

X-Ray Crystal Structure of a Cationic Rhodium Hydride Complex with a *cis*-Chelating Diphosphine Ligand [$\{\text{Rh}(\text{dipp})\text{H}\}_2(\mu\text{-H})_2(\mu\text{-ClO}_4)\text{ClO}_4$ {dipp = $\text{Pr}_2\text{P}[\text{CH}_2]_3\text{PPr}_2$ }

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An X-ray crystallographic study of a rhodium hydride complex containing a *cis*-chelating diphosphine, isolated from the reaction of a cationic rhodium(I) hydrogenation catalyst precursor $[\text{Rh}(\text{dipp})(\text{kbd})\text{ClO}_4]$ [dipp = $\text{Pr}_2\text{PC}_3\text{H}_6\text{PPr}_2$, kbd = norbornadiene] with H_2 , has revealed the structure as $[\{\text{Rh}(\text{dipp})\text{H}\}_2(\mu\text{-H})_2(\mu\text{-ClO}_4)]\text{ClO}_4$, suggesting the presence of a rhodium *cis*-dihydride species $[\text{Rh}(\text{dipp})(\text{H})_2\text{S}_2]^+$ (S = solvent), as an intermediate.

Recently the reaction of cationic phosphinerhodium(I) complexes, $[\text{Rh}(\text{diphosphine})(\text{diene})]^+$, (**1**), with H_2 has received much attention in relation to catalytic hydrogenation.¹ Such cationic rhodium(I) complexes containing a *cis*-chelating diphosphine ligand were thought to take up no more than 2 equivalents of H_2 , resulting only in the formation of a solvated complex, $[\text{Rh}(\text{diphosphine})\text{S}_2]^+$, (**2**), (S = solvent) and not to afford hydrides.² We have shown that when the diphosphine is a highly basic one such as dipp, dipb, or cydiop [dipp = $\text{Pr}_2\text{PC}_3\text{H}_6\text{PPr}_2$, dipb = $\text{Pr}_2\text{PC}_4\text{H}_8\text{PPr}_2$, cydiop = 1,4-bis(dicyclohexylphosphino)-2,3-*O*-isopropylidene-2,3-dihydroxybutane] rhodium hydride complexes of formula ' $\text{Rh}(\text{diphosphine})(\text{H})_2(\text{ClO}_4)$ ' (**4**) can be isolated from the reaction mixture, but we could not obtain a crystal suitable for X-ray analysis.^{3,4} Subsequently Brown *et al.* demonstrated a rapid reversible addition of H_2 to $[\text{Rh}(\text{diphos})(\text{MeOH})_2]^+$ (**2**) giving a low concentration of a dihydride $[\text{Rh}(\text{diphos})(\text{MeOH})_2(\text{H})_2]^+$ (**3**).⁵ More recently Butler *et al.* have isolated a rhodium hydride species containing an unusual trihydride bridge $[\{\text{Rh}(\text{diphosphine})\text{H}\}_2(\mu\text{-H})_3]\text{ClO}_4$ using *rac*-(PhBu) $^+\text{PC}_5\text{H}_4)_2\text{Fe}$ as a diphosphine ligand.⁶ With a more basic ferrocenyl diphosphine ($\text{Pr}_2\text{PC}_5\text{H}_4)_2\text{Fe}$ they detected a new hydride species in the ^1H n.m.r. spectrum,⁷ which may be similar to (**4**). Here we report the X-ray crystal structure of the rhodium hydride ' $\text{Rh}(\text{dipp})(\text{H})_2(\text{ClO}_4)$ ' (**4a**), which has been isolated as pale yellow crystals from the reaction of $[\text{Rh}(\text{dipp})(\text{kbd})]\text{ClO}_4$ (**1a**) with excess of H_2 in methanol.^{4†}

† Crystal data: $\text{C}_{30}\text{H}_{72}\text{Cl}_2\text{O}_8\text{P}_4\text{Rh}_2$, $M = 961.51$, orthorhombic, space group *Pcam*, $F(000) = 2000$, $a = 16.585(3)$, $b = 11.246(2)$, $c = 23.361(2)$ Å, $U = 4357(1)$ Å³, $Z = 4$, $D_c = 1.466$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 11.65$ cm⁻¹, crystal size, $0.55 \times 0.4 \times 0.15$ mm. Data were collected on a Rigaku-denki AFC-4 automated diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) using ω -2 θ scan ($2\theta_{\text{max}} < 55^\circ$) 293 K; 5132 unique reflections were measured. No absorption corrections were applied. The structure was solved by Patterson and difference-Fourier techniques and refined with anisotropic thermal parameters by block-diagonal least-squares methods to an R of 0.064. At this stage all hydrogen atoms were located from a difference-Fourier map. Hydride atoms were refined isotropically and alkyl hydrogen atoms were included as fixed contributions. Current refinement is to conventional $R = 0.041$ and $R_w = 0.051$ for 2477 reflections [$I > 3\sigma(I)$] and 224 parameters with weights $w = [\sigma^2(F_o) + 0.0022|F_o| + 0.00075|F_o|^2]^{-1}$. A final difference-Fourier map was featureless with maximum residual of 0.57 e Å⁻³. All calculations were performed with UNICS programs on ACOS 900 and 850 computers.

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.

The molecular structure of the (**4a**) cation is shown in Figure 1 along with selected bond lengths and angles and the atom numbering scheme. The structure reveals several interesting features. A perchlorate and a dihydride bridge connect two $\text{Rh}(\text{dipp})\text{H}$ groups forming a dinuclear cation $[\{\text{Rh}(\text{dipp})\text{H}\}_2(\mu\text{-H})_2(\mu\text{-ClO}_4)]^+$ with a perchlorate counter anion; both rhodium atoms are in the +3 oxidation state. The bidentate intramolecular perchlorate bridge is to our knowledge the first example for a rhodium complex, though it is known for several copper complexes.^{8,9} Overall the cation has C_s symmetry with a mirror plane including the bridging dihydrides and O(1)-Cl(1)-O(2) atoms of the bridging perchlorate ligand. Each rhodium atom has distorted octahedral geometry. The present structure is consistent with the ^1H and ^{31}P n.m.r. spectra,⁴ indicating that the dinuclear structure is maintained in solution. The Rh-Rh distance [2.671(1) Å] is similar to the Rh-Rh separation [2.681(1) Å] in the μ -dihydride complex $[\{\text{Rh}(\text{C}_5\text{Me}_5)\}_2(\mu\text{-H})_2(\mu\text{-OAc})]^+$.¹⁰ This result shows that the hydride and the perchlorate form strong bridges, and this is reflected in the low catalytic activity of the hydrides (**4**) in hydrogenation compared with the very high catalytic activity

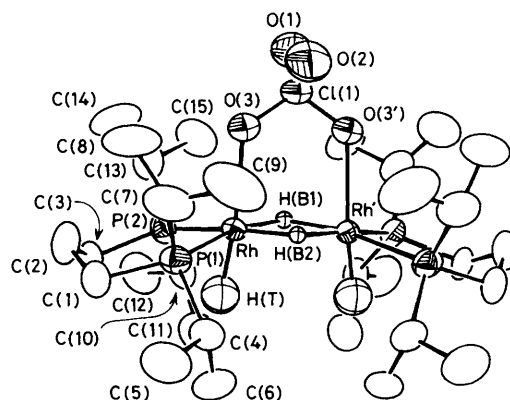
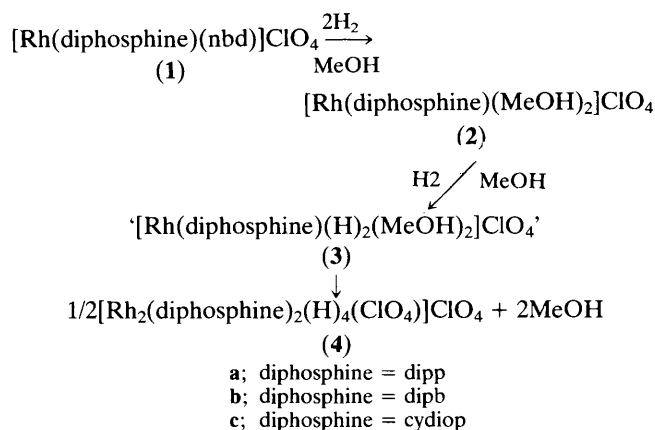


Figure 1. ORTEP drawing (50% probability contours for all atoms) of the cation $[\text{Rh}_2(\text{dipp})_2(\text{H})_4(\text{ClO}_4)]^+$ in (**4a**) (from MeOH). Selected interatomic distances (Å) and angles ($^\circ$): Rh-Rh' 2.671(1), Rh-P(1) 2.276(2), Rh-P(2) 2.273(2), Rh-O(3) 2.304(5), Rh-H(T) 1.57(9), Rh-H(B1) 1.73(6), Rh-H(B2) 1.55(6), Cl(1)-O(1) 1.426(6), Cl(1)-O(2) 1.424(7), Cl(1)-O(3) 1.469(6), P-C and C-C distances in the phosphine ligand are 1.818–1.866 and 1.444–1.558 Å, respectively; P(1)-Rh-P(2) 94.9(1), O(3)-Rh-P(1) 101.8(1), O(3)-Rh-P(2) 100.2(1), O(3)-Rh-Rh' 86.8(1), P(1)-Rh-Rh' 130.8(1), P(2)-Rh-Rh' 131.5(1), P(1)-Rh-H(B1) 168(2), P(1)-Rh-H(B2) 101(2), P(2)-Rh-H(B1) 93(2), P(2)-Rh-H(B2) 161(2), O(3)-Rh-H(T) 171(3), O(3)-Rh-H(B1) 86(2), O(3)-Rh-H(B2) 86(2), H(B1)-Rh-H(B2) 70(3), H(B1)-Rh-H(T) 95(4), H(B2)-Rh-H(T) 103(4), P(1)-Rh-H(T) 79(3), P(2)-Rh-H(T) 71(3), Rh-H(B1)-Rh' 101(3), Rh-H(B2)-Rh' 119(4).



Scheme 1. nbd = norbornadiene.

shown by the parent diene complexes (1);⁴ the binuclear hydride complexes themselves are not considered to be active hydrogenation catalysts. The formation of the hydride (4a) can reasonably be explained by supposing that a *cis*-dihydride species $[\text{Rh}(\text{dipp})(\text{H})_2\text{S}_2]^+$ (3a) is formed initially followed by rapid dimerization, as shown in Scheme 1.

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