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Formation of an Asymmetric Rh–Hg–Rh Bridged Complex

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Abstract

Reaction of $HgCl_2$ with $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]Cl$ (dppm = bis(diphenylphosphino)methane) gives $[Rh_2Cl_3(\mu\text{-}HgCl)(CO)_2(\mu\text{-}dppm)_2]$ in which only one Rh is oxidised by insertion into a Hg–Cl bond, and which consequently contains an unusual asymmetric Rh–Hg–Rh bridge.

Introduction

The reactions of mercury(II) halides with complexes of the transition metals are various, and include insertion of the metal centre into a mercury–halogen bond, or formation of simple adducts in which the transition metal complex acts as a Lewis base [1]. Oxidation of *trans*-$[RhCl(CO)(PR_3)_2]$ (PR_3 = PPh_2Et, PPh_2Pr^i, PPh_2CH_2SPh, but not PPh_3) by $HgCl_2$ to form $[RhCl_2(HgCl)(CO)(PR_3)_2]$ has been demonstrated [2]. Recently it was reported [3] that $HgCl_2$ reacts with $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]$ to form $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}HgCl_2)]$, **1**. A symmetric Rh–Hg–Rh bridge is formed as each electron-rich Rh centre acts as a Lewis base. Herein I report the formation of a complex containing an unusual and, to date, unique asymmetric Rh–Hg–Rh bridge.

Experimental

Preparation of $[Rh_2Cl_3(\mu\text{-}HgCl)(CO)_2(\mu\text{-}dppm)_2]$

To a dichloromethane solution of $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]Cl$ (0.455 mmol), prepared *in situ*, was added $HgCl_2$ (0.117 g, 0.431 mmol), which rapidly dissolved with concurrent formation of a red solution. The solvent slowly evaporated under a stream of CO to leave a dark, glassy product. The residue was washed with alcohol, then ether, and then extracted with dichloromethane (30 mL). The dichloromethane solution was diluted with ethanol (20 mL), and then placed under a stream of N_2. When the major proportion of dichloromethane had evaporated red-brown crystals of $[Rh_2Cl_3(\mu\text{-}HgCl)(CO)_2(dppm)_2]$ were separated, and dried under vacuum. All attempts to prepare crystals suitable for X-ray crystallography have yielded only microcrystals or gross multiples. Analysis found: C, 44.4; H, 3.2; Cl, 10.1%; M, 1337. Calculated: C, 45.5; H, 3.2; Cl, 10.3%; M, 1373.

Reaction of $[Rh_2Cl_3(\mu\text{-}HgCl)(CO)_2(\mu\text{-}dppm)_2]$ *with CO*

Recrystallization of the above product from dichloromethane/ethanol under a stream of CO gave a material which appeared to be (IR spectrum) the same product, but with lesser amounts of an impurity containing a bridging CO ligand. However, a solution of the same complex in dichloromethane-d_2 under an atmosphere of CO exhibited ^{31}P and ^{13}C NMR resonances due to both starting material and a carbonyl-bridged dirhodium complex containing a Rh–Rh bond [4].

Results and Discussion

Reaction of CO with $[Rh_2Cl_2(CO)_2(\mu\text{-}dppm)_2]$, in which each Rh centre has 16 electrons, gives $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]Cl$, **2**, in which each Rh centre has 18 electrons [4]. The reaction is reversible. Reaction of an equimolar amount of $HgCl_2$ with a solution of **2** in CH_2Cl_2 under an atmosphere of CO rapidly gave a dark red solution of crude $[Rh_2Cl_3(\mu\text{-}HgCl)(CO)_2(\mu\text{-}dppm)_2]$, **3**. Recrystallization of **3** from CH_2Cl_2/EtOH (5:1) under a stream of N_2 gave pure **3** as deep red-brown microcrystals. Complex **3**, which is not an electrolyte, is assigned the formula above and the structure shown in Fig. 1 on the basis of elemental analyses, molecular weight, and the following spectroscopic evidence.

The IR spectrum exhibits bands at 2068 and 2026 cm^{-1} assigned to the carbonyl ligands bonded to Rh_B and Rh_A respectively. Weak bands (200 to 400 cm^{-1}) are observed at 372, 355, 304 and 244 cm^{-1}, and are assigned as metal–ligand stretches. The ^{31}P NMR spectrum of **3** (Fig. 2; –50 °C, CD_2Cl_2, ^1H decoupled) shows two doublets of triplets, each

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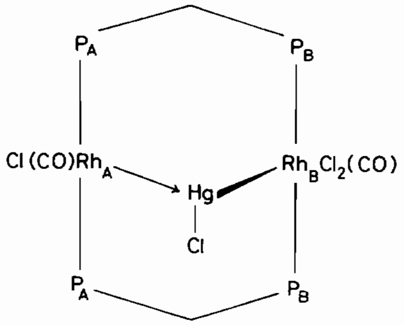

Fig. 1. Structure of $[Rh_2Cl_3(\mu\text{-}HgCl)(CO)_2(\mu\text{-}dppm)_2]$, 3 ($P\frown P$ = dppm).

with distinctive satellites due to coupling to ^{199}Hg. The triplet structure (J = 10 Hz) is due to coupling between P_A and P_B. The value of $^1J_{Rh_AP_A}$ (106 Hz) is lower than corresponding values for *trans*-$[RhCl(CO)(PR_3)_2]$ [5], and is consistent with the proposed interaction between Rh_A and Hg. The value for $^1J_{Rh_BP_B}$ (83 Hz) is very similar to the corresponding parameter for $[RhCl_2(HgCl)(CO)(PR_3)_2]$ [2], and confirms that oxidation of Rh_B has occurred by insertion into a Hg–Cl bond. Coupling of Hg to P_B (192 Hz) is reduced in comparison to $[RhCl_2(HgCl)(CO)(PR_3)_2]$ [2], probably due to the interaction of Hg also with Rh_A. The value of $^2J_{HgP_A}$ is even lower, consistent with the weaker interaction of Hg with Rh_A. It is noteworthy that the values of $J_{Rh_AP_B}$ and $J_{Rh_BP_A}$ are each so small that no coupling is observed. This is consistent with the absence of a Rh–Rh bond, in contrast to complex 1 [3].

The ^{13}C NMR spectrum of a solution of the ^{13}CO (90% ^{13}C enriched) complex showed two distinct environments for ^{13}C, each coupled to one ^{103}Rh and two ^{31}P nuclei (δ_{C_A} 189.3 ppm, $^1J_{Rh_AC_A}$ 79, $^2J_{P_AC_A}$ 14 Hz; δ_{C_B} 183.8 ppm, $^1J_{Rh_BC_B}$ 68, $^2J_{P_BC_B}$ 10 Hz). The ^{31}P NMR spectrum of this material was the same as for the ^{12}CO complex, except that coupling of each ^{31}P nucleus to one adjacent ^{13}C nucleus was observed.

On the basis of the above evidence it is concluded that $HgCl_2$ reacts with 2 to form the 1:1 addition complex 3, that this reaction involves oxidation of only one rhodium centre by insertion into a mercury–chlorine bond, and that 3 contains an asymmetric Rh–Hg–Rh bridge of a kind previously unknown.

The ^{31}P NMR spectrum of a solution prepared from 3 under an atmosphere of CO showed resonances not only due to 3, but also another predominant species. Neither crystals nor a pure solution of this latter species could be isolated. No $HgCl_2$ precipitated from solution under CO. The spectrum of the species formed possessed a single environment for ^{31}P (δ_P 31.3 ppm; $|^1J_{RhP} + {}^xJ_{RhP}|$, 93.4 Hz), and was second-order, resembling in character the spectrum of 2 [4]. The ^{13}C NMR spectrum was broad, overlapping with that of 3, and contained a

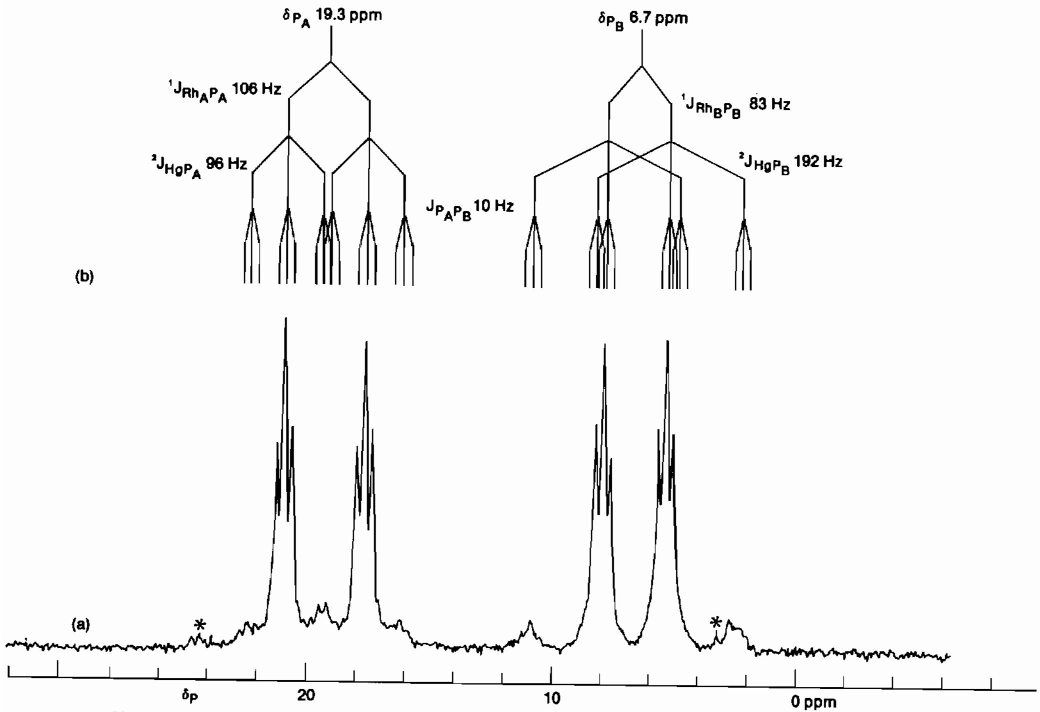

Fig. 2. (a) ^{31}P NMR spectrum of a solution of $[Rh_2Cl_3(\mu\text{-}HgCl)(CO)_2(\mu\text{-}dppm)_2]$, 3, in CD_2Cl_2, –50 °C, ^{1}H-decoupled. Chemical shifts are relative to external 85% H_3PO_4. Peaks marked by an asterisk are due to impurities. (b) Calculated positions of lines.

broad weak resonance (δ_C 208 ppm) due to a bridging ^{13}CO ligand. By comparison with the properties of **1** [3], it is possible that an equilibrium mixture is established under CO, consisting of **3** and a $HgCl_2$- and CO-bridged complex.

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