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Trinuclear Complexes Bridged by Bis(diphenylphosphinomethyl)phenylphosphine. The Synthesis and Structure of $[Rh_3(\mu\text{-}\{Ph_2PCH_2\}_2PPh)_2(\mu\text{-}CO)_2(CO)(\mu\text{-}S_2COEt)(S_2COEt)][BPh_4]\cdot 0.5CH_2Cl_2$ and Related Binuclear Compounds

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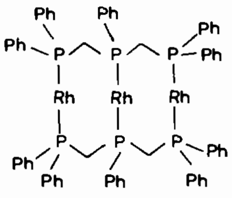
Bis(diphenylphosphinomethyl)phenylphosphine (dpmp) forms a group of rhodium clusters built around the $Rh_3(\mu\text{-dpmp})_2{}^{3+}$ core *1* [1, 2]. Ligands may bind in the plane perpendicular to the P–Rh–P axes, and we have shown that the disposition of these ligands in $[Rh_3(\mu\text{-dpm})_2(CO)_3X_2]^+$ (X = Cl, Br, I) is highly dependent on the identity of the anion. For X = Cl the arrangement in the plane is shown in *2* with long Rh···Rh separations (>3.1 Å) and a somewhat bent (157.4°) Rh···Rh···Rh group, while for X = I the arrangement is shown in *3* with much shorter Rh–Rh separations (3.003, 2.760 Å), a more strongly bent Rh–Rh–Rh angle (127.6(1)°) and a different array of bridging and terminal ligands. Structural studies of clusters of this sort are necessary to identify cooperative interactions between the metal centers and vacant coordination sites which may be useful in developing the reaction and cata-



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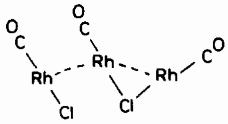

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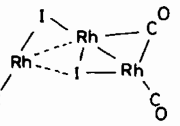

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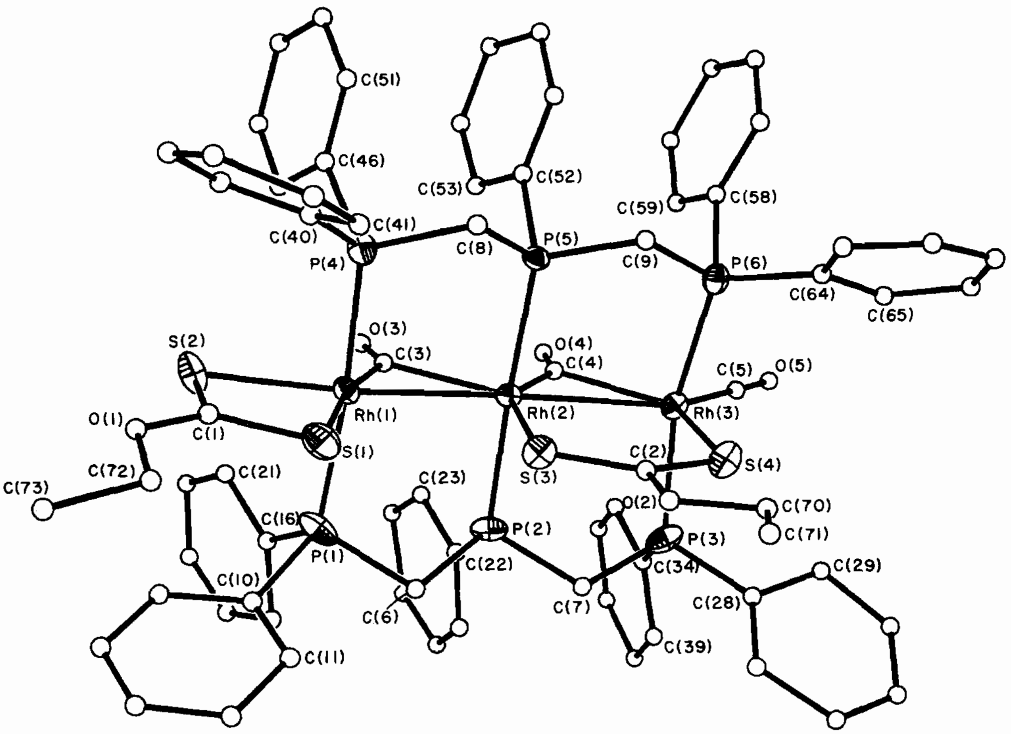

Fig. 1. A perspective drawing of the cation $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-}CO)_2(CO)(\mu\text{-}S_2COEt)(S_2COEt)]^+$.

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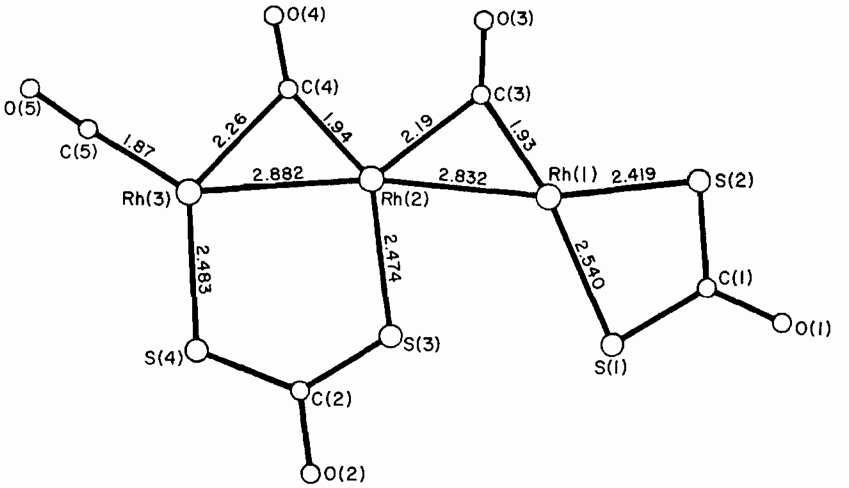
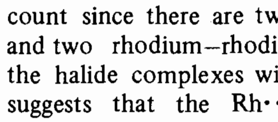


Fig. 2. A planar portion of the stucture of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})_2(CO)(\mu\text{-}S_2COEt)(S_2COEt)][BPh_4]$ showing some of the more interesting interatomic distances and angles.

lytic activity of these species. Here we describe yet another array of ligands which occurs when a bidentate 1,1-dithiolate ligand replaces the halide ligands in these clusters.

Purple crystals of $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})_2(CO)(\mu\text{-}S_2COEt)(S_2COEt)][BPh_4]$ are obtained upon treatment of a dichloromethane solution of $[Rh_3(\mu\text{-dpmp})_2(CO)_3(\mu\text{-Cl})Cl][BPh_4]$ with an excess of sodium ethylxanthate in ethanol followed by precipitation with ethanol and recrystallization from dichloromethane/ether. The infrared spectrum indicates that terminal and bridging carbonyl groups are present: ν(CO), 1956s, 1806s, 1780 w cm^{-1}. Purple $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})_2(CO)(\mu\text{-}S_2CNEt_2)(S_2CNEt_2)][BPh_4]$ is obtained similarly using potassium diethyl-dithiocarbamate; ν(CO), 1950s, 1819s, 1775 m cm^{-1}.

The structure of the xanthate compound has been established from an X-ray diffraction study*. The results are shown in Fig. 1 which gives a perspective view of the cation. Figure 2 shows the planar section of the cation which contains the $Rh_3(CO)_3(S_2COEt)_2$ unit. The cation contains one terminal and two rather unsymmetrical carbonyl groups. One xanthate ligand forms a chelate ring about Rh(1) while the other forms a bridge between Rh(2) and Rh(3). The Rh–Rh–Rh angle of 170.5(1)° is more nearly linear than the corresponding angles in the related halide-containing cations. The Rh–Rh distances are in the range which normally is found between bonded rhodium atoms with carbonyl bridges. The unsymmetrical nature of the bridging carbonyl groups can be understood by considering the two limiting bonding structures *4* and *5*. (These diagrams show only a planar section of the complex). In *4*, each carbonyl acts as a two electron donor toward one rhodium and the total electron count is 18 at Rh(1) whereas Rh(2) and Rh(3) are electron-deficient, 16-electron centers. With *5*, however, each rhodium atom achieves an 18 electron count since there are two bridging carbonyl groups and two rhodium–rhodium bonds. Comparison of the halide complexes with this xanthate compound suggests that the Rh···Rh separations and the Rh–Rh–Rh angle are independently variable in these trinuclear compounds. Thus the xanthate complex has relatively short Rh···Rh separations and is the most nearly linear of the group. The chloride containing cation is bent with significantly longer Rh···



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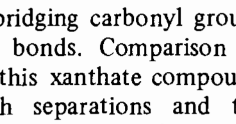

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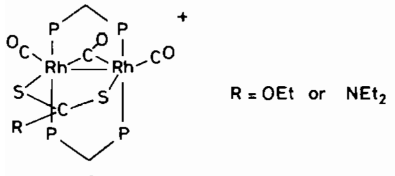
*Crystal data: Fragile dark red needles of $[Rh_3(\mu\text{-dpm})_2(\mu\text{-CO})_2(CO)(\mu\text{-}S_2COEt)(S_2COEt)][BPh_4]\cdot 0.5CH_2Cl_2$ were obtained by vapor diffusion of ether into a dichloromethane solution of the complex salt. It crystallizes in the space group $P\bar{1}$ (No. 2) with a = 13.287(2), b = 16.544(3), c = 24.485(6) Å, α = 106.96(2), β = 96.05(2), δ = 100.90(1)°, Z = 2 at 140 K. R = 11.7% for 6859 reflections with $I > 2\sigma I$ and 545 parameters. The presence of additional disordered dichloromethane molecules in the lattice and disorder in one phenyl ring of the tetraphenylborate as well as difficulty in finding a crystal which did not fragment on handling, have hampered our ability to achieve a better R value.

Rh separations and the corresponding iodide is more strongly bent but has short Rh$\cdots$Rh separations.

Since binuclear analogs of these trinuclear clusters were unknown, they have been prepared for comparative purposes from the reaction of $Rh_2(\mu\text{-}dpm)_2(CO)_2Cl_2$ [6] (dpm is bis(diphenylphosphino)-methane) with 1,1-dithiolates. With ethyl xanthate $[Rh_2(\mu\text{-}dpm)_2(\mu\text{-}S_2COEt)(\mu\text{-}CO)(CO)_2][BPh_4]$ is obtained as pale rose crystals. The infrared spectrum shows that terminal and bridging carbonyl ligands are present: ν(CO), 1993, 1980, 1787 cm^{-1}. The $^{31}P\{^1H\}$ NMR shows a typical AA'XX'X"X"' pattern with δ, 33.7 ppm and $|^1J(Rh,P) + {}^xJ(Rh,P)|$, 88.5 Hz. $[Rh_2(\mu\text{-}dpm)_2(\mu\text{-}S_2CNEt_2)(\mu\text{-}CO)(CO)_2][BPh_4]$ was obtained by an analogous route and displays similar spectroscopic properties: ν(CO) 1990sh, 1978, 1790 cm^{-1}; $^{31}P\{^1H\}$; δ, 33.5 ppm; $|^1J(Rh,P) + {}^xJ(Rh,P)|$, 90.0 Hz. These spectral data indicate that the cations have a symmetrical structure *6* which is similar to that of the double A-frame, $Rh_2(\mu\text{-}dpm)_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2^+$, [3] that has been characterized by X-ray diffraction. Thus these dinuclear complexes are similar to the portion of the structure of $[Rh_3(\mu\text{-}dpmp)_2(\mu\text{-}CO)_2(CO)(\mu\text{-}S_2CR)(S_2CR)]^+$ which involves the bridging carbonyl and bridging 1,1-dithiolate.



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Further studies of the chemistry of these clusters, which we know undergo oxidative-additions, are in progress.

Acknowledgements

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