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Preparation of a Rh–$SnCl_2$–Rh bridged A-frame complex, and the reversible reaction with CO and chloride to form the corresponding $SnCl_3^-$ complex

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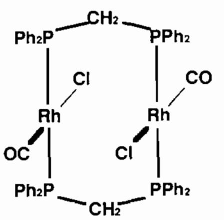
Abstract

Reaction of $SnCl_2\cdot 2H_2O$ with $[Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2]$ occurs to form $[Rh_2(\mu\text{-Cl})(\mu\text{-SnCl}_2)(CO)_2(\mu\text{-dppm})_2]Cl$. Reaction of this complex with CO causes a sequence of reactions resulting in the displacement of the tin ligand and the formation of $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2][SnCl_3]$.

Introduction

An extensive variety of complexes containing transition metal–Group 14 metal bonds is now known [1, 2]. The hydrogenation or hydroformylation catalytic activity of trihalogenostannio complexes of platinum group metals is frequently superior to that of the corresponding halogeno complexes [3, 4]. Binuclear dppm-bridged (dppm is bis(diphenylphosphino)-methane; dpam is the corresponding diarsine) A-frame complexes of rhodium(I) are catalytically active for hydrogenation [5–7], hydroformylation [5, 7] and the water gas shift reaction [5, 7, 8]. Consequently it was considered appropriate to investigate the reactions of $SnCl_2$ with $[Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2]$ (**1**), $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2][BPh_4]$ (**2**) or the diarsine analogues.



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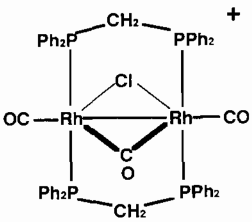

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Experimental

All reactions were performed in dry, oxygen-free solvents under an atmosphere of nitrogen or carbon monoxide. Complexes **1** and **2**, and the diarsine and bromo analogues, were prepared using procedures reported in the literature [9, 10]. Spectra were recorded using the following instruments: IR, Perkin-Elmer 283; NMR, Bruker WP80 (CD_2Cl_2 or $(CD_3)_2CO$ at −80 °C). Conductivities were measured using a Radiometer CDM2e conductivity meter.

Preparation of $[Rh_2(\mu\text{-Cl})(\mu\text{-SnCl}_2)(CO)_2(\mu\text{-dppm})_2]Cl$

Under an atmosphere of N_2, a mixture of **1** (0.435 g, 0.395 mmol) and $SnCl_2\cdot 2H_2O$ (0.182 g, 0.807 mmol) in dichloromethane (50 ml) was stirred, while methanol (10 ml) was added slowly. The reagents dissolved to form a dark red solution, from which a red–brown powder slowly separated as the bulk of the solvent was reduced. The product was recrystallized from CH_2Cl_2/MeOH to give, as red–brown crystals (78%), $[Rh_2(\mu\text{-Cl})(\mu\text{-SnCl}_2)(CO)_2(\mu\text{-dppm})_2]Cl$. *Anal.* Found: C, 47.1; H, 3.4; Cl, 10.6. Calc.: C, 48.4; H, 3.4; Cl, 11.0%. The complex is a 1:1 electrolyte in solution in acetone (Λ_M 62 Ω cm^{-1} M^{-1}). Crystals of the complex are stable in air for periods in excess of one year.

The analogous dpam complex can be prepared by a similar procedure, as a purple–brown powder (87%). *Anal.* Found: C, 41.6; H, 2.9; Cl, 10.0%; *M* (CH_2Br_2 solution), 1467. Calc.: C, 42.6; H, 3.0; Cl, 9.7%; *M*, 1467.

Preparation of $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2][SnCl_3]$

When a similar reaction was performed under an atmosphere of CO the initially red–orange solution became golden. The solvent was gradually reduced in bulk, and $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2][SnCl_3]$

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precipitated as yellow crystals (72%). *Anal.* Found: C, 47.7; H, 3.3; Cl, 11.4%; *M* (CH_2Br_2 solution), 1256. Calc.: C, 48.2; H, 3.3; Cl, 10.8%; *M*, 1319. The complex is a 1:1 electrolyte in solution in acetone (Λ_M 113 Ω cm^{-1} M^{-1}) or dichloromethane (Λ_M 71 Ω cm^{-1} M^{-1}).

Reversible reaction of [$Rh_2(\mu$-$Cl)(\mu$-$SnCl_2)(CO)_2$-(μ-dppm$)_2$]Cl with CO

A solution of [$Rh_2(\mu$-$Cl)(\mu$-$SnCl_2)(CO)_2(\mu$-dppm$)_2$]Cl in a mixture of CH_2Cl_2 and CH_3OH changed from red–orange to yellow upon reaction with CO. Slow evaporation of solvent gave yellow crystals of [$Rh_2(\mu$-$Cl)(CO)_2(\mu$-$CO)(\mu$-dppm$)_2$][$SnCl_3$].

When a solution of the latter complex was stirred under a stream of N_2, the colour slowly became darker and, after a period of hours, the former complex was recovered.

Results and discussion

When an equimolar amount of $SnCl_2 \cdot 2H_2O$ is added to a solution of **1** in a mixture of CH_2Cl_2 and CH_3OH, the 1:1 electrolyte [$Rh_2(\mu$-$Cl)(\mu$-$SnCl_2)(CO)_2(\mu$-dppm$)_2$]Cl is formed in high yield (eqn. (1)). The IR spectrum of the complex exhibits only terminal carbonyl bands (1982(vs), 1973(vs) cm^{-1}). The ^{31}P NMR of a solution of the complex in CD_2Cl_2 or $(CD_3)_2CO$ (−80 °C) is second order, and is not that expected for [$Rh_2(\mu$-$Cl)(CO)_2(\mu$-dppm$)_2]^+$ [10]. The parameters (CD_2Cl_2: δ_P 25.9 ppm (versus external H_3PO_4), $|^1J+^xJ|_{RhP}$ 106 Hz; $(CD_3)_2CO$: δ_P 24.7 ppm, $|^1J+^xJ|_{RhP}$ 106 Hz) demonstrate that all phosphorus nuclei are equivalent, and that the Rh–Rh interaction is non-bonding [10]. Satellites are observed for the spectrum in either solvent which are consistent with coupling to ^{117}Sn and ^{119}Sn, but not all separate satellites for coupling to each isotope are unequivocably discerned ($^2J_{SnP} \sim 114$ Hz) (Fig. 1). On warming to −70 °C the signals become broader, and at −50 °C the spectrum becomes a very broad doublet with ill-resolved Sn–P satellites

For all phosphorus nuclei to be equivalent and coupled to tin the complex cation must have a tin-bridged structure. A $SnCl_2$-bridged structure is both precedented [2] and consistent with all the spectroscopic data. The alternative structure, containing a (μ-SnCl) ligand and two terminal chloro ligands, would require the presence of a Rh–Rh bond, which is not consistent with the ^{31}P NMR spectrum. Oxidative addition of $HgCl_2$ across only one Rh centre of complex **1** affords the Rh(I)Rh(III) complex [$Rh_2Cl_3(\mu$-$HgCl)(CO)_2(\mu$-dppm$)_2$] [11], demonstrating that spacing between the closer Rh centres of **1** can easily increase to accommodate such a large ligand. On the evidence of the analytical, spectroscopic and conductivity data, and by comparison with the above precedents, it is concluded that the product of the reaction of **1** with $SnCl_2 \cdot 2H_2O$ is [$Rh_2(\mu$-$Cl)(\mu$-$SnCl_2)(CO)_2(\mu$-dppm$)_2$]Cl, and that the cation has the structure illustrated.

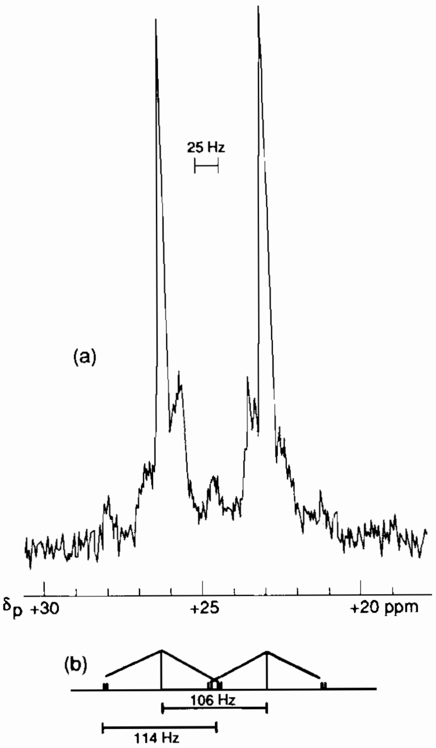
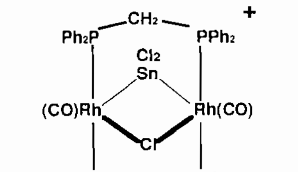


Fig. 1. (a) ^{31}P NMR (at −80 °C) of a solution of [$Rh_2(\mu$-$Cl)(\mu$-$SnCl_2)(CO)_2(\mu$-dppm$)_2$]Cl in $(CD_3)_2CO$, under N_2 (chemical shift vs. 85% H_3PO_4). (b) Proposed coupling $^2J_{SnP}$.

$$[Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2] + SnCl_2 \cdot 2H_2O \longrightarrow$$

$$[Rh_2(\mu\text{-Cl})(\mu\text{-SnCl}_2)(CO)_2(\mu\text{-dppm})_2]Cl + 2H_2O \quad (1)$$

When the reaction of [$Rh_2Cl_2(CO)_2(\mu$-dppm$)_2$] with an equimolar or excess amount of $SnCl_2 \cdot 2H_2O$ is performed under an atmosphere of CO, instead of N_2, the product is again a 1:1 electrolyte. However, the cation contains no tin ligand, but instead the $SnCl_3^-$ anion is present (eqn. (2)). The IR spectrum of the product shows carbonyl bands at 2012(s, sh), 1983(vs) and 1872(s) cm^{-1}, characteristic of the A-frame cation **2** [10]. Metal ligand bands are at 359(w), 287(w) and 251(w-m) cm^{-1}. The anion $SnCl_3^-$ exhibits bands close to 289 and 252 cm^{-1}, which are shifted to higher values upon coordination to a platinum-group metal [12, 13]. The ^{31}P NMR spectrum (−80 °C) shows only the second order spectrum characteristic of cation **2** [10]. On the basis of the analytical, spectroscopic and conductivity evidence, the product of the reaction under CO is shown to be [$Rh_2(\mu$-$Cl)(CO)_2(\mu$-$CO)(\mu$-dppm$)_2$][$SnCl_3$].



$[Rh_2(\mu\text{-Cl})(\mu\text{-SnCl}_2)(CO)_2(\mu\text{-dppm})_2]^+$

$$[Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2] + CO + SnCl_2\cdot 2H_2O \longrightarrow [Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2][SnCl_3] + 2H_2O \qquad (2)$$

Even when a large excess of $SnCl_2\cdot 2H_2O$ was present, the only rhodium containing product formed was that of eqn. (2), in which only one chloro ligand has reacted to form a $SnCl_3^-$ anion.

When a similar reaction was performed under CO with the bromo analogue of complex **1**, both addition of $SnCl_2$ and halogen exchange (Cl/Br) occurred, to form a mixture of products.

The $SnCl_2$-bridged complex, above, reacts reversibly with CO to afford the same product as eqn. (2). The reaction is slow and sequential. The highly complex ^{31}P NMR spectra taken during the reaction show transient signals due to one or more intermediates, the identities of which are unknown. Subsequently, signals due to $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2][SnCl_3]$ predominate, and this complex can be isolated (eqn. (3)).

$$[Rh_2(\mu\text{-Cl})(\mu\text{-SnCl}_2)(CO)_2(\mu\text{-dppm})_2]Cl + CO \rightleftharpoons \text{‘}Rh_2SnCl_4(CO)_3(\mu\text{-dppm})_2\text{’} \rightleftharpoons [Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2][SnCl_3] \qquad (3)$$

The above sequence of events is reversible. Bubbling N_2 through a solution of $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2][SnCl_3]$ causes the solution to become redder, and the $SnCl_2$-bridged complex $[Rh_2(\mu\text{-Cl})(\mu\text{-SnCl}_2)(CO)_2(\mu\text{-dppm})_2]Cl$ is recovered in high yield.

Although reaction (3) is reversible, it is unlikely to be the straightforward displacement of bridging $SnCl_2$ with CO, for such a reaction would not give the complex transient spectra observed. The existence of both bonded and ionic tin species in rhodium–tin complexes is reasonable [14–17]. The straightforward dissociation reaction (4) has been proposed for diene [15],

$$L_nRhSnCl_3 \rightleftharpoons L_nRh^+ + SnCl_3^- \qquad (4)$$

phosphite [16] and bidentate nitrogen heterocycle [17] complexes of rhodium. To date all attempts to exchange $SnCl_3^-$ or Cl^- anions of the products of reactions (1) or (2) with BPh_4^-, in solvents of high dielectric constant, have yielded only mixtures of products, consistent with a system more complex than reaction (4). Reaction (3) therefore represents an unusual reversible reaction, in which a bridging tin ligand is transformed into a $SnCl_3^-$ anion, rather than simple ionization.

The reaction of only one terminal chloro (or bromo) ligand of a binuclear complex to form a $SnCl_3^-$ complex is precedented. However, the binuclear complexes $[M_2Cl(SnCl_3)(\mu\text{-dppm})_2]$ (M = Pd [18], Pt [19]) react further with excess $SnCl_2$ readily to form $[M_2(SnCl_3)_2(\mu\text{-dppm})_2]$, in contrast to the system herein reported.

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