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Preliminary communication

SYNTHESIS AND X-RAY CHARACTERIZATION OF $Rh_4(CO)_8[P(OPh)_3]_4$ AND $Rh_6(CO)_{12}[P(OPh)_3]_4$

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Summary

The structures of the compounds $Rh_4(CO)_8[P(OPh)_3]_4$ and $Rh_6(CO)_{12}$-$[P(OPh)_3]_4$ have been determined and shown to be derived from those of the parent species $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ by replacement of terminal carbonyl groups.

An investigation of the reactivity of the carbonyl cluster compounds $M_4(CO)_{12}$ (M = Co, Rh, Ir) toward phosphorus-donor ligands has given a variety of stable substitution products [1, 2]. With triphenylphosphite, $Rh_4(CO)_{12}$ gives mono-, di-, tri-, and tetra-substituted species, depending on the relative amounts of the reagents [1, 2]. The more highly substituted derivative, $Rh_4(CO)_8[P(OPh)_3]_4$ (I), can be obtained even with a large excess of $P(OPh)_3$ in THF at room temperature for 3 h. Crystals obtained by recrystallization from THF/i-PrOH have been subjected to X-ray analysis.*

The structure of I is shown in Fig. 1 (neglecting the OPh groups) and is derived from that of $Rh_4(CO)_{12}$, with one terminal CO ligand per metal atom replaced by a phosphite ligand. The $Rh_4(CO)_8P_4$ moiety has an approximate C_s symmetry. The Rh—Rh distances have a mean value of 2.72 Å, similar to the corresponding mean values in $Rh_4(CO)_{12}$ (2.73 Å) [3] and in $Rh_4(CO)_8(Ph_2PCH_2PPh_2)_2$ (2.71 Å) [4]. The Rh—P bond lengths range in the interval 2.20—2.25(2) Å (mean 2.23 Å) and are, on average, shorter than the Rh—P(phosphine) distances

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*Crystal data: I, monoclinic, $P2_1/n$, a = 15.24(3), b = 35.95(6), c = 15.45(2) Å, β 101.82(12)°. II, orthorhombic, $Aba2$, a = 19.654(5), b = 21.474(7), c = 19.955(4) Å. The intensities were collected on a Philips PW1100 four-circle diffractometer. The structure solutions were based on conventional Patterson and Fourier methods and the refinements were carried out by block-matrix least-squares up to the current R values of 8.7% for 1354 observed reflections (I) and of 5.0% for 3480 reflections (II), respectively.

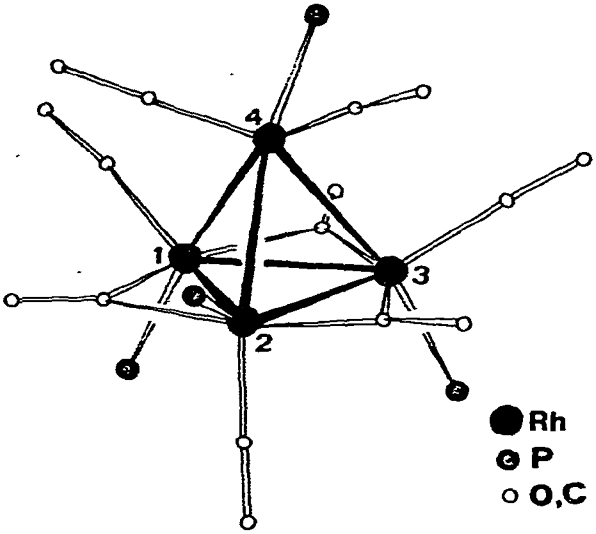

Fig. 1. Structure of $Rh_4(CO)_8[P(OPh)_3]_4$. The metal—metal distances are: 1—2, 2.732(7), 1—3, 2.753(9), 1—4, 2.711(8), 2—3, 2.738(8), 2—4, 2.712(8) and 3—4, 2.703(8) Å.

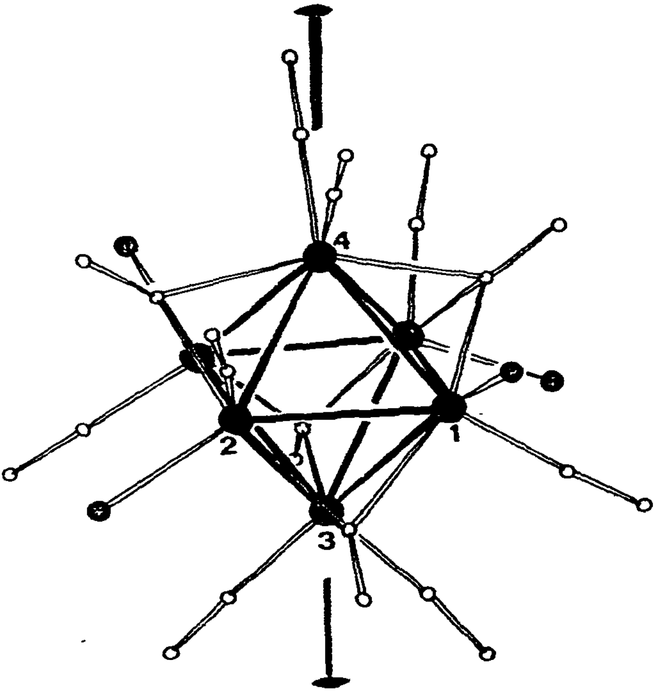

Fig. 2. Structure of $Rh_6(CO)_{12}[P(OPh)_3]_4$. The independent metal—metal distances are: 1—2, 2.801(2): 1—2', 2.825(2); 1—3, 2.758(2); 1—4 2.792(2), 2—3, 2.809(2) and 2—4, 2.750(2) Å.

in $Rh_4(CO)_8(Ph_2PCH_2PPh_2)_2$ (mean 2.30 Å), in agreement with the previously reported data for phosphite and phosphine ligands [5]. Because of the limited number and poor quality of the intensity data the Rh—C and C—O distances are rather scattered, and subject to large uncertainties (mean values 1.83, 1.18 Å for terminal and 2.00, 1.29 Å for bridging carbonyls).

Refluxing $Rh_6(CO)_{16}$ and $P(OPh)_3$ in a molar ratio of 1/6 in dichloromethane for 8 h gave the tetrasubstituted species $Rh_6(CO)_{12}[P(OPh)_3]_4$ (II) (yield 65%). Recrystallization from THF/i-PrOH gave crystals which have been studied by X-ray diffraction.

The $Rh_6(CO)_{12}P_4$ moiety of II is shown in Fig. 2. The molecule lies on a two-fold crystallographic symmetry axis. The ligand arrangement is similar to that of $Rh_6(CO)_{16}$ with replacement of four terminal CO ligands by phosphite ligands, alternately disposed two above and two below the same Rh_4 plane, in such a way as to minimize the intramolecular non-bonded contacts. The Rh—Rh distances have a mean value of 2.79 Å, comparable to those in $Rh_6(CO)_{16}$ (2.78 Å) [6], $[Rh_{12}(CO)_{30}]^{2-}$ (2.77 Å) [7], and $[Rh_6(CO)_{15}I]^-$ (2.75 Å) [8]. The Rh—P distances (mean 2.27 Å) are somewhat longer than in the tetranuclear species. The mean Rh—C and C—O bond lengths are 1.85 and 1.16 Å, respectively, for terminal and 2.18 and 1.19, respectively, for triply-bridging carbonyl groups.

The structural results show that: (a) in order to minimize non-bonded intramolecular contacts the bulky phosphorus-donor ligands are disposed as far as possible from each other, and generally one per metal atom; and (b) steric repulsions limit the extent of substitution. These repulsions principally involve the carbonyl groups and the atoms bonded to the phosphorus atoms (via the oxygens in the case of the phosphites).

In $Rh_6(CO)_{12}[P(OPh)_3]_4$ the four $P(OPh)_3$ ligands give rise to an overcrowded structure with (OC)· · ·(OPh) contacts down to 2.85 Å. Consequently the C—Rh—C angles involving the terminal CO groups are forced to lower values (mean 88°) than in $[Rh_{12}(CO)_{30}]^{2-}$ (mean 95°) and in $[Rh_6(CO)_{15}I]^-$ (mean 94°). It thus seems unlikely that another $P(OPh)_3$ could be bonded, and furthermore it is understandable that with PPh_3, which gives rise to more steric hindrance, the maximum number of substituents is three [2].

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