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Ionic Ruthenium(IV) Trihydrides as Intermediates in the Heterolytic Fission of Dihydrogen by Five-co-ordinate Hydridoruthenium(II) Cations. Direct Evidence for an Oxidative Addition–Reductive Elimination Pathway

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Summary The cations $[RuH(L_2)_2(MeOH)]^+$ [L_2 = $(PMe_2Ph)_2$, $(PMePh_2)_2$, or bis(diphenylphosphino)ethane (dpe)] and the salts $[RuH(L_2)_2]PF_6$ [L_2 = bis(diphenylphosphino)-propane (dpp) and -butane (dpb)], formed from stoicheiometric ligand additions to $[(cod)RuH(NH_2NMe_2)_3]PF_6$ (cod = cyclo-octa-1,5-diene) in methanol under argon, react *in situ* with dihydrogen to give the trihydrides $[RuH_3(L_2)_2]PF_6$ for L_2 = $(PMe_2Ph)_2$, dpe, or dpp, and the dihydrides $[RuH_2(L_2)_2]$ for L_2 = $(PMePh_2)_2$ or dpb; the equilibrium $[RuH_3(L_2)_2]^+ \rightleftharpoons [RuH_2(L_2)_2] + H^+$ is demonstrated and used to prepare $[RuH_3(L_2)_2]PF_6$ for L_2 = $(PMePh_2)_2$ or dpb, and $[RuH_2(L_2)_2]$ for L_2 = dpp.

A NUMBER of d^6 ruthenium(II) complexes in solution are known to activate molecular hydrogen in catalytic reactions through a heterolytic splitting process.[1] Although it has been suggested for some systems, *e.g.* in the conversion of $[RuCl_2(PPh_3)_3]$ into $[RuHCl(PPh_3)_3]$, that this heterolysis reaction occurs *via* initial homolytic activation in an oxidative addition step,[2] no direct evidence for a ruthenium(IV) intermediate has yet been obtained. Though the formation[3] of $[RuH_4(PPh_3)_3]$ from dihydrogen and the dihydride $[RuH_2(PPh_3)_4]$ may be cited as an example of an oxidative addition to a ruthenium(II) system, the reactivity of this complex is in fact similar to that of reversibly-bonded molecular dioxygen compounds[4] in that all its reactions to date[5] involve initial loss of dihydrogen. Thus $[RuH_4(PPh_3)_3]$ might be effectively considered as a ruthenium(II) complex containing neutral dihydrogen, which occupies the vacant co-ordination position and acts as an electron donor with little weakening of the H–H bond.[2] We have now synthesised† a series of five-co-ordinate (or effectively five-co-ordinate) ruthenium(II) cations which are highly reactive, and from our initial investigations into their ability to activate dihydrogen we have obtained direct evidence for an oxidative addition–reductive elimination pathway in the heterolytic splitting of molecular hydrogen by ruthenium(II) systems.

We have recently synthesised the salt $[(cod)RuH(NH_2NMe_2)_3]PF_6$ from the polymer $[(cod)RuCl_2]_x$ and NH_2NMe_2 in methanol containing NH_4PF_6 and found that treatment of (**1**) in an alcohol with stoicheiometric amounts of the appropriate tertiary diphosphine gave the five-co-ordinate hydrides $[RuH(L_2)_2]PF_6$ (**2**) [L_2 = dpp (hydride resonance at τ 22·3) or dpb (hydride resonance at τ 24·3)]. As the size of the chelate ring is reduced the tendency to bond a sixth ligand increases, and thus reactions of (**1**) with dpe in ethanol gave only the solvolysed salt $[RuH(dpe)_2(EtOH)]PF_6$ (**3**) [ν(OH) 3540m and ν(Ru–H) 2040w cm^{-1}]. These complexes are all crystalline and reasonably stable in an inert atmosphere but slowly decompose in air over a period of a few days. The cations $[RuH(L_2)_2(MeOH)]^+$ [L_2 = $(PMe_2Ph)_2$ or $(PMePh_2)_2$] were formed *in situ* as red species from (**1**) and 4 mol. equiv. of PMe_2Ph or $PMePh_2$ in methanol solution.

These hydrido-phosphine complexes readily react with

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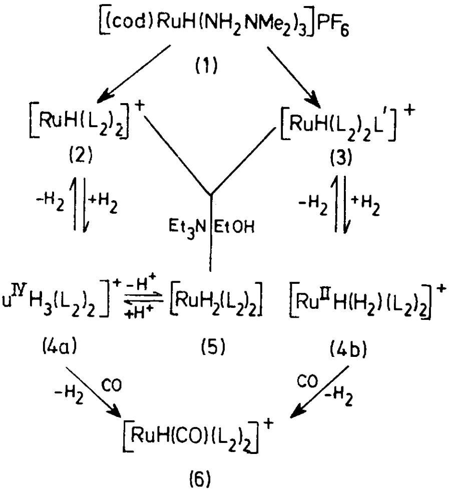
† Satisfactory microanalyses were obtained for all complexes reported.

dihydrogen at ambient temperature and pressure to form respectively [$RuH_3(L_2)_2$]PF_6 (**4**) [L_2 = $(PMe_2Ph)_2$, dpe, or dpp] and [$RuH_2(L_2)_2$] (**5**) [L_2 = $(PMePh_2)_2$[6] or dpb]. The salts [**4**; L_2 = $(PMe_2Ph)_2$ or dpe] slowly lose 1 mol. equiv. of dihydrogen on warming in an alcohol under argon to produce the monohydrides, whilst (**4**; L_2 = dpp) loses dihydrogen only on prolonged heating. The stoicheiometry of (**4**) was confirmed by the 1 mol equiv. of molecular hydrogen liberated and the quantitative conversion into *trans*-[$RuH(CO)(dpp)_2$]PF_6 [^{1}H n.m.r. spectrum: τ 14·8 (q, *J* 21 Hz)] and *cis*-[$RuH(CO)(PMe_2Ph)_4$]PF_6 [^{1}H n.m.r. spectrum: τ 18·6 {d (*J* 75 Hz) of q (*J* 24 Hz)}], respectively, when [**4**; L_2 = dpp or $(PMe_2Ph)_2$] was shaken with a measured amount of CO. The ^{1}H n.m.r. hydride resonance of [**4**; L_2 = $(PMe_2Ph)_2$] in CD_2Cl_2 at 30 °C was observed as a broad peak which integrated in the ratio of 1:8 with the phosphine methyls.



SCHEME. The complex [**2**; L_2 = $(PMePh_2)_2$] is solvolysed. (**2**) and (**4a**): L_2 = dpp, dpb, or $(PMePh_2)_2$; (**3**) and (**4b**): L_2 = dpe, L′ = EtOH, and L_2 = $(PMe_2Ph)_2$, L′ = MeOH; (**5**): L_2 = dpe, dpp, dpb, or $(PMePh_2)_2$; (**6**): L_2 = dpe, dpp (*trans*-configuration), or $(PMe_2Ph)_2$ (*cis*-configuration). dpe, dpp, and dpb are bis(diphenylphosphino)-ethane, -propane, and -butane respectively, and cod = cyclo-octa-1,5-diene.

When a CH_2Cl_2 solution of [$RuH_3(dpp)_2$]PF_6 was treated with Et_3N, conversion into [$RuH_2(dpp)_2$] was rapidly effected, and this represents the first example of the reductive elimination of H^+ from a relatively stable ruthenium(IV) hydride. Similar treatment of [**4**; L_2 = $(PMe_2Ph)_2$ or dpe], however, gave only the monohydrides and may indicate that the H–H bond is not ruptured in these complexes. Addition of a slight excess of HPF_6 to the dihydrides [**5**; L_2 = $(PMePh_2)_2$, dpp, or dpb] gave the trihydride [**4**; L_2 = $(PMePh_2)_2$, dpp, or dpb] which, for L_2 = $(PMePh_2)_2$ or dpb, was unstable and readily reconverted into the dihydride on recrystallization. All the dihydrides [**5**; L_2 = $(PMePh_2)_2$, dpe,[7] dpp, or dpb] were also prepared from the monohydride and Et_3N in ethanol, probably *via* a ruthenium ethoxide intermediate (Scheme).

We are at present extending this study to possible heterolytic fissions of other molecules with bond energies similar to or lower than that of dihydrogen. For example, additions of PhC≡CH to a solution of [$RuH(dpe)_2(MeOH)$]$^+$ appears, on initial investigation, to give the neutral complex [Ru(C≡CPh)(CH=CHPh)$(dpe)_2$] probably *via* similar oxidative addition–deprotonation steps.

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