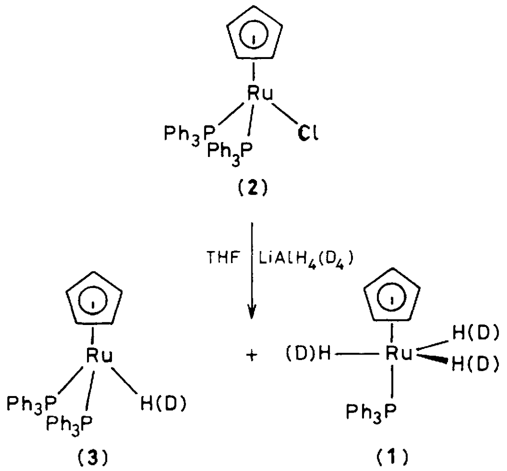
$(\eta^5\text{-}C_5H_5)Ru(PPh_3)H_3$: A Stable Ruthenium(IV) Trihydride

Stephen G. Davies,* Steven D. Moon, and Stephen J. Simpson
The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, U.K.

Reduction of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ (**2**) with $LiAlH_4$ in tetrahydrofuran leads to the trihydride $(\eta^5\text{-}C_5H_5)Ru(PPh_3)H_3$ (**1**) together with, as a minor product, the expected monohydride $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2H$ (**3**) which can be prepared efficiently by treatment of the chloride (**2**) with NaOMe; reduction of $(\eta^5\text{-}C_5H_5)Ru(Ph_2PCH_2CH_2PPh_2)Cl$ (**4**) with $LiAlH_4$ gives only the monohydride $(\eta^5\text{-}C_5H_5)Ru(Ph_2PCH_2CH_2PPh_2)H$ (**5**).

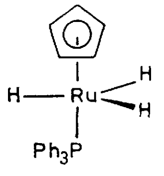
Hydridoruthenium(IV) species have been frequently proposed as intermediates in catalytic reactions such as olefin isomerisation[1] and intramolecular H–D exchange.[2] Neutral compounds such as $RuH_4(PAr_3)_3$ (Ar = Ph, $p\text{-}MeC_6H_4$, *etc.*) are unstable with respect to dihydrogen loss and might best be considered as ruthenium(II) co-ordinated to a neutral dihydrogen donor ligand.[3] Cationic compounds such as $[RuH_3(L_2)_2]^+PF_6^-$ $\{L_2 = (PMe_2Ph)_2$, $Ph_2P[CH_2]_2PPh_2$, $Ph_2P[CH_2]_3PPh_2\}$[4] and $[(\eta^6\text{-}C_6Me_6)RuH_3(PR_3)]^+PF_6^-$ (R = Me, Ph)[5] have been prepared and are moderately stable. We now report the preparation of the thermally stable ruthenium(IV) trihydride $(\eta^5\text{-}C_5H_5)Ru(PPh_3)H_3$ (**1**).

Treatment of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ (**2**) with $LiAlH_4$ in diethyl ether has been reported to yield $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2H$ (**3**);[6] however in our hands poor yields of hydride-containing materials were obtained. Treatment of (**2**) with $LiAlH_4$ in tetrahydrofuran (THF) gave on work-up a mixture of the trihydride $(\eta^5\text{-}C_5H_5)Ru(PPh_3)H_3$ (**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^+)], ^{31}P n.m.r. spectroscopy [(C_6D_6) δ 73.1 p.p.m.], and ^1H n.m.r. spectroscopy [(C_6D_6) δ 7.8—7.0 (m, Ph), 4.8 (s, C_5H_5), −9.8 (d, *J* 18 Hz, RuH)] led to its formulation as $(\eta^5\text{-}C_5H_5)Ru(PPh_3)H_3$ (**1**). The off-resonance decoupled ^{31}P n.m.r. spectrum of (**1**) was a broad quartet, confirming the presence of three metal hydride ligands.

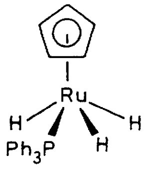


The use of $LiAlD_4$ in THF followed by D_2O work-up gave the corresponding trideuteride $(\eta^5\text{-}C_5H_5)Ru(PPh_3)D_3$. The ^2H n.m.r. spectrum of the trideuteride showed no deuterium incorporation into the triphenylphosphine or cyclopentadienyl ligands.

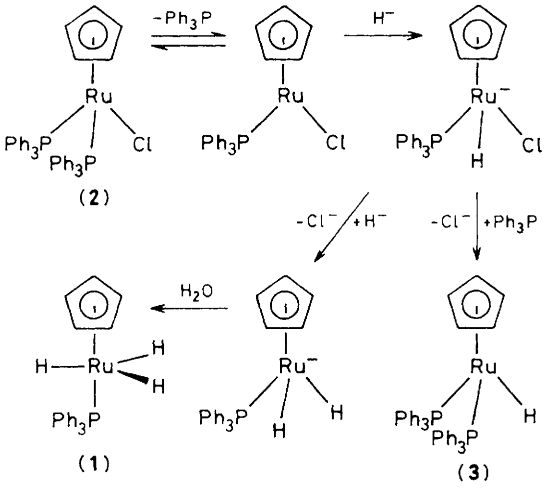
The trihydride (**1**) would be expected to adopt either the trigonal bipyramidal (**1a**) or the square based pyramidal (**1b**) structure. The C_{3v} structure (**1a**) should exhibit two i.r. active stretching modes ($A_1 + E$) while the C_s structure (**1b**) should exhibit three i.r. active modes ($2A' + A''$). The i.r. spectrum of (**1**) consists of two absorptions attributable to ν(Ru–H) at 2040 and 1995 cm^{-1}. In the ^1H 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 ^1H



(1a)



(1b)



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.[7] The spectrum of (**1**) is unchanged from −80 to 70 °C, in contrast to that of the recently prepared (η^5-C_5Me_5)Os(CO)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.[8]

The closely related tribromide (η^5-C_5Me_4Et)Ru(CO)Br_3 has been crystallographically characterised and possesses the C_s structure, though disordered, in the solid state.[9] Presumably (η^5-C_5Me_5)Os(CO)H_3 also has this structure. The i.r. and ^1H 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 $LiAlH_4$. Treatment of (**2**) with $LiAlD_4$ followed by H_2O gave (**1**) containing *ca.* 30% hydrogen at the metal centre. We note that (**3**) does not react with $Ph_2P[CH_2]_2PPh_2$ in toluene at reflux in contrast to the chloride (**2**),[10] *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**).

(η^5-C_5H_5)Ru($Ph_2PCH_2CH_2PPh_2$)X
(**4**) X = Cl
(**5**) X = H

In contrast to the reaction of (**2**) and consistent with the mechanism in Scheme 1, the reaction of (η^5-C_5H_5)Ru(Ph_2PCH_2-CH_2PPh_2)Cl (**4**) with $LiAlH_4$ in THF leads cleanly to (η^5-C_5H_5)-Ru($Ph_2PCH_2CH_2PPh_2$)H (**5**) characterised by elemental analysis, mass [*m/z* 566 (M^+)], ^{31}P n.m.r. [(C_6D_6) δ 91.0 p.p.m.] and ^1H n.m.r. spectroscopy [(C_6D_6) δ 7.3 (m, Ph), 4.8 (s, C_5H_5), 2.0 (m, 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 ^1H n.m.r. [(C_6D_6) δ −11.1 (t, *J* 34 Hz, RuH)] and ^{31}P n.m.r. spectroscopy [(C_6D_6) δ 67.5 p.p.m.]. The reaction to yield (**3**) presumably proceeds by β-elimination from an initially formed methoxy complex.[11]

We thank the British Petroleum Company Limited for a Fellowship (S. J. S.) and Johnson Matthey Chemicals Limited for a generous loan of ruthenium.

Received, 15th August 1983; Com. 1114

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