

Preliminary communication

**The reactivity of the metal–metal bond in the dimer
 $[(\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3)_2\text{Rh}_2(\mu\text{-CO})_2] \cdot (\text{CH}_3)_2\text{CO}$.
 Synthesis and X-ray structure of a paramagnetic dinuclear
 rhodium complex**

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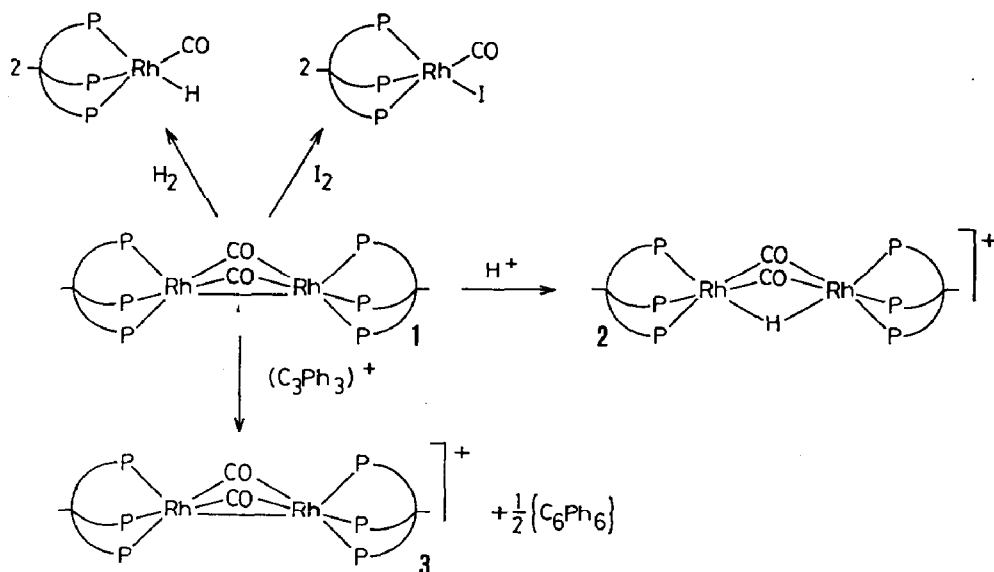
Abstract

The dimeric rhodium(0) complex $[(\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3)_2\text{Rh}_2(\mu\text{-CO})_2]$ (**1**), undergoes oxidative-addition reactions with H_2 and H^+ , with metal–metal bond breaking, to form a monomeric and a dinuclear hydride derivative, respectively. The oxidation of **1** by electrochemistry or chemical agents affords the paramagnetic cation $[(\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3)_2\text{Rh}_2(\mu\text{-CO})_2]^+$. The structure of this latter, which has been determined by X-ray diffraction, closely resembles that of the uncharged species **1**, but with a shorter Rh–Rh bond distance.

The current high level of interest in binuclear metal complexes stems mainly from the possibility of increasing understanding of important catalytic processes by gaining more knowledge of the requirements for the making and breaking of metal–metal bonds [1].

We recently reported an improved synthesis of the rhodium(0) dimer (triphos) $_2\text{Rh}_2(\mu\text{-CO})_2$ (**1**) (triphos = 1,1,1-tris(diphenylphosphinomethylethane) (Scheme 1), in which the presence of a formal metal–metal single bond has been suggested by an X-ray study [2].

Now we report some reactions of **1** in which the metal–metal bond is variously involved (Scheme 1).



Scheme 1

Complex **1** in THF at room temperature undergoes oxidative-addition reactions with H_2 or I_2 to form the previously reported monomeric derivatives (triphos)Rh(CO)H and (triphos)Rh(CO)I, respectively [3]. The reaction with molecular hydrogen, which occurs rapidly at atmospheric pressure, is not reversed by bubbling carbon monoxide through the solution of the hydride.

When a THF solution of **1** is treated with an equimolar amount of CF_3COOH a yellow-green solution is obtained, from which, after addition of NaBPh_4 , crystals of formula [(triphos) $_2$ Rh $_2$ (CO) $_2$ H](BPh $_4$) (**2**) can be isolated [4*]. The IR and the ^1H NMR spectra at room temperature are consistent with a bioctahedral structure with two carbonyls and a hydride bridging the two rhodium atoms (Scheme 1) [5*]. The IR (Nujol) spectrum shows the presence of only bridging carbonyls ($\nu(\text{CO})$ 1790s, 1820m cm^{-1}), which are, as expected, at higher frequency than those found for **1**, ($\nu(\text{CO})$ 1730s, 1750m cm^{-1}). The ^1H NMR (299.943 MHz, CD_2Cl_2 , 293 K) spectrum has a resonance at high field (1H, δ -7.45 ppm) (Fig. 1), consisting of a triplet of pseudo nonets due to coupling of the hydride to two phosphorus ($^2J(\text{H}-\text{P}_{\text{trans}})$ 63 Hz), two rhodium ($^1J(\text{H}-\text{Rh})$ 10 Hz), and four phosphorus atoms ($^2J(\text{H}-\text{P}_{\text{cis}})$ 5 Hz) [5*]. This assignment was confirmed by the $^1\text{H}\{^{31}\text{P}\}$ spectra. Although the dimeric structure is retained upon protonation of **1** the metal-metal bond is formally cleaved. The observed basicity of the Rh-Rh bond in **1** strongly suggests the possibility of successive 2×1 electron oxidations of the dimer. This, and the increasing attention being given to the electrochemical characterization of dirhodium complexes [6], prompted us to investigate the electrochemistry of **1**. Figure 2 shows the cyclic voltammogram exhibited by [(triphos) $_2$ Rh $_2$ (CO) $_2$] in THF solution. There are two distinct anodic processes, each showing a directly associated reduction peak in the reverse scan. Analysis of cyclic voltammograms with scan rates varying from 0.02 to 10 V s^{-1} , together with the results of controlled

* Reference number with asterisk indicates a note in the list of references.

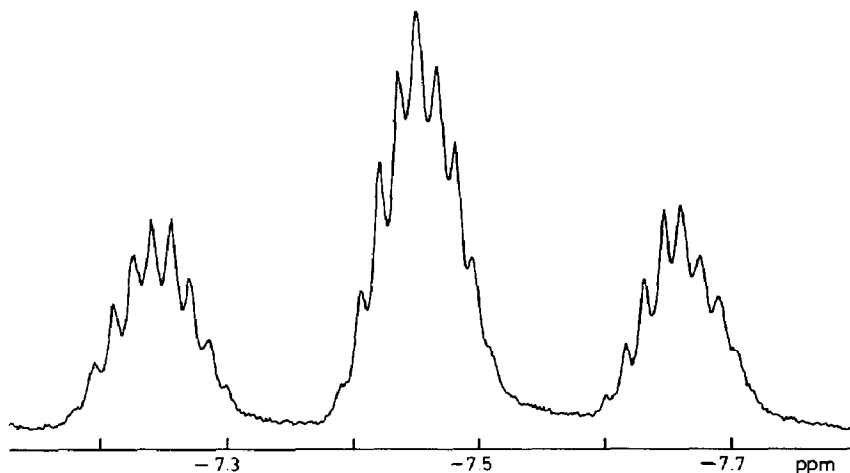


Fig. 1. Hydride absorption in the ^1H NMR spectrum of **2** (CD_2Cl_2 , 293 K).

potential coulometry, indicate that each anodic step involves a simple one-electron quasi-reversible process. The formal electrode potentials for these chemically reversible redox changes are: $E_{0/1}^0 = -0.61$ V, $E_{1+/2+}^0 = +0.06$ V (vs. S.C.E.) [7*].

In the light of this redox behaviour, we attempted to make $[(\text{triphos})_2\text{Rh}_2(\mu\text{-CO})_2]^+$ and $[(\text{triphos})_2\text{Rh}_2(\mu\text{-CO})_2]^{2+}$ by chemical oxidation. Treatment of **1** with triphenylcyclopropenyl perchlorate [6*] in the presence of NaBPh_4 gave brown crystals of formula $[(\text{triphos})_2\text{Rh}_2(\text{CO})_2](\text{BPh}_4) \cdot (\text{CH}_3)_2\text{CO}$ (**3**) [10*]. The IR (Nujol) spectrum clearly showed the presence of only bridging carbonyls ($\nu(\text{CO})$ 1760s, 1790m cm^{-1}). The solid is paramagnetic with μ_{eff} of 1.84 BM, at room temperature, indicating the presence of one unpaired electron in the dimeric unit. The powder ESR spectrum yielded a g value of 2.07.

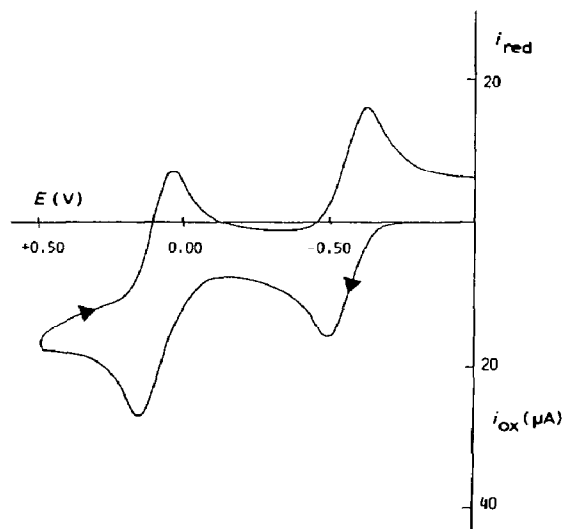


Fig. 2. Cyclic voltammogram recorded at a platinum electrode in a deaerated solution of THF containing **1** (1.6×10^{-3} mol dm^{-3}) and $[\text{NB}_4]\text{ClO}_4$ (0.1 mol dm^{-3}). Scan rate 0.2 V s^{-1} .

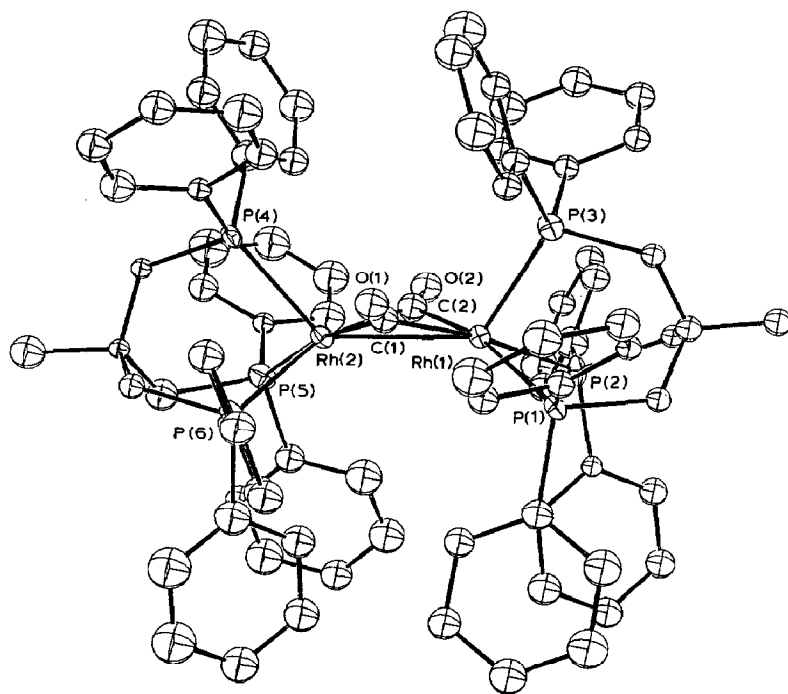


Fig. 3. Perspective view of the complex cation of **3**. Ortep drawing with 30% probability ellipsoids. Selected bond distances (Å) and angles (°): Rh(1)–Rh(2) 2.746(4), Rh–P range 2.336(9)–2.415(9), Rh–C range 1.98(4)–2.05(4), P(1)–Rh(1)–C(2) 165.0(10), P(2)–Rh(1)–C(1) 171.8(9), P(5)–Rh(2)–C(1) 169.8(9), P(6)–Rh(2)–C(2) 159.9(10), C(1)–Rh(1)–C(2) 87.6(14), C(1)–Rh(2)–C(2) 89.8(13), Rh(1)–C(1)–Rh(2) 86.5(13), Rh(1)–C(2)–Rh(2) 85.9(14).

A complete X-ray structural determination was carried out for **3** [11*]. The crystal structure involves dimeric complex cations $[(\text{triphos})\text{Rh}(\text{CO})]_2^+$, BPh_4^- anions, and acetone molecules of solvation.

A perspective view of the cation is given in Fig. 3. The structure of the dimer, in which two almost eclipsed (triphos)Rh fragments are held together by two carbonyl groups, very closely resembles that of the uncharged species **1**, the main difference being in values of the metal–metal bond distances (2.822(2) in **1** and 2.746(4) Å in **3**, respectively). The shortening of the Rh–Rh bond distance is consistent with the results of Hoffmann's MO calculations, which predicted a change 0.13–0.16 Å on going from d^8 – d^8 to d^9 – d^9 dimers [12]. In addition to the shortening of the Rh–Rh separation, there is a substantial flattening of the inner Rh–(CO)₂–Rh ring; the dihedral angles Rh(1)C(1)Rh(2)/Rh(1)C(2)Rh(2) are 138.1 and 146.6° in the uncharged and monocharged species, respectively.

References

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- 2 C. Allevi, M. Golding, B.T. Heaton, C.A. Ghilardi, S. Midollini and A. Orlandini, *J. Organomet. Chem.*, 326 (1987) C19.

- 3 J. Ott, L.M. Venanzi, C.A. Ghilardi, S. Midollini and A. Orlandini, *J. Organomet. Chem.*, 291 (1985) 89.
- 4 Procedure for **2**: CF_3COOH (11.4 mg, 0.1 mmol) was added to a solution of $[(\text{triphos})_2\text{Rh}_2(\mu\text{-CO})_2] \cdot (\text{CH}_3)_2\text{CO}$ (157 mg, 0.1 mmol) in 40 ml of THF. The resulting yellow-green solution was treated with a solution of NaBPh_4 (35 mg, 0.1 mmol) in 10 ml of n-butanol. Yellow-green crystals of **2** rapidly separated. Yield: 67%. Satisfactory elemental analyses were obtained. All operations were carried out under nitrogen.
- 5 The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** recorded at 293 K (80.961 MHz, CD_2Cl_2) shows a pattern of four broad lines. The inner pair of lines make up one third of the total intensity and are centered at $\delta -1.7$ ppm, with a splitting of 174 Hz. The outer pair of lines are centred at $\delta -3.75$ ppm with a splitting of 1498 Hz, and have approximately twice the line width of the inner lines $W_{1/2}$ 275 Hz. We attribute this spectrum to second order effects in the $(\text{AB}_2\text{X})_2$ spin system.
- 6 W.E. Geiger and N.G. Connelly, *Adv. Organomet. Chem.*, 24 (1987) 87; P. Piraino, G. Bruno, S. Lo Schiavo, F. Laschi and P. Zanello, *Inorg. Chem.*, 26 (1987) 2205, and refs. therein; F.A. Cotton, K.R. Dunbar and M.G. Verbruggen, *J. Am. Chem. Soc.*, 09 (1987) 5498.
- 7 Under these conditions the ferrocenium/ferrocene reference couple is at +0.56 V vs. S.C.E.
- 8 The ability of triphenylcyclopropenyl to act as a mild oxidizing agent towards organometallic species with formation of dicyclopropenyl has been noted previously [9]. Furthermore, when **1** is treated with $\text{C}_3\text{Ph}_3\text{Br}$ the following reaction is observed: $1 + 2\text{C}_3\text{Ph}_3\text{Br} \rightarrow 2(\text{triphos})\text{Rh}(\text{CO})\text{Br} + \text{C}_6\text{Ph}_6$.
- 9 F. Cecconi, S. Midollini and A. Orlandini, *J. Chem. Soc., Dalton Trans.*, (1983) 2263 and refs. therein.
- 10 Procedure for **3**: solid $\text{C}_3\text{Ph}_3\text{ClO}_4$ (75 mg, 0.2 mmol) was added to a solution of **1** (157 mg, 0.1 mmol) in 40 ml of THF. When the mixture was kept at 50 °C for ca. 20 min the $\text{C}_3\text{Ph}_3\text{ClO}_4$ dissolved, a brown solution was formed, and brown crystals of formula $[(\text{triphos})_2\text{Rh}_2(\text{CO})_2]\text{ClO}_4$ separated. Well-shaped crystals of formula $[(\text{triphos})_2\text{Rh}_2(\text{CO})_2]\text{BPh}_4 \cdot (\text{CH}_3)_2\text{CO}$ were obtained by recrystallizing the perchlorate salt from acetone/n-butanol solution in the presence of NaBPh_4 . Yield: 58%. Satisfactory elemental analyses were obtained. All operations were carried out under nitrogen.
- 11 Monoclinic, space group $P2_1/a$, a 26.165(11), b 20.082(9), c 18.526(8) Å, β 93.38(6)°, V 9717.84 Å³, $\mu(\text{Mo-K}_\alpha)$ 4.82 cm⁻¹; Philips PW 1100 diffractometer; $\lambda(\text{Mo-K}_\alpha)$ 0.7107 Å; $5^\circ \leq 2\theta \leq 40^\circ$; 2400 absorption corrected reflections with $I \geq 3\sigma(I)$; Patterson and Fourier methods; full-matrix least-squares refinement, $R = 0.070$ and $R_w = 0.069$. Tables of atom coordinates, bond lengths and angles will be deposited with the Cambridge Crystallographic Data Centre.
- 12 A.R. Pinhas and R. Hoffmann, *Inorg. Chem.*, 18 (1979) 654.