscopy revealed that,

in addition to the doublet for **3** and the multiplet for PF_6^- (below), there was a broad resonance at –28 ppm (pwhh 400 Hz), so the sample was recrystallised repeatedly from Me_2SO/MeOH until it was free of the impurity. Yield 5.0 mg (1.4%). ^1H NMR (400 MHz, DMSO-d_6): 2.10 br m, 12 H (PCH_2CH_2P); 1.92 br s, 18 H (PMe); 1.88 br s, 18 H (PMe). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): 31.0 br s (PCH_2CH_2P); 18.3 br s (PMe); 17.7 br s (PMe). ^{19}F NMR (376 MHz, DMSO-d_6): –103 d, J_{PF} = 708 (PF_6^-). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6): 33.3 d, J_{RhP} = 79 (dmpe); –143.5 septet, J_{PF} = 708 (PF_6^-). For $C_{18}H_{48}F_9N_{1.5}O_{4.5}P_{7.5}Rh$ (863.8) calculated: 25.02% C, 5.60% H, 2.43% N; found: 25.29% C, 5.59% H, 3.33% N.

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