Metal Hydrides from Cationic Rhodium(I) Catalyst Precursors. *X*-Ray Structure of [(L–L)HRh(μ-H)$_3$RhH(L–L)]ClO$_4$ [L–L = *rac*-Fe(η^5-C$_5$H$_4$PPhBu^t)$_2$]

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The hydrogenation catalyst precursor [(L–L)RhNBD]ClO$_4$ reacts with H$_2$ (1 atm, 30 °C, MeOH) to yield [(L–L)HRh(μ-H)$_3$RhH(L–L)]ClO$_4$ [L–L = *rac*-Fe(η^5-C$_5$H$_4$PPhBu^t)$_2$; NBD = norbornadiene].

Brown and coworkers[1] have recently described an elegant and useful test for the reversibility of hydrogen addition to metal complexes in solution. Of particular interest is their result indicating a rapid addition of hydrogen to the catalytically important cationic rhodium species [(diphos)RhS$_2$]$^+$, (**1**), [diphos = 1,2-bis(diphenylphosphino)ethane, S = MeOH] to give an undetectable concentration of a dihydride [(diphos)RhS$_2$(H)$_2$]$^+$. This hydride was formulated as such because Otsuka and coworkers[2] have suggested that this is the composition of the incompletely characterized solids obtained from the reaction of [(L–L)RhNBD]ClO$_4$, (**2**), with H$_2$ {L–L = (C$_6$H$_{11}$)$_2$P[CH$_2$]$_4$P(C$_6$H$_{11}$)$_2$ or (C$_6$H$_{11}$)$_2$PCH–CH[CH$_2$P-(C$_6$H$_{11}$)$_2$]OCMe$_2$O; NBD = norbornadiene}.

These results are of considerable interest because species such as (**1**) are not generally believed to react with hydrogen directly to afford hydrides[3] although hydride formation accompanying internal metallation has been observed.[3,4]

We now report that hydrides are easily obtained from cationic rhodium complexes (**2**) where L–L is one of a wide range of ferrocenylphosphines [η^5-C$_5$H$_{5-n}$(PR$_2$)$_n$]Fe-[η^5-C$_5$H$_3$(PR$_2$)C(H)MeNMe$_2$-1,2] and Fe(η^5-C$_5$H$_4$PR$_2$)$_2$

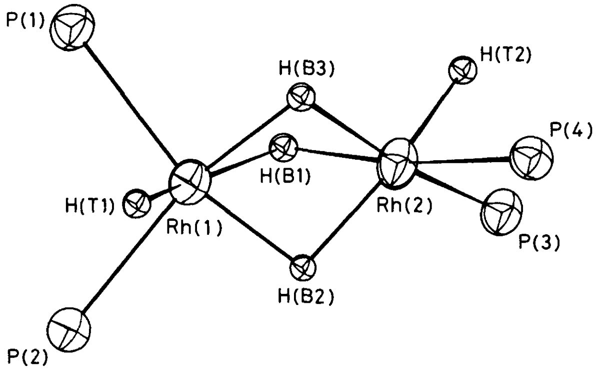


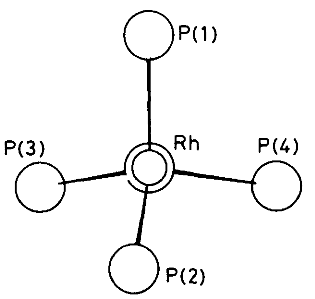
Figure 1. The 'RhPH' skeletal structure of compound (**3**). Some important bond distances [corresponding values for (**4**) are given in parentheses]: Rh(1)–Rh(2) 2.5943(9) [2.720(2)], Rh(1)–P(1) 2.351(2) [2.394(3)], Rh(1)–P(2) 2.300(2) [2.376(4)], Rh(1)–H(T1) 1.64(6), Rh(1)–H(B) (av.) 1.79(8) Å; bond angles: P(1)–Rh(1)–P(2) 103.50(7) [104.6(2)], H(T1)–Rh(1)–H(B1) 165(3), H(T1)–Rh(1)–P(1) 84(2), H(B)–Rh(1)–H(B) (av.) 72(3)°.

(R = Bu^t, Pr^i, or Ph: n = 0—2). The hydrides are formed in a variety of solvents by treating (**2**) with hydrogen (1 atm, 30 °C). The n.m.r. spectra of the products are complex, and variable temperature studies show the existence of a number of equilibria involving fluxional species. In two instances so far it has been possible to isolate crystals of products [(**3**) and (**4**)], suitable for X-ray investigation,† from cooled MeOH solutions. The structure of one of these, [(**3**)] is shown in Figure 1. The single counter ion is perchlorate.

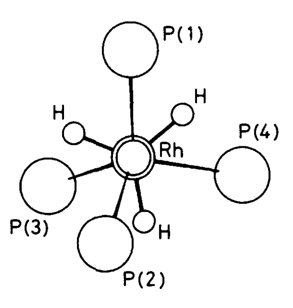
$[(\text{diphos})\text{RhS}_2]^+$
(**1**)

A symmetrical trihydride bridge is present in (**3**) together with two terminal hydrogen atoms, both rhodium atoms being in the 3+ oxidation state. This structure is very similar to that of the iridium analogue $[\text{Ir}_2(\mu\text{-H})_3\text{H}_2(\text{PPh}_3)_4]\text{PF}_6$,[5] although here the H atoms were not located during the structure analysis because of disorder.

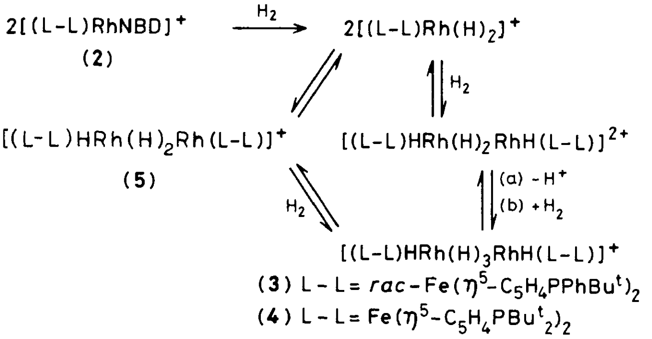
Neutral binuclear Rh$^{\text{I}}$---Rh$^{\text{III}}$ hydride species have been characterized in the solid state where a dihydride bridge was found, and in solution where some n.m.r. spectra have been interpreted in terms of a trihydride bridged species.[6,7] The cation $\{[(\text{C}_5\text{H}_5)\text{P}(\text{CHMe}_2)_3\text{Rh}]_2(\mu\text{-H})_3\}^+$ with a Rh$^{\text{III}}$–Rh$^{\text{III}}$ bond has been identified recently.[8]



(A)



(B)



Scheme 1

Crystals of the cationic hydride (**4**) obtained from [(**2**); L–L = $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PBu}^t{}_2)_2$] are not good enough to allow the number and disposition of hydrogen atoms to be determined with any certainty. A view of (**4**) looking down the Rh---Rh vector is shown in (A). This should be compared with a similar view (B) of (**3**). In (A) and (B) all groups around the P atoms have been omitted for clarity and only the three bridging H atoms of (**3**) are shown. The similarity of the overall ligand dispositions in the two indicates that the complexes could have the same structure. For the present, only minor differences in the conformation of the chelate rings in the two complexes can be used to counter this conclusion. Chemically the similarity is to be expected because the eight electron donating Bu^t groups in (**4**) should encourage oxidative addition of hydrogen to give two Rh$^{\text{III}}$ species.

Possible routes to (**3**) and (**4**) are as in Scheme 1; (**5**) is probably present in solution and is the expected structure of a cation with a dihydrogen bridge. The reversible loss of a proton has been established for dihydrides obtained in similar systems involving monodentate ligands [equation (1)].[9]

$$[\text{L}_2\text{RhNBD}]^+ \xrightarrow{\text{H}_2} [\text{L}_2\text{RhH}_2]^+ \overset{-\text{H}^+}{\rightleftharpoons} \text{L}_2\text{RhH} \qquad (1)$$

Both isolated hydride complexes dissolve in a variety of solvents to give solutions which are catalytic for olefin hydrogenation (1 atm H_2, 30 °C) but which contain a number of species (fluxional and non-fluxional) in equilibrium. As hydrides are also obtained from the reaction of $\{$**2**; L–L = $\text{Pr}^i{}_2\text{P}[\text{CH}_2]_2\text{PPr}^i{}_2\}$ with hydrogen [10] it is important to apply the test of Brown and coworkers[1] to these systems to obtain information about the involvement of hydrides in the catalytic cycle. These results will be reported in due course.

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† *Crystal data:* $[(\text{L–L})\text{HRh}(\mu\text{-H})_3\text{RhH}(\text{L–L})]\text{ClO}_4$ [L–L = *rac*-$\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PPhBu}^t)_2$], (**3**), $\text{C}_{60}\text{H}_{77}\text{ClFe}_2\text{O}_4\text{P}_4\text{Rh}_2\cdot\text{CH}_3\text{OH}$, M = 1371.2, monoclinic, space group $P2_1/n$, a = 18.708(4), b = 14.857(2), c = 21.853(4) Å, β = 92.95(2)°, Z = 4, U = 6065.9 Å^3, D_c = 1.501 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 11.89 cm^{-1}, present R factor = 0.045 for 5732 reflections with $I/\sigma(I) \geqslant 2.3$ collected on a Nonius CAD-4 diffractometer in the 2θ range 3—45°. $[(\text{L–L})\text{HRh}(\mu\text{-H})_3\text{RhH}(\text{L–L})]\text{ClO}_4$ [L–L = $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{PBu}^t{}_2)_2$], (**4**), $\text{C}_{52}\text{H}_{93}\text{ClFe}_2\text{O}_4\text{P}_4\text{Rh}_2$, M = 1259.2, monoclinic, space group $P2_1/c$, a = 15.276(3), b = 14.751(2), c = 25.950(3) Å, β = 89.15(1)°, Z = 4, U = 5846.8 Å^3, D_c = 1.430 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 12.26 cm^{-1}, present R factor = 0.059 for 4180 reflections with $I/\sigma(I) \geqslant$ 2.3 collected as for compound (**3**).

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

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