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Preliminary communication

PHOSPHORUS-BRIDGED RHODIUM CLUSTERS

II*. SYNTHESIS AND CHARACTERIZATION OF $Rh_4(\mu\text{-}PPh_2)_4(CO)_5(PPh_3)$

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Summary

Decomposition of $RhH(CO)(PPh_3)_3$ (Ph = phenyl) in nonane at 120°C under CO/H_2 yielded a dark brown compound. The compound was established at $Rh_4(\mu\text{-}PPh_2)_4(CO)_5(PPh_3)$ by X-ray crystallography, the structure bears certain similarities to that of $Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2$.

The thermal decomposition of $IrH(CO)(PPh_3)_3$ produced *trans*-$Ir_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_3)_2$ which contains an iridium—iridium double bond [1, 2]. In contrast, the thermal decomposition of $RhH(CO)(PPh_3)_3$ yielded the novel triangular complex, $Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2$ [3].

As part of a study of the chemistry of $RhH(CO)(PPh_3)_3$, a suspension of the hydride in nonane was heated at 120°C under 60 psig CO/H_2 (1/1) overnight to produce a suspension of brown solids. A high pressure liquid chromatogram of these solids (on Waters μ-Porasil using 20 percent THF in hexane) indicated that I was obtained with only small amounts of impurities. The infrared spectrum of I exhibited bands at 1980, 1840, and 1800 cm^{-1} (CH_2Cl_2) indicating the presence of both terminal and bridging CO ligands. No structural information could be derived from the very complex $^{31}P\{^1H\}$NMR spectrum of I. Consequently, the compound was characterized by X-ray crystallography.

Crystals suitable for a stuctural determination were obtained from a CH_2Cl_2 / hexane solution. I crystallized in the monoclinic space group, $P2_1/c$:*a* 17.586(7) Å; *b* 14.438(9) Å; *c* 25.259(8) Å; β 97.08 (3)°; and Z = 4**. The 3418 unique reflections with $F_0^2 > 3\sigma(F_0^2)$ were used to solve the structure. The positions of the four rhodium and five phosphorus atoms were located by direct methods.

*Ref. 3 is Part I of this series.

**The X-ray crystal structure determination was carried out at Molecular Structure Corp., College Station, Texas, using an Enraf—Nonius CAD4 automated diffractometer and the Enraf—Nonius Structure Determination Package on a PDP 11/45 computer.

Positions of the remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. The rhodium and phosphorus atoms were refined with anisotropic temperature factors, and the other non-hydrogen atoms with isotropic temperature factors; $R = 0.067$. Thus, I was determined to be $Rh_4(\mu\text{-}PPh_2)_4(CO)_5(PPh_3)$*,**.

The structure of I (Fig. 1) is based on a pseudo-tetrahedron of rhodium atoms. Three of the rhodium atoms (Rh(1)—Rh(3)) are bridged by diphenylphosphide ligands (P(1), P(2), and P(4)). Qualitatively, P(2) and P(4) are coplanar with Rh(1)—Rh(3), while P(1) is considerably out of that plane. This arrangement is quite similar to that of the Rh_3P_3 skeleton of $Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2$ [3]. The fourth rhodium atom (Rh(4)) is directly bonded to each of the three other rhodium atoms, to two bridging CO's, a diphenylphosphide, (P(3)), and to a PPh_3 molecule (P(5)). The compound has a total of 36 valence electrons, so each rhodium atom satisfies the 18-electron rule. Rhodium—rhodium bond lengths vary from 2.771(2) to 2.903(2) Å (2.844, ave.) and are consistent with those previously reported [3, 4]. Rhodium—diphenylphosphide bond lengths vary from 2.253(5) to 2.323(6) Å and agree well with those found in $Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2$ [3].

Meek and Kreter [5] have recently reported the synthesis and characterization of an anionic cluster, $Rh_4(\mu\text{-}PPh_2)_5(CO)_6^-$, $Li(THF)_4^+$.

Further chemical and spectroscopic studies are in progress and will be reported later.

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*A black prismatic crystal measuring approximately 0.07 × 0.2 × 0.3 mm was sealed in a thin-walled glass capillary under nitrogen. The capillary was then mounted on Molecular Structure Corporation's Enraf—Nonius CAD4 fully-automated diffractometer. The crystal diffracted well; peak widths at half-height for several intense reflections (ω-scans) were 0.2°.

The automatic centering and autoindexing procedure of the Enraf—Nonius Structure Determination Package indicated a primitive monoclinic cell. The space group was determined to be $P2_1/c$ by the extinctions $h0l$, ($l \neq 2n$) and $0k0$ ($k \neq 2n$).

Data were collected at 23 ± 1°C using a graphite-crystal monochromator; Mo-K_α radiation and the θ—2θ scan technique were used. Peak intensities were recorded using scan rates from 4 to 20°/min and a scan range from 2θ (Mo-K_{α_1}) −0.6° to 2θ (Mo-K_{α_2}) +0.6°. A total of 12129 unique reflections were collected in the $0° < 2\theta < 45°$ region of which 3418 had $F_{obs}^2 > 3\sigma(F_{obs}^2)$. Three standard reflections were measured periodically during data collection; no significant changes were observed. No absorption correction was applied in view of the small linear absorption coefficient −11.67 cm^{-1}. The unique data were reduced to a set of relative F_{obs}^2 after Lorentz and polarization corrections were made.

**A table of atom positional and thermal parameters and the table of stucture factors have been deposited as NAPS, Document No. 03683 (19 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $5.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

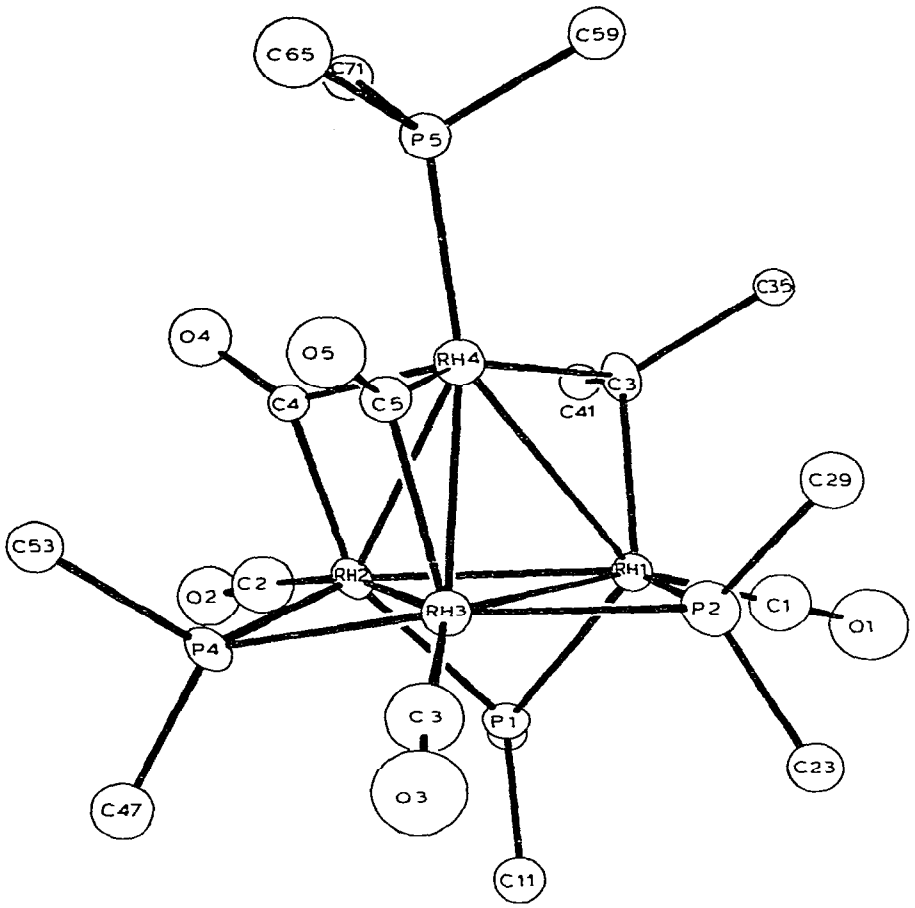

Fig. 1. ORTEP Drawing of $Rh_4(\mu\text{-}PPh_2)_4(CO)_5(PPh_3)$. For sake of simplicity only the carbon atoms bonded to phosphorus in the PPh_3 and $\mu\text{-}PPh_2$ ligands are shown. The main bond lengths (in Å) are: Rh(1)—Rh(2), 2.771(2); Rh(1)—Rh(3), 2.853(2); Rh(2)—Rh(3), 2.815(2); Rh(1)—Rh(4), 2.897(2); Rh(2)—Rh(4), 2.827(2); Rh(3)—Rh(4), 2.903(2); Rh(1)—P(1), 2.315(5); Rh(1)—P(2), 2.287(6); Rh(2)—P(1), 2.293(5); Rh(2)—P(4), 2.253(5); Rh(3)—P(2), 2.306(5); Rh(3)—P(4), 2.320(5); Rh(1)—P(3), 2.323(6); Rh(4)—P(3), 2.288(5); and Rh(4)—P(5), 2.279(6).

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