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Preliminary communication

SYNTHESIS AND CHARACTERIZATION OF $Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2$: A NOVEL TRIANGULAR RHODIUM CLUSTER

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Summary

Thermal decomposition of $RhH(CO)(PPh_3)_3$ (Ph = phenyl) in nonane at 120°C yielded a green solid in high yield. The complex was established as $Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2$, (I), by X-ray crystallography. I was found to be coordinately unsaturated in the solid state and in solution.

There have been two reports [1,2] of the thermal decomposition of $IrH(CO)(PPh_3)_3$ to *trans*-$Ir_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_3)_2$, a complex containing a metal—metal bond of order two. We report here a preliminary study of the thermal decomposition of $RhH(CO)(PPh_3)_3$, a complex isoelectronic and presumably isostructural with $IrH(CO)(PPh_3)_3$.

Thermal decomposition of $RhH(CO)(PPh_3)_3$ occurs in a wide variety of solvents above 80°C. The reaction, however, is carried out most conveniently in a non-solvent, n-nonane, at 120°C overnight under nitrogen, whereupon a green solid is deposited in ca. 85% yield. The green solid is stable in air for short periods, but solutions of the complex decompose rapidly on exposure to air.

The compound exhibits two carbonyl bands in the IR at 1985 and 1945 cm^{-1} (CH_2Cl_2). The ^1H NMR spectrum indicates only phenyl protons, while the $^{31}P\{^1H\}$NMR spectrum exhibits three complex multiplets centered at −52.0, −146.0, and −269.7 ppm (downfield from external H_3PO_4) having the relative areas, 1.8:1:1.8. These data are clearly inconsistent with the anticipated formulation, *trans*-$Rh_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_3)_2$.

Crystals suitable for X-ray crystallography were obtained from CH_2Cl_2/hexane. The compound crystallized in the orthorhombic space group $Pna2_1$: a 35.736(7), b 12.498(8), c 14.484(5) Å, $Z = 4$. The structure was solved using 2566 reflections having $F_0^2 \geqslant 3\sigma(F_0^2)$. The positions of the three rhodium and five phosphorus atoms were located by direct methods then refined by least squares refinement. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. The rhodium and phosphorus atoms were refined

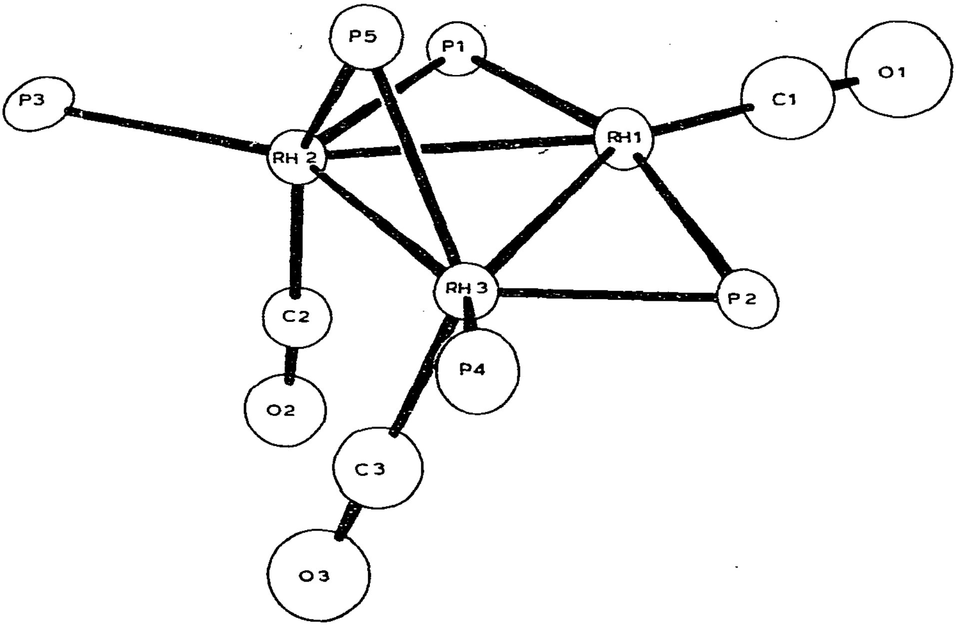

Fig. 1. ORTEP Drawing of $Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2$. For sake of clarity, phenyl groups have been omitted. The main bond lengths (in Å) are: Rh1—Rh2, 2.790(2); Rh1—Rh3, 2.821(2); Rh2—Rh3, 2.744(2); Rh1—P1, 2.268(6); Rh1—P2, 2.290(6); Rh2—P1, 2.316(6); Rh3—P2, 2.323(6); Rh2—P5, 2.332(5); Rh3—P5, 2.331(5); and Rh1—P5, 3.073(5).

with anisotropic temperature factors, and the other non-hydrogen atoms with isotropic temperature factors; $R = 0.054$.*,**

The structure of I is based on a triangle of rhodium atoms as shown in Figure 1. The unique rhodium atom, Rh1, as implied by the inert gas rule, is two electrons short of the rare gas configuration and is thus coordinatively unsaturated. This is manifested in two structural features: a nonbonding interaction between Rh1 and the phosphorus atom in the unique diphenylphosphide bridge, P5 (3.073(5)Å); and, what seems to be an unsymmetrical displacement of phosphorus atoms P1 and P2 of the two similar diphenylphosphide groups

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*A dark green prismatic crystal measuring approximately 0.2 × 0.2 × 0.2 mm was sealed in a thin-walled glass capillary under nitrogen. The capillary was then mounted on Molecular Structure Corporation's (College Station, Texas) 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 (on a PDP 11/45 computer) indicated a primitive orthorhombic cell. The extinctions, $0kl$ $(k + l \neq 2n)$ and $h0l (h \neq 2n)$, were consistent with the $Pna2_1$ or $Pnma$ space groups; the choice of $Pna2_1$ were confirmed by successful refinement of the structure.

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 $2\theta(\text{Mo-}K_{\alpha_1}) - 0.6°$ to $2\theta(\text{Mo-}K_{\alpha_2}) + 0.6°$. A total of 4750 unique reflections were collected in the $0° < 2\theta < 45°$ region of which 2566 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 (9.08 cm^{-1}). The unique data were reduced to a set of relative F_{obs}^2 after Lorentz and polarization connections were made.

**Supplementary material is available from NAPS Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10017.

towards Rh1. The latter is analogous to asymmetric bridging carbonyls [3,4]. A chemical manifestation of coordinative unsaturation is the observation that I reacts rapidly and reversibly with CO in solution as shown by the appearance of a new IR band at 2000 cm^{-1} which subsequently disappears on purging the system with argon.

Steric effects may account for the formation of the observed tri-rhodium structure versus the anticipated, *trans*-$Rh_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_3)_2$. In the latter, molecular models indicate that there are severe steric interactions between the phenyl groups on the terminal triphenylphosphines and those on the μ-phosphido groups, while in the tri-rhodium structure these interactions are less severe.

In analogy, $Pt(PPh_3)_4$, has been reported to undergo a thermal decomposition [6] to a dimer, $Pt_2(\mu\text{-}PPh_2)_2(PPh_3)_2$, as well as a trimer, $Pt_3(\mu\text{-}PPh_2)_2(Ph)(PPh_3)_2$. Presumably with platinum, steric constraints are less stringent than with rhodium.

Satisfactory elemental analyses for $Rh_3(\mu\text{-}PPh_2)_3(CO)_3(PPh_3)_2$ were obtained. Further chemical and spectroscopic investigations of I are in progress.

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