

Novel Binuclear Cationic Complexes of Rhodium(I) and Iridium(I)

Sir:

There is intense interest in the preparation and characterization of polynuclear metal complexes and in their use for the study of multicentered catalysts.¹ We wish to report the preparation of a series of cationic binuclear complexes of rhodium(I) and iridium(I) one of which appears to be the first example wherein a metal-metal bond is simultaneously bridged by chloride and carbonyl ligands. These compounds significantly extend the known "A-frame" type complexes, of which the recently reported $[\text{Rh}_2(\text{CO})_2(\mu\text{-S})(\text{DPM})_2]^2$ (DPM = bis(diphenylphosphino)methane) is the first structurally characterized example.

Successive treatment of an ethanolic solution of $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ (ref. 3) with equimolar quantities of DPM in chloroform and $\text{NaB}(\text{C}_6\text{H}_5)_4$ in ethanol under a CO atmosphere produced a yellow solid. Recrystallization from chloroform-ethanol under CO yielded yellow crystals of $\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\mu\text{-CO})(\text{DPM})_2\text{B}(\text{C}_6\text{H}_5)_4$ (**1**). Complex **1** is obtained analytically pure and exhibits $\nu_{\text{C}=\text{O}}$ at 1992 (s), 1977 (vs), and 1863 (s) cm^{-1} (Nujol mull). In CH_2Cl_2 solution $\nu_{\text{C}=\text{O}}$ occurs at 2008 (sh), 1991 (vs), and 1873 (m) cm^{-1} .

Complete characterization of **1** was achieved via a single-crystal x-ray diffraction study. Complex **1** crystallizes in the space group $P\bar{1}$ with $a = 14.451$ (2), $b = 17.661$ (2), $c = 13.726$ (1) Å; $\alpha = 102.06$ (1), $\beta = 95.59$ (1), $\gamma = 75.56$ (1)°; $V = 3313.8$ Å³ ($Z = 2$, $\rho_{\text{calcd}} = 1.416$, $\rho_{\text{obsd}} = 1.40$ (2) g/cm^3). Intensity data were collected on an automated Picker, four-circle diffractometer using two crystals and Cu K α radiation ($2\theta \leq 128^\circ$; scan range, 1.9° in 2θ plus correction for α_1 - α_2 separation). Of the 9390 unique intensities, 8523 had $F_o^2 \geq 3\sigma(F_o^2)$ and were used in the solution and refinement of the structure. Conventional Patterson methods provided the location of the heavy atoms. Location of the remaining atoms and refinement of the model was accomplished by the successive application of the usual Fourier and least-squares techniques. At the present stage of refinement (decomposition correction, isotropic thermal parameters, phenyls treated as rigid groups with C—C = 1.392 Å); $R = 0.116$ and $R_w = 0.171$.⁴ As shown in Figure 1, each rhodium atom is coordinated by five donor atoms in a significantly distorted trigonal-bipyramidal arrangement (C₁-Rh₁-C₂, 113.4 (5); C₁-Rh₁-Cl, 144.2 (4); C₂-Rh₁-Cl, 102.4 (3); C₂-Rh₂-C₃, 118.8 (5); C₃-Rh₂-Cl, 137.7 (4); C₂-Rh₂-Cl, 103.5 (3)°). The Rh₁-Rh₂ distance of 2.841 (1) Å is somewhat longer than those considered to involve normal two-electron Rh—Rh bonds (2.617 (3) to 2.796 (8) Å);⁵ however, several features of the structure strongly indicate that a metal-metal bond is present. (1) The acute angles at chlorine (Rh₁-Cl-Rh₂, 66.39 (7)°) and at C₂ (Rh₁-C₂-Rh₂, 87.7 (4)°) together with the C₂- -Cl distance of 3.441 Å are indicative of considerable compression of this four-membered ring along the Rh—Rh axis. (2) The intraligand P- -P distances of 3.364 (P₁- -P₂) and 3.429 Å (P₃- -P₄) are both significantly longer than the Rh₁-Rh₂ distance again indicating a compression along the metal-metal axis (Figure 1).⁶ (3) Conventional electron counting yields a 17-electron configuration for each metal so that a metal-metal interaction is necessary to account for the observed diamagnetism. In addition $|^1J_{\text{Rh-Rh}}| = 127.8$ Hz (vide infra) which indicates significant Rh—Rh interaction.

Even at the present stage of refinement, the bridging chlorine and carbonyl ligands are unsymmetrically placed (Rh₁-C₂, 2.09 (1); Rh₂-C₂, 2.01 (1); Rh₁-Cl, 2.578 (3); Rh₂-Cl, 2.610 (3) Å). This is consistent with the facile CO exchange (vide infra) and the ready formation of $[\text{Rh}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Cl})(\text{DPM})_2]\text{Cl}$ from $[\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DPM})_2]^8$ and CO in polar solvents. Complex **1** is thus an

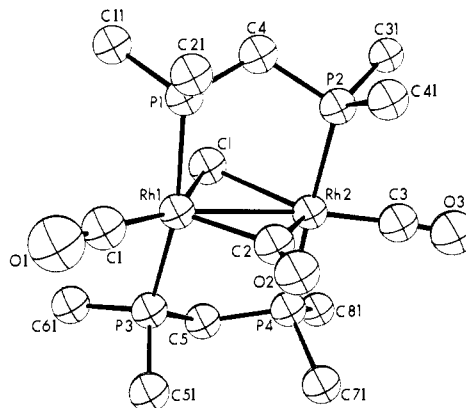


Figure 1. A perspective view of the inner coordination sphere of $[\text{Rh}_2(\text{CO})_2\text{Cl}(\text{DPM})_2]^+$. Only the first carbon atom of each phenyl ring is shown.

analogue of $[\text{Rh}_2(\text{CO})_2(\mu\text{-S})(\text{DPM})_2]$ with a molecule situated in the postulated active site.²

Complex **1** is also novel in that it is the second example of a system wherein reversible binding of carbon monoxide to a bridging site occurs.⁹ Thus on flushing a dichloromethane or acetone solution of **1** with argon or dinitrogen the lowest energy CO band disappears and an orange complex (**2**) can be isolated which analyzes for $[\text{Rh}_2(\text{CO})_2\text{Cl}(\text{DPM})_2]\text{B}(\text{C}_6\text{H}_5)_4$ and shows $\nu_{\text{C}=\text{O}}$ at 1997 (s) and 1978 (vs) cm^{-1} (Nujol mull) and 2006 (s), 1992 (vs) cm^{-1} (CH_2Cl_2 solution). Regeneration of **1** occurs readily by briefly passing CO through a dichloromethane solution of **2**. This together with the observed 1:1 electrolyte behavior ($\Lambda(10^{-3}\text{ M}) = 99 \Omega^{-1}\text{ cm}^2\text{ equiv}^{-1}$, acetone solution) suggests formulation of **2** as $[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\text{DPM})_2]\text{B}(\text{C}_6\text{H}_5)_4$, a cationic analogue of $[\text{Rh}_2(\text{CO})_2(\mu\text{-S})(\text{DPM})_2]$.

Exchange experiments with ¹³CO show that the terminal carbonyl ligands in both **1** and **2** are also readily exchanged. Thus on flushing a dichloromethane solution of either complex with ¹³CO (1–2 min at 25 °C), the original CO bands *essentially completely disappear* and are replaced by bands at 1964 (sh), 1945 (s), and 1832 (m) cm^{-1} . Subsequent flushing with dinitrogen removes the lowest energy band to give the fully enriched analogue of **2**.

Further insight into the CO exchange process is obtained by treating a solution of **2** in dichloromethane with increasing amounts of ¹³CO at -70 °C and examining aliquots of the resulting solution at room temperature. Initially one observes new bands at 1951 and 1873 cm^{-1} and a marked decrease in the intensity of only the 2006- cm^{-1} band. As more ¹³CO is added, the first two bands continue to grow at the expense of the third and a new band appears at 1830 cm^{-1} . Concurrent with the increase in the intensity of the 1830- cm^{-1} band is a decrease in the 1992- cm^{-1} band which in the initial stages appears to remain at its original intensity. These observations imply that the **1** which is initially formed contains ¹²CO in the bridging position and is enriched in ¹³CO at *only one terminal position*. This in turn strongly suggests that the CO exchange and the interconversion of **1** \rightleftharpoons **2** occur via a bridge-terminal exchange (eq 1). Analogues of **1** and **2** containing bis(diphenylarsino)methane can be prepared similarly and show the same CO exchange behavior.

Complex **2** reacts readily with SO₂ to give red crystals analyzing as $[\text{Rh}_2(\text{CO})_2\text{Cl}(\text{SO}_2)(\text{DPM})_2]\text{B}(\text{C}_6\text{H}_5)_4$ (**3**) with $\nu_{\text{C}=\text{O}}$ at 2014 (vs) and 1984 (s) cm^{-1} and ν_{SO} at 1229 (m) and 1068 (m) cm^{-1} . These latter values are similar to those found for $[\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{SO}_2)(\text{DPPP})_2]$ (DPPP = 1,3-bis(diphenylphosphino)propane)¹⁰ and for $[\text{Fe}_2(\text{CO})_8(\mu\text{-SO}_2)]$ ¹¹ which contain terminal and bridging SO₂ molecules, respectively; so the determination of the mode of SO₂ coordination must await

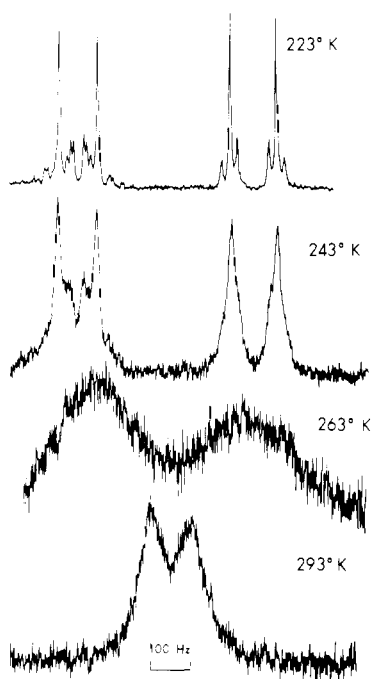
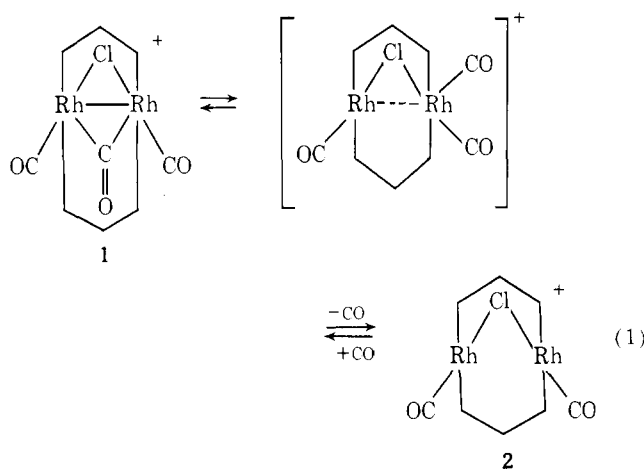


Figure 2. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a mixture of $[\text{Rh}_2(\text{CO})_3\text{Cl}(\text{DPM})_2]^+$ (left) and $[\text{Rh}_2(\text{CO})_2\text{Cl}(\text{DPM})_2]^+$ (right) in CD_2Cl_2 under N_2 at selected temperatures.



the results of a crystal structure analysis of **3** now in progress. The arsine analogue of **3** is prepared similarly.

$[\text{Rh}_2(\text{CO})_2(\mu\text{-Cl})(\mu\text{-CO})(\text{DPM})_2]^+$ can also be obtained as the $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ salt (**4**) from a 50% excess of $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ or $[\text{Rh}_2\text{Cl}_2(\text{c-C}_8\text{H}_{12})_2]$ under CO. By this route, $[\text{Ir}_2(\text{CO})_2(\mu\text{-Cl})(\mu\text{-CO})(\text{DPM})_2][\text{Ir}(\text{CO})_2\text{Cl}_2]$ (**5**) can be obtained from the analogous iridium(I) precursors. Complex **5** shows $\nu_{\text{C}=\text{O}}$ for the cation at 2000 (sh) 1993 (vs), and 1843 (m) cm^{-1} . The anion shows $\nu_{\text{C}=\text{O}}$ at 2058 (m) and 1982 (s) cm^{-1} . The conductivity of $84 \Omega^{-1} \text{cm}^2 \text{equiv}^{-1}$ in acetone indicates it to be a 1:1 electrolyte.

Figure 2 shows the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum obtained from a solution of **1** in CD_2Cl_2 under N_2 . The 233 K spectrum shows two complex, second-order patterns attributable to **1** (δ 26.0 ppm vs. external H_3PO_4) and **2** (δ 15.4 ppm), respectively.¹² The presence of **2** is consistent with the ready loss of CO from **1**. On warming, rapid CO exchange between **1** and **2** appears to occur. The spectrum of **1** has been successfully analyzed as an AA'A''A'''XX' system with $^1J_{\text{Rh-P}} = 118.3 \text{ Hz}$, $^2J_{\text{Rh-P}} = -24.1 \text{ Hz}$ and $^1J_{\text{Rh-Rh}} = 127.8 \text{ Hz}$. The analysis of the spectrum of **2** is less satisfactory because of the near coincidence of many of the weaker lines. However the close resemblance to the $^{31}\text{P}\{^1\text{H}\}$ spectrum of $[\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DPM})_2]^+$

indicates that the metal-metal interaction in **2** should be similar to that proposed for this neutral dimer.¹⁰ Support for this comes from the electronic spectrum of **2** which shows an analogous "proximity shifted" band at 443 nm (CH_2Cl_2 solution) which is absent in the spectrum of **1**. Complex **2** thus presents an interesting contrast to $[\text{Pd}_2\text{Cl}_2(\text{DPM})_2]^9$ in that addition of the bridging carbonyl leads to the formation of a metal-metal bond.

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References and Notes

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- (3) Prepared by passing CO through a refluxing solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in aqueous ethanol for 4 h.
- (4) $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$; $R_w = \frac{[\sum w|F_o| - |F_c|]^2 / \sum wF_o^2}{1/2}$.
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- (6) This is to be contrasted with the situation in the related complex $[\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{C}_6\text{H}_5)_2\text{AsCH}_2\text{As}(\text{C}_6\text{H}_5)_2]^7$ where the Rh-Rh separation is 3.396 (1) Å, while the intraligand As-As distance is 3.288 Å. The Rh-Rh interaction here is clearly repulsive.
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- (12) Confirmed by independent measurements on **1** under CO and **2** under N_2 .
- (13) In **2** the separation of the major peaks ($^1J_{\text{Rh-P}} + ^2J_{\text{Rh-P}}$) is 113.0 Hz while for $[\text{Rh}_2(\text{CO})_2\text{Cl}_2(\text{DPM})_2]^+$ the resonance is centered at δ 16.0 ppm with $^1J_{\text{Rh-P}} + ^2J_{\text{Rh-P}} = 114.0 \text{ Hz}$.

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An Unusual Reaction of Tri-*tert*-butylphosphine with Rhodium(III) and Iridium(III) Chlorides

Sir:

Recent studies¹ demonstrate that tertiary phosphines containing bulky substituents on phosphorus often form unusual products with transition metals. For example, the hydrido complexes^{2,3} $[(t\text{-Bu})_3\text{P}]_2\text{MH}_2\text{Cl}$, where M = Rh or Ir are obtained from the reactions of tri-*tert*-butylphosphine with hydrated iridium(III) and rhodium(III) chlorides. Recently, we found⁴ that tri-*tert*-butylphosphine undergoes a facile reaction with platinum(II) and palladium(II) chlorides to form the internally metallated complexes of the type $[(t\text{-Bu})_2\text{PC}(\text{CH}_3)_2\text{CH}_2]\text{M}[(t\text{-Bu})_3\text{P}]\text{Cl}$ (where M = Pt or Pd). The formation of internally metallated hydrido complex $[(t\text{-Bu})_2\text{PC}(\text{CH}_3)_2\text{CH}_2]\text{IrHCl}(\text{NC}_6\text{H}_7)_2$ by the reaction of