

Preliminary communication

**ACTIVATION OF C—H BONDS BY RUTHENIUM HYDRIDE COMPLEXES.
 DEUTERATION OF TRIISOPROPYL AND TRICYCLOHEXYLPHOSPHINE
 USING C₆D₆ OR C₇D₈ AS THE DEUTERIUM SOURCE**

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Summary

Complexes of the type RuH₄P₃ (P = P(Prⁱ)₃, P(C₆H₁₁)₃ or P(N(C₂H₅)₂)₃) in solution in deuterated aromatic solvents undergo H-D exchange between the solvent and the coordinated phosphines. The reaction works better with RuH₄-P(Prⁱ)₃, in which about 70% of the phosphine protons can be so exchanged. A mechanism involving dissociation of a phosphine followed by activation of the solvent C—D bond and the phosphine C—H bond is proposed.

Activation of C—H bonds by metal complexes has been extensively studied in the past ten years [1,2] and especially so in the past year. As far as arenes and alkanes are concerned, four main types of system have been employed: (i) Low valent organometallic (mainly hydride) complexes either alone as in the case of lutetium [3], or activated, chemically, e.g. by being made electron-deficient by use of a consumed chemical Bu^tCH=CH₂ [4,5], or photochemically by loss of H₂ or CO [6–8]. Some of these systems can lead to compounds such as alkenes [5], benzaldehyde [9], or the imine C₆H₅CHNCH₂(CH₃)₃ [10] from benzene or deuterobenzene.

(ii) Porphyrinato complexes which can catalytically hydroxylate alkanes [11–16] or bring about simple C—H activation [17].

(iii) Acid solutions containing transition metal salts which can dehydrogenate [18] or oxidize [19] saturated hydrocarbons.

(iv) Polyhydrides or low valent complexes of transition metals which catalytically exchange H—D [20,21]. A typical reaction is the exchange between benzene and deuterium catalyzed by ReH₅(PPh₃)₃. Such systems are also capable of incorporating deuterium into their ligands, e.g. Nb(C₅H₅)₂(C₂H₄)-(C₂H₅) or Rh(C₅H₅)(C₂H₄)₂, but the mechanisms are likely to involve one oxida-

TABLE 1

TOTAL CONVERSION AND APPROXIMATE RATE OF DEUTERATION AS MEASURED BY INTEGRATION OF THE ^1H NMR SPECTRA

Complex	Temperature ($^{\circ}\text{C}$)	Solvent	Time (h)	Conversion (%)	Rate (cps)
$\text{RuH}_4(\text{PPr}^i_3)_3$	36	C_6D_6	168	70	0.26
$\text{RuH}_4(\text{PPr}^i_3)_3$	36	C_7D_8	96	10	0.06
$\text{RuH}_4(\text{PPr}^i_3)_3$	110	C_7D_8	0.1	50	>315
$\text{RuH}_4(\text{PCy}_3)_3$	36	C_6D_6	12	25	2.1
$\text{RuH}_4(\text{PCy}_3)_3$	36	C_7D_8	24	15	0.6
$\text{RuH}_4(\text{PCy}_3)_3$	110	C_7D_8	0.1	5	^a

^a This system reaches a maximum, so the order of magnitude of the rate is unknown.

tive addition of a C—D bond followed by an insertion, rather than two C—D and C—H activations. After photolytic activation $\text{CpMo}(\text{dpme})\text{H}_3$ can cause exchange hydrogen between some organic compounds and C_6D_6 [22].

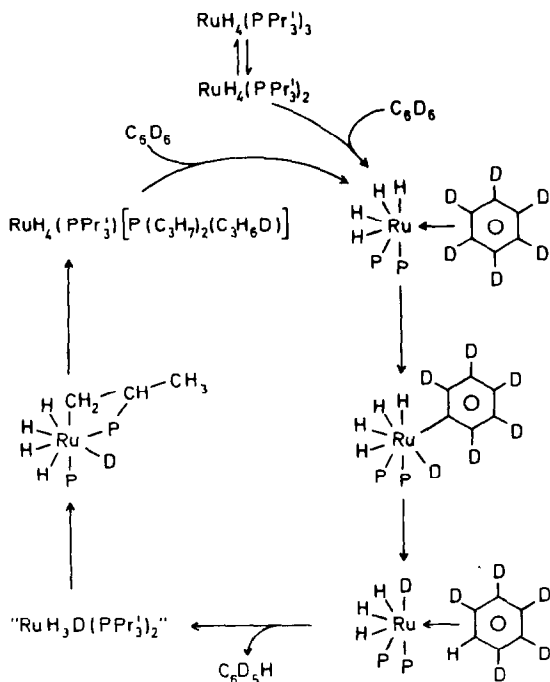
In continuation of our studies of ruthenium polyhydride chemistry [23,24] we now describe a system capable of activating spontaneously (i.e. without added chemicals or irradiation) C—H bonds of both arene solvents and phosphine ligands, which result in deuteration of the phosphine ligand with C_6D_6 or $\text{C}_6\text{D}_5\text{CD}_3$ as the deuterium source.

The reactions of $\text{Ru}(\text{COD})(\text{COT})$ with hydrogen in the presence of phosphines have been shown to involve complex processes [23], from which $\text{Ru}(\text{COD})(\text{COT})\text{P}$ and $\text{RuH}_6(\text{PCy}_3)_2$ were isolated by precipitation and polynuclear products such as $\text{Ru}_2\text{H}_x(\text{PPr}^i_3)_4$ or a similar PCy_3 complex detected [23]. Obviously other complexes must have been formed during the reaction at least as transient species; we have isolated one type, and shown RuH_4P_3 ((1) $\text{P} = \text{PPr}^i_3$; (2) $\text{P} = \text{PCy}_3$; (3) $\text{P} = \text{P}(\text{NET}_2)_3$), to be formed in moderate yield from the reaction of $\text{Ru}(\text{COD})(\text{COT})$ with three equivalents of phosphine at room temperature under hydrogen. These complexes are very air-sensitive, white crystalline solids, which show characteristic broad bands at about 1950 cm^{-1} in their IR spectra, like the well known $\text{RuH}_4(\text{PPh}_3)_3$ [25]. Their highfield ^1H NMR and $\{^1\text{H}\}^{31}\text{P}$ NMR spectra recorded immediately after dissolution are also as expected (^1H NMR (1) $\delta -9.05$ q, $J(\text{PH})$ 7 Hz (C_7D_8); (2) $\delta -9.3$ br (C_6D_{12}); ^{31}P NMR (1) $\delta 69.8$ s (C_6D_6); (2) $\delta 64.3$ s (C_6D_6). The changes in the spectra are more interesting. This is very rapid for both (1) and (2) in C_6D_6 and involve the appearance of a second highfield peak which has a triplet pattern ((4) $\delta -7.5$ t, $J(\text{PH})$ 8 Hz, $\text{P} = \text{PPr}^i_3$; (5) $\delta -7.5$ br.t, $\text{P} = \text{PCy}_3$). This is accompanied by a rapid decrease in intensity of all the hydride signals due to deuteration (in the case of PCy_3 , the signals disappear within 15 min, but for PPr^i_3 a weak signal for (1) and (4) always remains as well as one for $\text{Ru}_2\text{H}_x\text{P}_4$) and increase in the intensity of the peak for $\text{C}_6\text{D}_{6-x}\text{H}_x$ ($x > 1$) which is present throughout. In the case of (3), no hydride signal is visible due to extremely rapid H—D exchange with the solvent. The reaction with PCy_3 * and $\text{P}(\text{NET}_2)_3$ is rapid, and reaches its maximum conversion after 12 h at 36°C (25% deuteration of PCy_3 , representing about 2 protons exchanged per hour; 40% deuteration of $\text{P}(\text{NET}_2)_3$). With PPr^i_3

* All the deuterations proceed in the dark at 36°C unless otherwise stated.

the reaction is slower, but about 70%* of the initial phosphine is deuterated within 7 days at 35°C. Addition of more C_6D_6 displaces the statistical equilibration to reach a deuteration value of 76%. Effective deuteration of PPr^i_3 is confirmed by the mass spectrum of solid residues obtained after evaporation to dryness of reaction mixtures from three different experiments (one of which was performed in $C_6D_5CD_3$). The peak of the free phosphine at m/e 160 corresponding to the starting material was replaced by a series of peaks at m/e 160–180 (highest abundances in the range 175–178), attributed to partially deuterated phosphines. We did not observe the parent ion for this kind of product, although some fragments such as Ru-deuterated phosphine are visible. The same reaction is observed when (1) or (2) are dissolved in $C_6D_5CD_3$ but is slower (such as in the case of the known examples of H–D exchange in arenes catalyzed by hydride complexes [20,21]); after 4 days only about 10% of the phosphine protons had been exchanged. Heating the reaction mixture for one minute at 110°C caused a large increase of the reaction rate in the case of (1) (ca. 50% exchange yield). Similar behaviour was observed with (2) but once again the degree of conversion was far smaller (see Table 1). In C_6D_{12} , the reactions are more complicated, and these will be described later.

A possible mechanism for the reaction is given in Scheme 1. Since the phosphines employed are bulky, it is probable that in solution RuH_4P_3 undergoes dis-



SCHEME 1. Proposed mechanism for the H–D exchange between C_6D_6 and PPr^i_3 , catalyzed by $RuH_4(PPr^i_3)_3$.

* As measured by comparison of the integrated signal of phosphine protons with that for benzene in the 1H NMR spectrum. The signals for isopropyl and methyl protons decrease at similar rates.

sociation of a phosphine to give the undercoordinated "RuH₄P₂" species, namely (4) and (5). These species would be isoelectronic with ReH₅P₂ obtained by Caulton et al. [26] by photolysis. The species RuH₄P₂C₆R₆ (R₆ = H₆, D₆, D₅CD₃ ...) obtained by coordination of the arene according to an η² mode as in the rhenium [27] or rhodium [28] case, might also be present as an intermediate; the two transient species probably exist in an equilibrium. The undercoordinated complex so formed is highly reactive and has three possible reaction modes: (i) formation of a dinuclear complex and deactivation of the system, (ii) η²-coordination of benzene and C—H or C—D activation, or (iii) activation of a C—H bond of the phosphine ligand. The last two processes would be likely to occur at similar rates, and so allow the H—D scrambling to take place.

This reaction is obviously catalytic with respect to ruthenium, since deuteration of 70% of the initial phosphine in RuH₄(PPrⁱ)₃ represents about 44 catalytic cycles (0.26 cycle per hour). In the case of PCy₃ it is noteworthy that the 25% conversion corresponds to a 3/8 deuterium to hydrogen ratio in PCy₃, which could indicate exchange with deuterium for the proton in position 1, and for the axial protons in position 2 and 6. Similarly for P(NEt₂)₃, the 40% limit corresponds to the exchange of the methylene protons of the ethyl groups.

The observation that toluene is less readily activated than benzene is significant since it rules out the possibility of electrophilic attack such as has been observed [20,21], and favours precoordination of the arene. In this case the methyl group would be bulky enough to slow down the reaction considerably. The very large increase in the reaction rate at 110°C might suggest a change in mechanism (the presence of colloids, for example) but the fact that the limit of deuteration of PCy₃ remains the same favours a homogeneous mechanism. It is possible that at higher temperature another phosphine or one mole of H₂ is eliminated, giving rise to the increase in reactivity.

In conclusion, we note that the reaction we have described is typical of transition metal polyhydrides and the novelty of our system is that the reaction occurs spontaneously, i.e. it does not require heating or photochemical initiation, and gives high yields of deuterated species through a series of inter- and intra-molecular C—H activations.

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