

A Family of Hydride Complexes of Rhodium. Crystal Structure of the Paramagnetic Rhodium(III)–Rhodium(II) Complex [(triphos)Rh(μ -H)₃Rh(triphos)](BPh₄)₂·DMF [triphos = MeC(CH₂PPh₂)₃, DMF = dimethylformamide]

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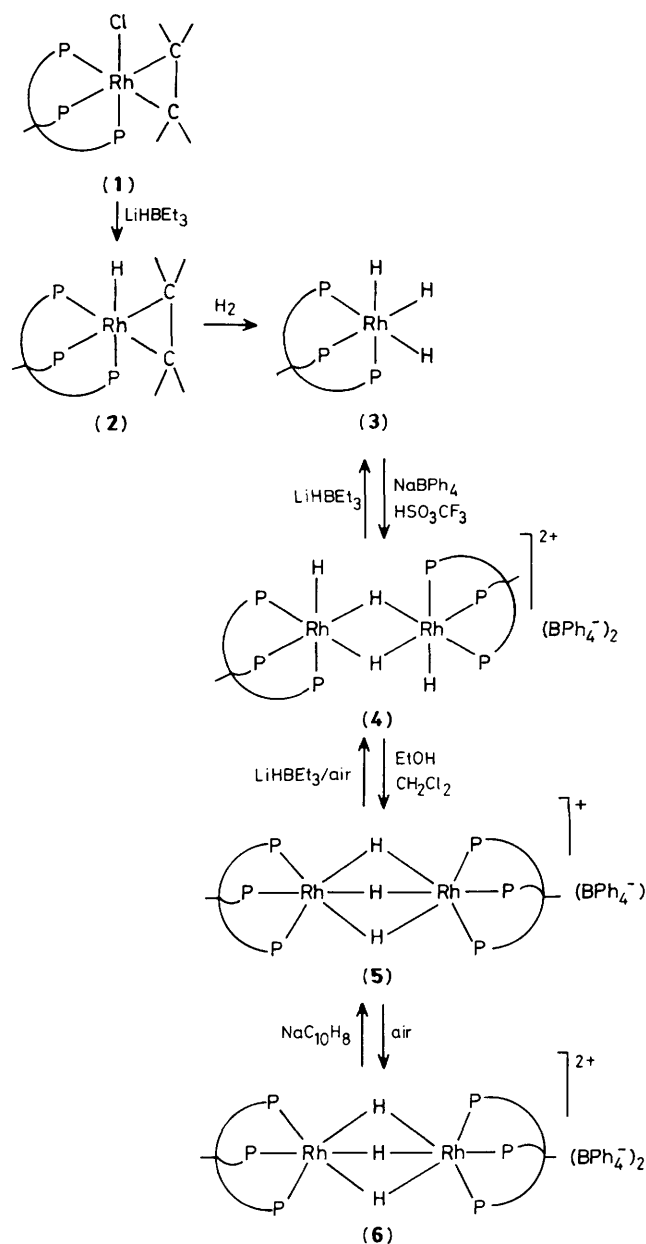
A family of rhodium hydrides including mono- and bi-nuclear, mono- and poly-hydride, diamagnetic and paramagnetic members has been prepared; the structure of the paramagnetic rhodium hydride [(triphos)Rh(μ -H)₃Rh(triphos)](BPh₄)₂·DMF [triphos = MeC(CH₂PPh₂)₃, DMF = dimethylformamide] has been established by X-ray methods: three hydride ligands bridge two rhodium atoms which are separated by a short distance [2.644(1) Å].

Hydrido(phosphine) complexes of rhodium play a considerable role in several homogeneous catalytic processes.¹ In this context, we believe that the following sequence of reactions which generates a novel family of rhodium hydrides may be of interest. The chemical results, summarized in Scheme 1, include mono- and bi-nuclear, mono- and poly-hydride, diamagnetic and paramagnetic complexes of rhodium with the trichelate ligand triphos, MeC(CH₂PPh₂)₃.

By treatment of (triphos)RhCl(C₂H₄)[†] (**1**) in tetrahydrofuran (THF) with an equimolar amount of LiHBEt₃, pale yellow crystals of (triphos)RhH(C₂H₄) (**2**) are obtained in 65% yield [i.r. (Nujol) 1965 cm⁻¹ ν (Rh–H); ¹H n.m.r. (CD₂Cl₂, 293 K) 3.07 (m), 1.71 (m) δ (C₂H₄); –11.8 doublet of doublets, δ (H_{hydride}), ²J(H–P_{trans}) 162, ²J(H–P_{cis}) 0, J(Rh–H) 19 Hz]. On bubbling H₂ through a THF solution of the hydrido(ethylene) complex (**2**), colourless crystals of the known trihydride (triphos)RhH₃ (**3**) are formed in 85% yield. The latter compound reacts with an equimolar amount of HSO₃CF₃ evolving H₂ and producing an orange solution from which yellow orange crystals of [(triphos)HRh(μ -H)₂RhH(triphos)](BPh₄)₂ (**4**) precipitate upon addition of NaBPh₄ in 80% yield [i.r. (Nujol) 1980 cm⁻¹ ν (Rh–H_t); ¹H n.m.r.

(CD₂Cl₂, 203 K) –10.6 (m) δ (H_{hydride}), 4H; λ_M (EtNO₂) 98 cm² Ω^{-1} mol⁻¹]. Compound (**4**) is stable as a solid but slowly decomposes in CH₂Cl₂ solution even in an inert atmosphere to give red orange crystals of [(triphos)Rh(μ -H)₃-Rh(triphos)]BPh₄·2CH₂Cl₂ (**5**) [i.r. (Nujol) 1665 cm⁻¹ broad ν (Rh–H–Rh); λ_M (EtNO₂) 44 cm² Ω^{-1} mol⁻¹]. It takes ca. 12 h to convert 1 g of (**4**) into 0.85 g of (**5**). We note that this process which, in practice, corresponds to the elimination of a proton from (**4**), is greatly accelerated by the presence of a base such as a tertiary phosphine. However, the reverse reaction, from (**5**) to (**4**) does not proceed by treatment of (**5**) with strong acids. It has been ascertained that (**4**) can be formed from (**5**) only by reaction of the latter compound with LiHBEt₃, followed by exposure in air of the resultant deep red solution. Evidently, an intermediate step of the reaction (**5**) to (**4**) is the formation of another member of the family, namely a binuclear uncharged species containing four hydride ligands which is easily oxidized by atmospheric oxygen to (**4**). Unfortunately, we have not been able to isolate this intermediate in a pure form. Compound (**5**) has a magnetic moment at 293 K which ranges, over ten preparations, only from 1.65 to 1.70 μ_B . No appreciable variation of the magnetic susceptibility with temperature (296–84 K) was observed. Red crystals of [(triphos)Rh(μ -H)₃Rh(triphos)](BPh₄)₂·DMF (**6**) (DMF = dimethylformamide) are obtained in 75% yield by exposure in

[†] The synthesis and the crystal structure of (**1**) are the subject of a manuscript in preparation.



Scheme 1

air of a DMF solution of (5) for 12 h, followed by addition of NaBPh_4 in *n*-butyl alcohol [i.r. (Nujol) 1655 cm^{-1} $\mu(\text{Rh}-\text{H}-\text{Rh})$; λ_{M} (EtNO_2) $101\text{ cm}^2\ \Omega^{-1}\ \text{mol}^{-1}$]. Compound (6) is paramagnetic with a magnetic moment corresponding to one unpaired spin ($2.20\ \mu_{\text{B}}$). Reduction by $\text{NaC}_{10}\text{H}_8$ of (6) in THF yields (5). Thus, it can be safely assumed that (5) has the same primary dimeric framework as (6), whose precise stereochemistry has been ascertained by an *X*-ray analysis (see below). As a final synthetic remark, (4) gives the trihydride (3) when treated with an excess of LiHBEt_3 . Interestingly, when an equimolar amount of the latter reagent is used, the reaction gives red violet crystals of a monocharged dimeric complex which contains five hydride ligands. Treatment of this complex with LiHBEt_3 yields the trihydride (3). A proper characterization of this new member of the family is presently being attempted.

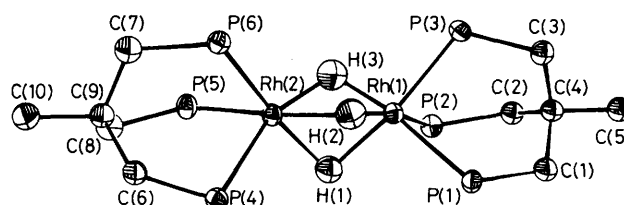


Figure 1. ORTEP drawing of the $[(\text{triphos})\text{Rh}(\mu\text{-H})_3\text{Rh}(\text{triphos})]^{2+}$ complex cation of (6). Hydrogen atoms of the ethylenic chains and phenyl rings are omitted for clarity. Some relevant bond distances (\AA): $\text{Rh}(1)-\text{Rh}(2)$, 2.644(1); $\text{Rh}(1)-\text{P}(1)$, 2.315(3); $\text{Rh}(1)-\text{P}(2)$, 2.302(3); $\text{Rh}(1)-\text{P}(3)$, 2.302(3); $\text{Rh}(2)-\text{P}(4)$, 2.329(2); $\text{Rh}(2)-\text{P}(5)$, 2.316(4); $\text{Rh}(2)-\text{P}(6)$, 2.326; mean $\text{Rh}(1)-\text{H}_b$, 1.73(6); mean $\text{Rh}(2)-\text{H}_b$, 1.91(7). Bond angles ($^\circ$): mean $\text{H}_b-\text{Rh}(1)-\text{H}_b$, 77(3), mean $\text{H}_b-\text{Rh}(2)-\text{H}_b$, 67(3).

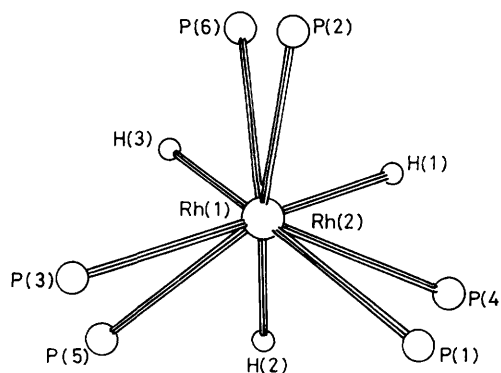


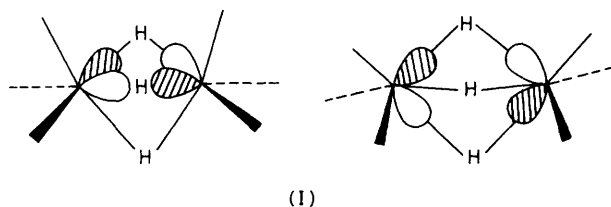
Figure 2. Perspective view of the $[(\text{triphos})\text{Rh}(\mu\text{-H})_3\text{Rh}(\text{triphos})]^{2+}$ complex cation looking down the $\text{Rh}(1)-\text{Rh}(2)$ vector.

The structure of (3) is already present in the literature,² whereas a structural determination of (6) has been performed by us \ddagger (Figure 1). As in other species of the type $\text{L}_6\text{M}_2(\mu\text{-H}_3)$, the skeleton of (6) is close to that of two face sharing octahedra although here the two (triphos)Rh units are rotated by *ca.* 15° from a mutually eclipsed orientation (see Figure 2). The $\text{Rh}-\text{Rh}$ separation of 2.644(1) \AA is slightly longer than that found in the complex $[(\text{L}-\text{L})\text{HRh}(\mu\text{-H})_3\text{Rh}(\text{L}-\text{L})]\text{ClO}_4$ ³ [$\text{L}-\text{L} = \text{rac-Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPhBu}^t)_2$] which contains one less valence electron (30) and for which a triple $\text{Rh}-\text{Rh}$ bond is formally predicted.

The magnetic features of both compounds (5) and (6) deserve some comments. The monocation (5) is 'formally' isoelectronic (32 valence electrons) with the complex $[(\text{as}_3)\text{Co}(\mu\text{-H})_3\text{Co}(\text{as}_3)]^+$,⁴ [$\text{as}_3 = \text{MeC}(\text{CH}_2\text{AsPh}_2)_3$] which

\ddagger Crystal data for (6): $\text{C}_{130}\text{H}_{121}\text{B}_2\text{P}_6\text{Rh}_2 \cdot \text{Me}_2\text{NCHO}$, $M = 2169.78$, triclinic, space group $P1$, $a = 16.868(4)$, $b = 15.863(4)$, $c = 14.026(3)$ \AA , $\alpha = 111.74(2)$, $\beta = 91.01(2)$, $\gamma = 116.25(2)^\circ$, $U = 3052(2)$ \AA^3 , $Z = 1$, $D_c = 1.18\text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 3.89\text{ cm}^{-1}$. The structure was solved by Patterson and Fourier techniques and refined to an R factor of 0.059 ($R_w = 0.064$) using 9149 reflections with $I > 3\sigma(I)$ measured on a Philips PW 1100 diffractometer up to $2\theta = 50^\circ$ ($\text{Mo-K}\alpha$ radiation, $\lambda = 0.71069$ \AA). The three bridging hydrogen atoms were found from a difference Fourier map and their positional and isotropic thermal parameters were refined. During the refinement the phenyl rings were treated as rigid groups of D_{6h} symmetry.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



has a very comparable primary geometry. However (5) has a much lower μ_{eff} . (1.7 vs. 3.1 μ_{B}). Complex (6) with its unpaired electron has no other precedent.

An exhaustive MO treatment of three hydrido dimers of the type $L_6M_2(\mu-H_3)$ was performed by Dedieu, Albright, and Hoffmann,⁵ and may in principle be adapted to the present cases. The degenerate set of MOs, shown in (I), is well separated in energy from any other level and thus it is the most probable candidate to be populated by one or two electrons. § This fact raises interesting questions. Given one or two electrons in an e orbital of a threefold symmetric system, a Jahn-Teller distortion should be in principle expected.⁶ The structure of (6) shows that the L_6M_3 skeleton has C_3 symmetry but since the co-ordinates of the hydrogen atoms are not very reliable one cannot exclude that their disposition about the Rh-Rh vector is somewhat asymmetrical. However, even if this is the case, the degeneracy of the levels in (I) can hardly be affected owing to their intrinsic metal character. ¶ If the

§ Extended Hückel calculations specifically performed for the present case confirm the assignment.

¶ No degenerate combination of three hydrogen orbitals can significantly overlap with the metal combinations (I).

primary geometry of (6) is maintained in (5), the anomalous magnetism of the latter can be explained in terms of a significant spin-orbit coupling. This effect is consistent with the nature of the metal atoms, the orthogonality and separation of the contributing AOs in (I) which confer a sort of diradical character to the system.⁷ In addition, the spin-orbit coupling, favoured by such a chemical environment, may be able to quench in (6) the Jahn-Teller effect inherent to a 2E ground state.⁸

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