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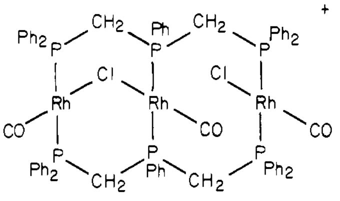
Communications

Flexibility in Complexes Bridged by Bis[(diphenylphosphino)methyl]phenylphosphine. Structure of $[Rh_3(\mu\text{-}(Ph_2PCH_2)_2PPh)_2(\mu\text{-}I)_2(\mu\text{-}CO)(CO)_2][BPh_4]$

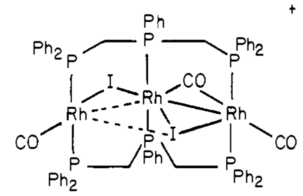
Sir:

In the development of polynuclear complexes built around polyphosphine backbones,[1] flexibility is essential if variations in metal–metal interactions (such as those found in the insertion of small molecules into metal–metal bonds[2] and in polynuclear oxidative additions[3]) are to be observed. Recently we reported the synthesis of the trinuclear rhodium(I) complex **1** and noted that it undergoes rapid bridge/terminal chloride exchange, which equilibrates the terminal phosphorus and rhodium environments in solution. In the attempt to slow down, and thus further characterize this process, we have metathesized, $[Rh_3(\mu\text{-dpmp})(\mu\text{-Cl})Cl(CO)_3]^+$ with iodide and bromide. The structural changes accompanying these reactions demonstrate the ability of this triphosphine to accommodate changes in not only the rhodium–rhodium separations but also the Rh–Rh–Rh angle.



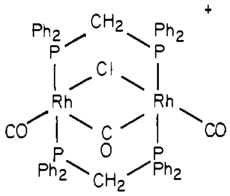
1, $Rh_3(\mu\text{-dpmp})_2(\mu\text{-Cl})Cl(CO)_3^+$

Treatment of rose-colored $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-Cl})Cl(CO)_3][BPh_4]$ in dichloromethane with a methanolic solution of sodium iodide, followed by precipitation with additional methanol and recrystallization from dichloromethane/ether, yields brown crystals of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-I})_2(\mu\text{-CO})(CO)_2][BPh_4]$ (**2**). The infrared spectrum of the solid shows the presence of both terminal (ν(CO) 1988, 1974 cm^{-1}) and bridging (1832 cm^{-1}) carbonyl groups. The $^{31}P\{^1H\}$ NMR spectrum of the complex shows three distinct phosphorus environments (δ_1 24.3, J(P,P) = 47 Hz, ^1J(P,Rh) = 97 Hz; δ_2 17.8, ^1J(P,Rh) = 106.9 Hz, J(P,P) = 25.0 Hz; δ_3 13.9, ^1J(Rh,P) = 100.0 Hz, J(P,P) = 47, 25 Hz). The spectrum is unchanged over the temperature range −70 to +25 °C.



2, $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-I})_2(\mu\text{-CO})(CO)_2][BPh_4]$

In order to structurally characterize the cation, an X-ray crystallographic study of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-I})_2(\mu\text{-CO})(CO)_2][BPh_4]$ was undertaken.[4] The results are summarized in Figure 1, which shows a perspective drawing of the cation. The basic $Rh_3(dpmp)_2$ unit remains intact but is bent to accommodate the bridging iodo and carbonyl ligands. This is best appreciated by comparing the planar portions of the complexes that lie perpendicular to the P–Rh–P units. These are shown in Figure 2. In addition to the bending of the Rh–Rh–Rh portion, the Rh–Rh separations are also considerably shortened in the iodo structure. As with $[Rh_3(\mu\text{-dmpm})_2(\mu\text{-Cl})Cl(CO)_3]^+$,[1a] the structure of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-I})_2(\mu\text{-CO})(CO)_2]^+$ can be compared to the structure of known binuclear counterparts. The unit comprised of Rh(2), Rh(1), I(2), CO(1), and CO(2) closely resembles the structure of cation **3**, which has a Rh–Rh distance of 2.838 (1) Å.[5] In



3, $Rh_2(\mu\text{-dpm})_2(\mu\text{-Cl})(\mu\text{-CO})(CO)_2^+$

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(1) (a) Guimerans, R. R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 1677. (b) Farr, J. P.; Olmstead, M. M.; Balch, A. L. *Ibid.* **1980**, *102*, 6654. (c) Osborn, J. A.; Stanley, G. G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1025. (d) Schore, N. E.; Benner, L. S.; La Belle, B. E. *Inorg. Chem.* **1981**, *20*, 3200. (e) Rauchfuss, T. B.; Wilson, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 6769.

(2) (a) Balch, A. L. In "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 135, p 167. (b) Cowie, M.; Southern, T. G. *Inorg. Chem.* **1982**, *21*, 246. (c) Brown, M. P.; Fisher, J. R.; Puddephatt, R. J.; Seddon, K. R. *Ibid.* **1979**, *18*, 2808.

(3) (a) Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 8049. (b) Lewis, N. S.; Mann, K. R.; Gordon, J. G., II; Gray, H. B. *Ibid.* **1976**, *98*, 7461. (c) Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M.; Farr, J. P. *Ibid.* **1981**, *103*, 3764. (d) Bonnett, J. J.; Thorez, A.; Maisonnat, A.; Galy, J.; Poilblanc, R. *Ibid.* **1979**, *101*, 5940.

(4) Brown crystals of $[Rh_3(\mu\text{-}C_{32}H_{29}P_3)_2(\mu\text{-I})_2(\mu\text{-CO})(CO)_2][B(C_6H_5)_4]\cdot 1.28CH_2Cl_2$ were grown by diffusion of ethyl ether into a dichloromethane solution of the compound. They belong to the space group $P2_1/c$ (No. 14) with a = 11.242 (2) Å, b = 31.602 (5) Å, c = 26.910 (4) Å, β = 99.89 (2)°, Z = 4 at 140 K, and R = 10.9% for 9179 reflections with $I > 1.5\sigma(I)$ and 539 parameters. Three disordered molecules of dichloromethane were located, and their occupancies were refined to 0.559, 0.452, and 0.272. Nine peaks with heights ranging from 2.2 to 4.5 e Å^{-3}, which were well removed from the cation and anion, probably represent other occluded material, but they could not be assembled into any reasonable molecules.

(5) Olmstead, M. M.; Lindsay, C. H.; Benner, L. S.; Balch, A. L. *J. Organomet. Chem.* **1979**, *179*, 289.

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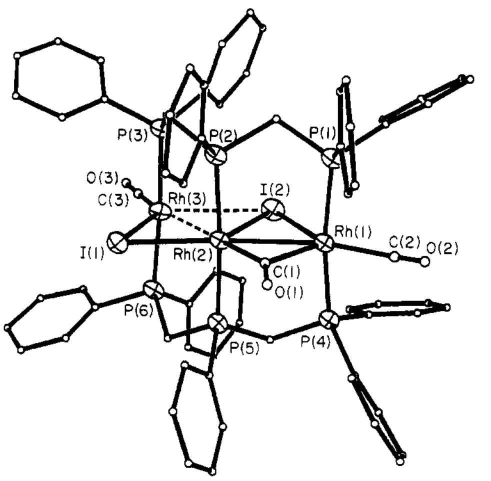


Figure 1. Perspective drawing of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}I)_2(\mu\text{-}CO)(CO)]^+$.

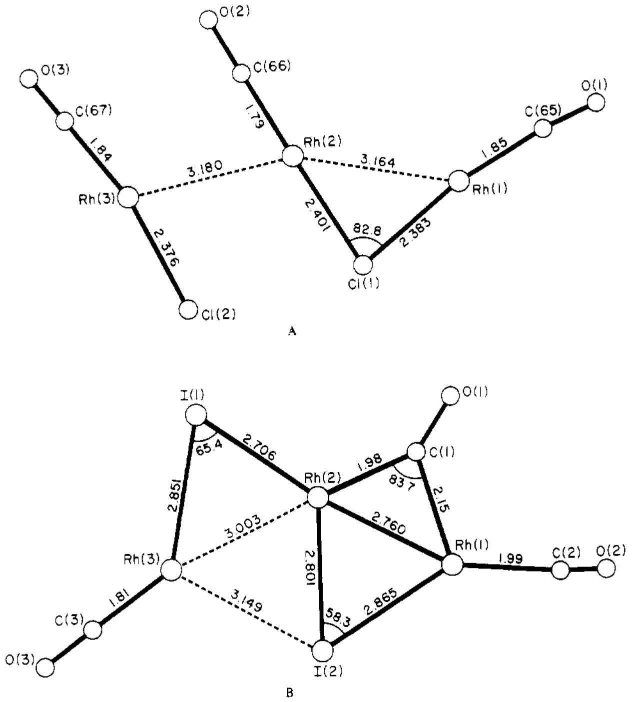
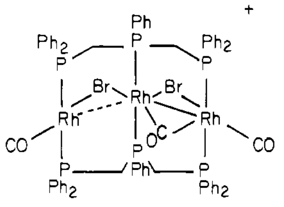


Figure 2. Drawings of planar sections of the structures of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}Cl)Cl(CO)_3]^+$ (A) and $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}I)_2(\mu\text{-}CO)(CO)_2]^+$ (B). For A, esd's are 0.003 Å for Rh–Rh, 0.03 Å for Rh–C, 0.006 Å for Rh–Cl, and 0.2° for Rh–Cl–Rh. For B, esd's are 0.002 Å for bonds involving Rh and I, 0.02 Å for Rh–C, 0.8° for Rh–C–Rh, and 0.1° for Rh–I–Rh; C(2) is disordered, and Rh(1)–C(2) is less accurate.

place of one of the terminal carbonyl groups in **3**, trinuclear **2** has a bridging iodide ligand and Rh(3). Rh(3) is pulled toward Rh(2) and also toward I(2). Although the Rh(3)–I(2) distance is longer than other Rh–I single-bond distances,[6] we still believe that an attractive interaction between these atoms is present and thus I(2) is three-coordinate.

Despite the rather crowded and cramped geometry of **2** (particularly relative to **1**), this molecule is reactive toward the addition of small molecules. For example it (unlike **1**) reacts with carbon monoxide to form a red adduct $[Rh_3(\mu\text{-dpmp})_2(CO)_4I_2][BPh_4]$ with bridging and terminal carbonyl groups (ν(CO) 1980, 1845, 1825, 1775 cm^{-1}).

Metathesis of **1** with sodium bromide yields brown $[Rh_3(\mu\text{-dpmp})_2Br_2(CO)_3][BPh_4]$, which has an infrared spectrum (ν(CO) 1977, 1962, 1813 cm^{-1}) similar to that of **2** and distinct from **1** with only terminal carbonyls. However, its $^{31}P\{^1H\}$ NMR spectrum is clearly indicative of a fluxional molecule that shows three phosphorus environments at −80 °C (δ_1 23.5, ^1J(P,Rh) = 114.7 Hz, J(P,P) = 25 Hz; δ_2 18.8, ^1J(P,Rh) = 100 Hz, J(P,P) = 50, 25 Hz; δ_3 16.3, ^1J(P,Rh) = 105.9 Hz, J(P,P) = 50 Hz). On warming, the two terminal phosphorus resonances broaden and coalesce so that at 25 °C they are present as a single broad line at 19 ppm. In order to account for this fluxional behavior, we suggest that the bromo compound has a structure similar to that of **2** but with the location of the bridging bromide and carbonyl ligands reversed as shown in **4**. With this structure, movement of the bridging carbonyl serves to render the terminal rhodium and phosphorus environments equivalent. Structure **4** necessarily lacks a counterpart of the Rh(3)–I(1) interaction found in **2**. The smaller size of bromide relative to iodide would require even more compression for the bromo analogue of **2** to exist. Consequently, the size difference between bromide and iodide contributes to the difference in these structures.



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Registry No. **1**, 84774-75-4; **2**, 86372-63-6; **4**, 86365-43-7.

Supplementary Material Available: A list of atomic fractional coordinates and thermal parameters for $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}I)_2(\mu\text{-}CO)(CO)_2][BPh_4]\cdot 1.28CH_2Cl_2$ (3 pages). Ordering information is given on any current masthead page.

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(6) For comparison, terminal Rh–I units have lengths of 2.735 (1) Å (trans to Rh–Rh) in $[(p\text{-}CH_3C_6H_4NC)_8Rh_2I_2]^{2+}$ (Olmstead, M. M.; Balch, A. L. *J. Organomet. Chem.* **1978**, *148*, C15), 2.761 (1) Å (trans to Rh–Rh) in $[(C_6H_5CH_2NC)_{12}Rh_3I_2]^{3+}$ (Balch, A. L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1979**, *101*, 3128), and 2.709 (6) Å in $[Rh_6(CO)_{15}I]^-$ (Albano, V. G.; Bellon, P. L.; Sansoni, M. *J. Chem. Soc. A* **1971**, 678). Bridging Rh–I units have lengths of 2.73 Å (average) in $[Rh_7(CO)_{16}I]^{2-}$ (Albano, V. G.; Ciani, G.; Martinengo, S.; Chini, P.; Giordano, G. *J. Organomet. Chem.* **1975**, 88, 381) and 3.001 (2) and 2.679 (2) Å in $[Rh_2(\mu\text{-}I)_2I_4(COCH_3)_2(CO)_2]^{2-}$ (Adamson, G. W.; Daly, J. J.; Forster, D. *Ibid.* **1974**, *71*, C17).

Excited-State Distortions of Tetrakis(μ-trifluoroacetato)dimolybdenum(III)

Sir:

The electronic spectra and structure of binuclear molybdenum complexes containing formal quadrupole bonds are attracting increasing interest.[1-7] A highly resolved vibrational structure has been reported on the 23 000-cm^{-1} $\delta \rightarrow \pi^*$ transition in the title compound.[5] A Franck–Condon analysis

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(3) Cotton, F. A.; Martin, D. S.; Fanwick, P. E.; Peters, T. J.; Webb, R. *J. Am. Chem. Soc.* **1976**, *98*, 4681-4682.

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