

## $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_3\text{H}$ : A Stable Ruthenium(IV) Trihydride

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Reduction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}$  (**2**) with  $\text{LiAlH}_4$  in tetrahydrofuran leads to the trihydride  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_3\text{H}$  (**1**) together with, as a minor product, the expected monohydride  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{H}$  (**3**) which can be prepared efficiently by treatment of the chloride (**2**) with  $\text{NaOMe}$ ; reduction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}$  (**4**) with  $\text{LiAlH}_4$  gives only the monohydride  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{H}$  (**5**).

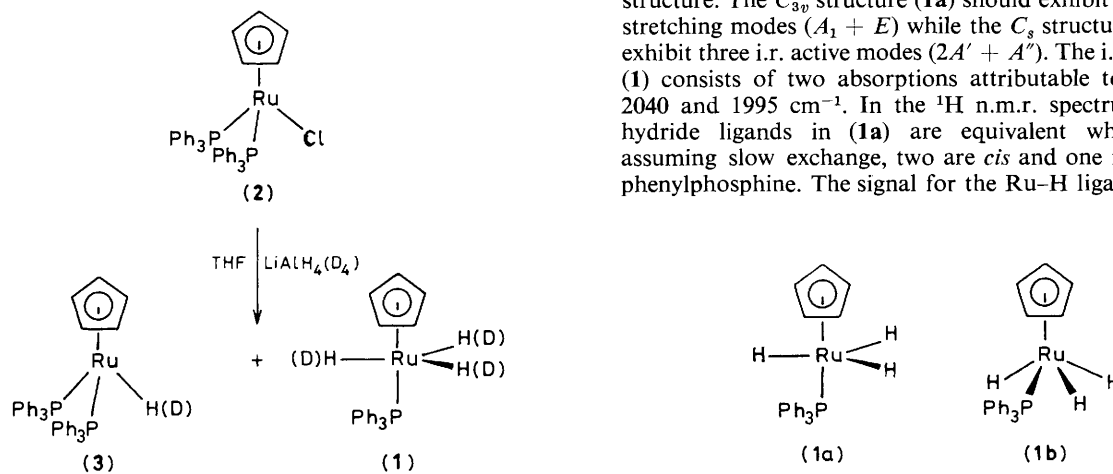
Hydridoruthenium(IV) species have been frequently proposed as intermediates in catalytic reactions such as olefin isomerisation<sup>1</sup> and intramolecular H-D exchange.<sup>2</sup> Neutral compounds such as  $\text{RuH}_4(\text{PAr}_3)_3$  (Ar = Ph, *p*-MeC<sub>6</sub>H<sub>4</sub>, etc.) are unstable with respect to dihydrogen loss and might best be considered as ruthenium(II) co-ordinated to a neutral dihydrogen donor ligand.<sup>3</sup> Cationic compounds such as  $[\text{RuH}_3(\text{L}_2)_2]^+\text{PF}_6^-$  { $\text{L}_2 = (\text{PMe}_2\text{Ph})_2$ ,  $\text{Ph}_2\text{P}[\text{CH}_2]_2\text{PPh}_2$ ,  $\text{Ph}_2\text{P}[\text{CH}_2]_3\text{PPh}_2$ }<sup>4</sup> and  $[(\eta^5\text{-C}_6\text{Me}_6)\text{RuH}_3(\text{PR}_3)]^+\text{PF}_6^-$  (R = Me, Ph)<sup>5</sup> have been prepared and are moderately stable. We now report the preparation of the thermally stable ruthenium(IV) trihydride  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_3\text{H}$  (**1**).

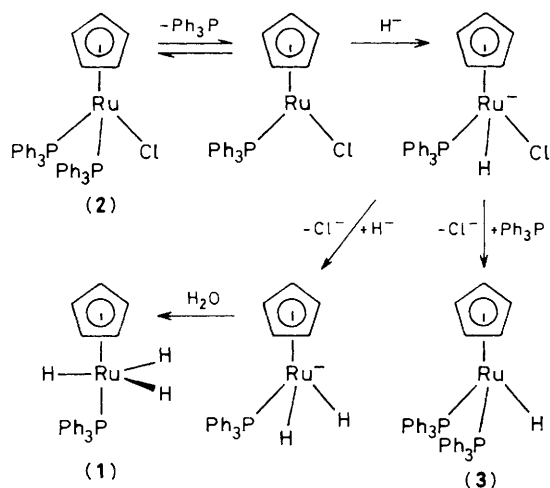
Treatment of  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{Cl}$  (**2**) with  $\text{LiAlH}_4$  in diethyl ether has been reported to yield  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_2\text{H}$  (**3**);<sup>6</sup> however in our hands poor yields of hydride-containing materials were obtained. Treatment of (**2**) with  $\text{LiAlH}_4$  in tetrahydrofuran (THF) gave on work-up a mixture of the trihydride  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_3\text{H}$  (**1**) and the monohydride (**3**)

in the ratio 4 : 1. These could be easily separated by crystallisation from diethyl ether. The yellow crystalline minor component was identified as the monohydride (**3**) by comparison with an authentic sample (see below). The major product, which was only moderately soluble in diethyl ether, crystallised as white needles. Characterisation by elemental analysis, mass spectroscopy [ $m/z$  432 ( $M^+$ )], <sup>31</sup>P n.m.r. spectroscopy [ $(\text{C}_6\text{D}_6)$   $\delta$  73.1 p.p.m.], and <sup>1</sup>H n.m.r. spectroscopy [ $(\text{C}_6\text{D}_6)$   $\delta$  7.8–7.0 (m, Ph), 4.8 (s, C<sub>5</sub>H<sub>5</sub>), –9.8 (d, *J* 18 Hz, RuH)] led to its formulation as  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_3\text{H}$  (**1**). The off-resonance decoupled <sup>31</sup>P n.m.r. spectrum of (**1**) was a broad quartet, confirming the presence of three metal hydride ligands.

The use of  $\text{LiAlD}_4$  in THF followed by D<sub>2</sub>O work-up gave the corresponding trideuteride  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{PPh}_3)_3\text{D}_3$ . The <sup>2</sup>H n.m.r. spectrum of the trideuteride showed no deuterium incorporation into the triphenylphosphine or cyclopentadienyl ligands.

The trihydride (**1**) would be expected to adopt either the trigonal bipyramidal (**1a**) or the square based pyramidal (**1b**) structure. The C<sub>3v</sub> structure (**1a**) should exhibit two i.r. active stretching modes ( $A_1 + E$ ) while the C<sub>s</sub> structure (**1b**) should exhibit three i.r. active modes ( $2A' + A''$ ). The i.r. spectrum of (**1**) consists of two absorptions attributable to  $\nu(\text{Ru-H})$  at 2040 and 1995 cm<sup>-1</sup>. In the <sup>1</sup>H n.m.r. spectrum, the three hydride ligands in (**1a**) are equivalent while for (**1b**), assuming slow exchange, two are *cis* and one is *trans* to triphenylphosphine. The signal for the Ru-H ligands in the <sup>1</sup>H



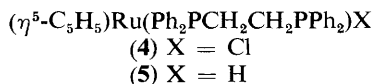


Scheme 1

n.m.r. spectrum of (1) is a sharp doublet ( $J$  18 Hz) with a coupling constant characteristic of the presence of a *cis* phosphine ligand.<sup>7</sup> The spectrum of (1) is unchanged from  $-80$  to  $70$  °C, in contrast to that of the recently prepared  $(\eta^5\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})\text{H}_3$  which exhibits a separate triplet and doublet in the ratio (1:2) for the metal hydride ligands at  $-50$  °C but a broad singlet at  $25$  °C.<sup>8</sup>

The closely related tribromide  $(\eta^5\text{-C}_5\text{Me}_5\text{Et})\text{Ru}(\text{CO})\text{Br}_3$  has been crystallographically characterised and possesses the  $C_s$  structure, though disordered, in the solid state.<sup>9</sup> Presumably  $(\eta^5\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})\text{H}_3$  also has this structure. The i.r. and  $^1\text{H}$  n.m.r. spectroscopic evidence is consistent with structure (1a) which is presumably favoured in this case by the steric requirements of the bulky triphenylphosphine ligand.

The monohydride (3) does not convert into the trihydride (1) in THF or benzene solution and transforms very slowly in warm THF ( $60$  °C) containing  $\text{LiAlH}_4$ . Treatment of (2) with  $\text{LiAlD}_4$  followed by  $\text{H}_2\text{O}$  gave (1) containing *ca.* 30% hydrogen at the metal centre. We note that (3) does not react with  $\text{Ph}_2\text{P}[\text{CH}_2]_2\text{PPh}_2$  in toluene at reflux in contrast to the chloride (2),<sup>10</sup> *i.e.* phosphine dissociation is much faster from the chloride (2) than from the hydride (3). It is unlikely therefore that (3) is a precursor to (1) and we propose the mechanism shown in Scheme 1 for the conversion of (2) to (1).



In contrast to the reaction of (2) and consistent with the mechanism in Scheme 1, the reaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}$  (4) with  $\text{LiAlH}_4$  in THF leads cleanly to  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{H}$  (5) characterised by elemental analysis, mass [ $m/z$  566 ( $M^+$ )],  $^{31}\text{P}$  n.m.r. [ $(\text{C}_6\text{D}_6)$   $\delta$  91.0 p.p.m.] and  $^1\text{H}$  n.m.r. spectroscopy [ $(\text{C}_6\text{D}_6)$   $\delta$  7.3 (m, Ph), 4.8 (s,  $\text{C}_5\text{H}_5$ ), 2.0 (m,  $\text{CH}_2$ ),  $-12.9$  (t,  $J$  34 Hz, RuH)]. Phosphine loss from the bidentate system is disfavoured and so a pathway leading to a ruthenium(IV) trihydride cannot be followed in this case.

While the new trihydride (1) is thermally stable in solution to *ca.*  $100$  °C and indefinitely stable under nitrogen in the solid state, solutions of (1) rapidly turn green in daylight.

It is possible to convert the chloride (2) cleanly into the monohydride (3), with sodium methoxide in methanol (78% yield). The monohydride (3) was characterised by  $^1\text{H}$  n.m.r. [ $(\text{C}_6\text{D}_6)$   $\delta$   $-11.1$  (t,  $J$  34 Hz, RuH)] and  $^{31}\text{P}$  n.m.r. spectroscopy [ $(\text{C}_6\text{D}_6)$   $\delta$  67.5 p.p.m.]. The reaction to yield (3) presumably proceeds by  $\beta$ -elimination from an initially formed methoxy complex.<sup>11</sup>

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