

Preparation of Polyhydride Complexes of Ruthenium by Direct Hydrogenation of Zerovalent Olefinic Derivatives. Mononuclear Complexes of the Type RuH_6L_2 and RuH_4L_3 . Spontaneous H-D Exchange between the Phosphine Protons and the Solvent Catalyzed by RuH_4L_3

Bruno Chaudret and René Poilblanc*

Laboratoire de Chimie de Coordination du CNRS, associé à l'Université Paul Sabatier, 31400 Toulouse, France

Received November 13, 1984

Hydrogenation of $\text{Ru}(\text{COD})(\text{COT})$ (1) in the presence of 2 equiv of PCy_3 leads to $\text{RuH}_6(\text{PCy}_3)_2$ (2), the first hexahydride of ruthenium. This compound loses hydrogen thermally, photochemically, or in vacuo to give the dinuclear complex $\text{Ru}_2\text{H}_6(\text{PCy}_3)_4$. Protonation of 2 with $\text{HBF}_4/\text{H}_2\text{O}$ leads to $[\text{Ru}(\text{H}_2\text{O})_5(\text{PCy}_3)](\text{BF}_4)_2$, whereas reaction with ethylene produces the metalated complex $\text{RuH}[\text{C}_6\text{H}_{10}\text{P}(\text{C}_6\text{H}_{11})_2][\text{P}(\text{C}_6\text{H}_{11})_3](\text{C}_2\text{H}_4)_2$. Hydrogenation of 1 in the presence of 3 equiv of a phosphine leads to RuH_4L_3 [$\text{L} = \text{PCy}_3$, $\text{P}-i\text{-Pr}_3$, $\text{P}(\text{NEt}_2)_3$]. These complexes are shown to dissociate a phosphine in solution to give " RuH_4L_2 " and to catalyze the spontaneous H-D exchange between the phosphine protons and a deuterated solvent through a series of inter- and intramolecular C-H activation reactions.

Introduction

Polyhydride complexes of third-row transition metals have been known for a long time and have been shown to be remarkably stable.¹ Among them we can quote OsH_6L_2 ² and ReH_7L_2 ³ [$\text{L}_2 = (\text{PPh}_3)_2$, $(\text{PET}_2\text{Ph})_2$, $(\text{PETPh}_2)_2$, diphos] which contain the highest number of hydrides per metal for a neutral complex. This type of complex has attracted renewed interest particularly since they have been found to be precursors for C-H activation reactions.⁴ Considering the second row of transition-metal tetrahydrides like $\text{RuH}_4(\text{PPh}_3)_3$ ⁵ or MoH_4L_4 ⁶ ($\text{L} = \text{PMePh}_2$, PEtPh_2 ; $\text{L}_2 = \text{dppe}$) has been known for about a decade, but the chemistry of the ruthenium complex has been found to be very close to that of $\text{RuH}_2(\text{PPh}_3)_4$ and it was thus proposed that the complex could probably be better described as $\text{RuH}_2(\text{H}_2)(\text{PPh}_3)_3$. Since then, neutron diffraction studies on different polyhydride complexes (especially $\text{OsH}_4(\text{PMe}_2\text{Ph})_3$)⁷ have shown the hydrides to be well separated.¹ It is worth noting that the crystal structure of a complex having one side on a dihydrogen ligand has recently been published,⁸ and this possibility cannot be entirely ruled out in the case of the ruthenium complex. $\text{RuH}_3\text{Cp}(\text{PPh}_3)_3$ has also been recently prepared.⁹ During the course of this work, Crabtree et al. prepared in low yield MoH_6L_3 ,¹⁰ the first hexahydride of the second-row transition metals, but the authors could not isolate the complexes. The methods used for the synthesis of such hydrides is often the low-temperature reduction of an analogous chloro complex. In our case, we chose an easier method: the direct hydrogenation at room tem-

perature and pressure of a zerovalent ruthenium(0) olefin complex, $\text{Ru}(\text{COD})(\text{COT})$ ¹¹ ($\text{COD} = 1,5\text{-cyclooctadiene}$; $\text{COT} = 1,3,5\text{-cyclooctatriene}$), in the presence of phosphines. This method has already been successfully used for the preparation of dihydrido tetrakis(phosphine) complexes¹² or dppm complexes.¹³

We describe the hydrogenation of $\text{Ru}(\text{COD})(\text{COT})$ in the presence of various phosphines which leads to complexes of the type $\text{Ru}(\text{COD})(\text{COT})\text{P}$, RuH_6P_2 , and RuH_4P_3 , according to the ligand and to the reaction conditions. Some reactions of the new products are also described; this includes an H-D exchange between the phosphine protons and the solvent occurring spontaneously in the case of RuH_4P_3 complexes. Preliminary accounts for this work have been published.^{14,15}

Results and Discussion

Reactions of $\text{Ru}(\text{COD})(\text{COT})$ with 2 Equiv of a Less Bulky Phosphine. This reaction of $\text{Ru}(\text{COD})(\text{COT})$ with 1 or 2 equiv of a small phosphine, L ($\text{L} = \text{PMe}_3$ or $\text{P}(\text{OMe})_3$), in the presence of or without H_2 , gives rise to decoloration of the initial bright yellow solution, and off-white crystals of $\text{Ru}(\text{COD})(\text{COT})\text{L}$ can be obtained. They show a band at 1630 cm^{-1} in their infrared spectrum and a complex ¹H NMR spectrum. The ³¹P NMR spectrum shows a singlet at $\delta 161$ ($\text{L} = \text{P}(\text{OMe})_3$), as expected. During the course of this work, Vitulli et al. have published independently the crystal structure of $\text{Ru}(\text{COD})(\text{COT})\text{P}(\text{OMe})_3$.¹⁶ The structure they found confirms our initial proposal mentioned in a preliminary communication.¹⁴ In order to ascertain the structure, we had undertaken a ¹³C NMR study; since this was not reported by these authors, we will describe it here. Thus, as reported earlier by Vitulli et al. the ¹³C NMR spectrum of $\text{Ru}(\text{COD})(\text{COT})$ is relatively simple showing six types of carbon: two aliphatic and four olefinic ones. This as well as the width of the

(1) Bau, R.; Carroll, W. E.; Hart, D. W.; Teller, R. G.; Koetzle, T. F. In "Transition Metal Hydrides"; Bau, R., Ed.; American Chemical Society: Washington, 1978; *Adv. Chem. Ser. No. 167*, p 73 and references therein.

(2) Douglas, P. G.; Shaw, B. L. *J. Chem. Soc. A* 1970, 335.

(3) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* 1969, 1963.

(4) Baudry, D.; Ephritikhine, M.; Felkin, H.; Holmes-Smith, R. *J. Chem. Soc., Chem. Commun.* 1983, 788 and references therein.

(5) Harris, R. O.; Hota, N. K.; Sadavoy, L.; Yuen, J. M. C. *J. Organomet. Chem.* 1973, 54, 259.

(6) Pennella, F. *J. Chem. Soc., Chem. Commun.* 1971, 158.

(7) Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* 1977, 99, 7557.

(8) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Waserman, H. J. *J. Am. Chem. Soc.* 1984, 106, 451.

(9) Davies, S. G.; Moon, S. D.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* 1983, 1278.

(10) Crabtree, R. H.; Hlatky, G. H. *J. Organomet. Chem.* 1982, 238, C21.

(11) Pertici, P.; Vitulli, G.; Paci, M.; Porri, L. *J. Chem. Soc., Dalton Trans.* 1980, 1961.

(12) Pertici, P.; Vitulli, G.; Porzio, W.; Zocchi, M. *Inorg. Chim. Acta Lett.* 1979, 37, L521.

(13) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* 1984, 1635.

(14) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* 1982, 1388.

(15) Chaudret, B. *J. Organomet. Chem.* 1984, 268, C33.

(16) Pertici, P.; Vitulli, G.; Porzio, W.; Zocchi, M.; Barili, P. L.; Deganello, G. *J. Chem. Soc., Dalton Trans.* 1983, 1553.

Table I. NMR Data for Some New Ruthenium Complexes^a

| complexes | ¹ H NMR hydride region | | | ³¹ P NMR | | |
|---|-----------------------------------|------|--------------------|---------------------|------|----------------------|
| | δ | mult | J _{PH} Hz | δ | mult | J _{PP} , Hz |
| RuH ₆ P ₂ (a) | -7.84 | br | | 79.2 | br | |
| [Ru(H ₂ O) ₅ (PCy ₃)](BF ₄) ₂ (b) | | | | 55.5 | s | |
| RuH[C ₆ H ₁₀ P(C ₆ H ₁₁) ₂][P(C ₆ H ₁₁) ₃](C ₂ H ₄) ₂ (a) | -7.1 | dd | 18.9, 26.2 | 82.2, 42.2 | dd | 283 |
| RuH ₄ (PCy ₃) ₃ (a) | -9.1 | br | | 69.8 | s | |
| "RuH ₄ (PCy ₃) ₂ (a) | -7.8 | t | 18 | | | |
| RuH ₄ (P- <i>i</i> -Pr) ₃ (a) | -9.0 | q | 7 | 64.3 | s | |
| "RuH ₄ (P- <i>i</i> -Pr) ₂ " (a) | -7.9 | t | 8 | | | |

^a a, in C₇H₈; b, in (CD₃)₂CO.

peaks imply the fluxionality of the molecule.

In contrast, ¹³C NMR spectra show the Ru(COD)(CO-T)L species to be rigid; 16 peaks are observed in both cases as expected (see Experimental Section). The most interesting feature is the shift to low field of two carbons of cyclooctatriene (δ ~118 and 138) which appear close to the position of free cyclooctadiene (δ 128.8) and accounts for the decoordination of one double bond of cyclooctatriene.

The molecules are rigid which may explain their relative lack of reactivity when compared to Ru(COD)(COT). For example, bubbling hydrogen through a pentane solution of Ru(COD)(COT) results in complete decomposition of the complex within 10 min whereas Ru(COD)(COT)L does not react with hydrogen at room temperature. It only reacts at 100 °C to give brown decomposition products which do not contain hydrides. The reactivity of Ru(COD)(COT) could be explained by the ease with which it can decoordinate on the C=C double bond and thus coordinate a ligand or give rise to oxidative-addition reactions.

Preparation and Reactivity of the Hexahydride RuH₆(PCy₃)₂. We have seen that the reaction of Ru(COD)(COT) with 2 equiv of a less bulky phosphine under hydrogen at room temperature only led to Ru(COD)(CO-T)L. Nevertheless, the same reaction using the bulky phosphine PCy₃ leads to hydrogenation and complete substitution of hydrocarbon ligands to yield a very air-sensitive white powder analyzing for RuH_x(PCy₃)₂ which could be recrystallized from toluene/hexane. The complex shows two strong terminal Ru-H bonds at 1927 and 1890 cm⁻¹ but no band in the bridging hydride region. A single peak is observed in both its ³¹P{¹H}NMR spectrum (δ 79.2) and high-field ¹H NMR spectrum (δ -7.84) (see Table I). The latter remains broad between 233 and 353 K. The best resolution is obtained near 273 K where a pseudo-triplet pattern is obtained (J_{P-H} = ca. 7 Hz). The compound is monomeric as shown by a cryoscopic molecular weight determination in benzene (found 570, calcd 667). Its physical properties (low solubility, white color) are in agreement with an 18-electron configuration and resemble those of other electron-saturated monomeric polyhydride complexes.¹ Despite the impossibility to count the hydride number using ³¹P NMR spectroscopy, this allows us to give the formulation RuH₆(PCy₃)₂ for the complex. It is worth noting that this is the first hexahydride of ruthenium. In fact PCy₃ is the only phosphine enabling us to isolate selectively the hexahydride complex, probably because of its low solubility.

With another bulky alkylphosphine like P-*i*-Pr₃, dinuclear complexes are directly obtained. In the case of the reaction of Ru(C₈H₈)₂(PPh₃)₂ with hydrogen¹⁷ the crude

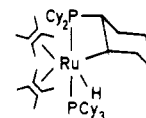


Figure 1. One possible structure for RuH[C₆H₁₀P(C₆H₁₁)₂][P(C₆H₁₁)₃](C₂H₄)₂. (Indeed the exact position of the metalated carbon was not determined.)

reaction mixture probably contains RuH₆(PPh₃)₂ but we have not been able to isolate it.

RuH₆(PCy₃)₂ is not very stable, and, when heated in an aromatic solvent, exposed to UV light, or placed in vacuo, it transforms invariably into a red dinuclear compound (see following paper). We may assume that the first step is the loss of one hydrogen molecule in each case. The complex behaves similarly in THF but can be recrystallized unchanged after dissolution at room temperature. No coordination of THF has been observed.

Surprisingly RuH₆(PCy₃)₂ does not react with H₂O in toluene. Nevertheless it reacts readily with HBF₄/H₂O in THF to yield the dication [Ru(H₂O)₅(PCy₃)](BF₄)₂ identified by microanalytical data as well as by IR and ¹H and ³¹P NMR spectroscopy. As for other known cases, protonation causes dramatic hydrogen evolution.

More interesting are the electrochemical properties. Thus RuH₆(PCy₃)₂ has not been found reducible in THF but can be oxidized through a one-electron process (quasi-reversible system; E_{PF} = 339.4 mV; E_{PB} = 18.5 mV; I_{PB}/I_{PF} = 0.89), probably to [RuH₆(PCy₃)₂]⁺. This compound is highly unstable and decomposes even at low temperature as monitored by EPR spectroscopy. We are presently looking for means to stabilize this paramagnetic hydride species.

Finally, we attempted a reaction with an olefin to test the reactivity of the complex. We found that bubbling ethylene through a suspension of RuH₆(PCy₃)₂ in hexane rapidly gives a red solution from which a white precipitate separates. The product analyzes for Ru(PCy₃)₂(C₂H₄)₂. A ³¹P NMR spectrum shows an AB pattern (δ(A) 82.2, δ(B) 42.2, J_{AB} 283.8 Hz). The large value of the P-P coupling constant suggests a trans configuration for the phosphines. The ¹H NMR spectrum is temperature dependent. Thus, if no hydride can be detected at 303 K, a broad peak at δ -7.1 appears at 290 K which becomes a doublet of doublet at 253 K (J_{P1H} = 18.9 Hz; J_{P2H} = 26.2 Hz). The signal remains unchanged down to 203 K. The low-field part of the spectrum is more puzzling. It shows four broad peaks at room temperature which change position according to the temperature, and either peaks of approximately equal intensity are eventually observed at 203 K (δ 5.35, 5.19, 4.3, 3.78, 3.41, 3.24, 2.98, and 2.74; the peak at δ 2.98 is split into a doublet). The peaks have not been attributed but probably arise from the eight nonequivalent ethylene protons. These data indicate that this molecule

(17) Chaudret, B.; Devillers, J.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* 1983, 641.

(18) Rhodes, L. F.; Zubowski, J. D.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* 1982, 21, 4185.

(19) Crabtree, R. H.; Hlatky, G. G.; Holt, E. M. *J. Am. Chem. Soc.* 1983, 105, 7302.

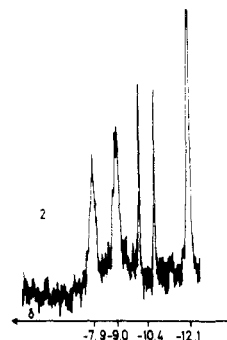
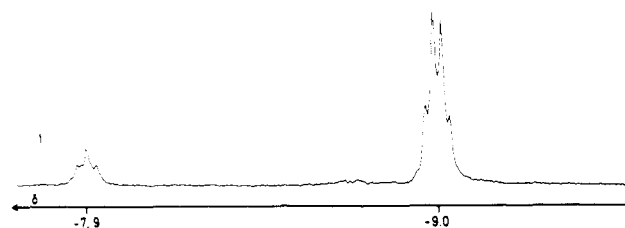
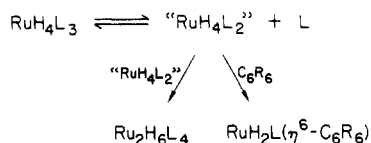
Scheme I. Reactions of RuH_4L_3 in Solution

Figure 2. High-field ^1H NMR of $\text{RuH}_4(\text{P-}i\text{-Pr})_3$: (1) immediately after dissolution (250 MHz), (2) after heating in C_6D_6 (60 MHz).

Signal A broadens at low temperature (from 303 to 203 K). Its chemical shift and pattern are in agreement with the proposed structure (see for example a single broad resonance at $\delta -7.1$ for $\text{RuH}_4(\text{PPh}_3)_3$).⁵ Signal B behaves similarly, and the triplet pattern is lost at -70°C .

These observations can be rationalized as follows: the tetrahydride RuH_4L_3 which gives rise to signal A dissociates reversibly a phosphine in solution through an exchange which is slow on the NMR time scale at room temperature to give "RuH₄L₂" which exhibits the hydride signal B. The presence of an aromatic cycle able to stabilize the complex by η^2 -coordination is ruled out by the same NMR evolution whether run in C_6D_6 or in C_6D_{12} . We believe this is the first NMR, observation in such a chemistry of a 16-electron polyhydride species. Coulton et al. have recently published a study of the C-H activation by $\text{ReH}_7(\text{PCy}_3)_2$ in which they show that the active species for H-D exchange is the transient 16-electron complex $\text{ReH}_5(\text{PCy}_3)_2$,²⁴ whose behavior is very similar to our "RuH₄P₂" (vide infra for H-D exchange for example). The bulkiness of the phosphine employed may explain the ready dissociation of one ligand and the observation of this unsaturated species. "RuH₄L₂" has a number of ways for achieving an 18-electron configuration: (a) recoordination of the lost phosphine; (b) intramolecular C-H activation to give a metalated species; (c) intermolecular C-H activation in the case of an aromatic solvent; (d) formation of a stable dinuclear complex through elimination of one H₂ mole; (e) formation of an η^6 -arene coordinated compound.

We have shown that these five possibilities occur in our system. Thus, (b) and (c) lead to H-D exchange between phosphine and solvent protons (vide infra), (d) gives rise to signal C near $\delta -12$ in ^1H NMR, and (e) is observed after the solution is heated in benzene-*d*₆: a sharp doublet at $\delta -10.4$ ($J_{\text{PH}} = 42.3$ Hz) (D) (Figure 2) appears together with a peak at $\delta 5.25$ attributed to the coordinated arene ring. These peaks are attributed by analogy with similar compounds recently prepared by Werner et al.²⁵ by a procedure different from that used for $\text{RuH}_2\text{L}(\eta^6\text{-C}_6\text{R}_6)$. It is noteworthy that these compounds have been used as

is fluxional. This fluxionality probably explains the non-observation of the hydride at room temperature. The other possibility (reversible insertion of one molecule of ethylene to give an ethyl group) would imply the presence of a mean peak on the spectrum.^{20,21} We propose the following structure for the complex $\text{RuH}[\text{C}_6\text{H}_{10}\text{P}(\text{C}_6\text{H}_{11})_2](\text{P}(\text{C}_6\text{H}_{11})_3)(\text{C}_2\text{H}_4)_2$ (see Figure 1) in which the metalation explains the inequivalence of the two trans phosphorus atoms. The mechanism is most probably the same as that observed in the case of the reaction of (triphenylphosphine)ruthenium hydrides with ethylene which leads to $\text{RuH}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$.²² The hydride ligands are removed by excess ethylene, and an unstable ruthenium(0) complex is formed [in our case, $\text{Ru}(\text{C}_2\text{H}_4)_2(\text{PCy}_3)_2$] which is able to activate one C-H bond of a phosphine ligand.

Preparation of the Tetrahydrides RuH_4L_3 [$\text{L} = \text{P-}i\text{-Pr}_3$, PCy_3 , or $\text{P}(\text{NEt}_2)_3$] and Their Reactions in Solution. The reaction of $\text{Ru}(\text{COD})(\text{COT})$ with 3 equiv of a phosphine L [$\text{L} = \text{P-}i\text{-Pr}_3$, PCy_3 , or $\text{P}(\text{NEt}_2)_3$] under hydrogen for 2 h yielded pale red (PCy_3) to brown ($\text{P-}i\text{-Pr}_3$, $\text{P}(\text{NEt}_2)_3$) hexane solutions. Recrystallization at -78°C afforded moderate yields (see Experimental Section) of the RuH_4L_3 complexes as extremely air-sensitive white ($\text{L} = \text{P-}i\text{-Pr}_3$, PCy_3) or pale brown [$\text{L} = \text{P}(\text{NEt}_2)_3$] crystals. Only terminal Ru-H stretches are seen in their infrared spectra as a very broad band near 1940 cm^{-1} like the well-known $\text{RuH}_4(\text{PPh}_3)_3$.⁵ The related complex $\text{RuH}_4(p\text{-FC}_6\text{H}_4)_3\text{P}_3$ has been recently prepared and has been shown to be able to dehydrogenate cyclooctane at 150°C in the presence of an hydrogen acceptor.²³

The reactions of these complexes in solution in deuterated aromatic solvents are especially interesting and somewhat surprising. Two phenomena can thus be observed at the same time: (i) a chemical modification of the complex and (ii) an H-D exchange between the phosphine protons and the solvent.

The complexes show an hydride signal (A) near $\delta -9$ in their high-field ^1H NMR spectrum recorded immediately after dissolution in a deuterated aromatic solvent (C_6D_6 , C_7D_8) [$\text{L} = \text{P-}i\text{-Pr}_3$, $\delta -9.0$ (q, $J_{\text{PH}} = 7$ Hz); $\text{L} = \text{PCy}_3$, $\delta -9.1$ (br q); $\text{L} = \text{P}(\text{NEt}_2)_3$, no signal] as well as a singlet in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum ($\text{L} = \text{P-}i\text{-Pr}_3$, $\delta 69.8$; $\text{L} = \text{PCy}_3$, $\delta 64.3$). Another signal (B) rapidly appears showing a triplet pattern [$\text{L} = \text{P-}i\text{-Pr}_3$, $\delta -7.9$ (t, $J_{\text{PH}} = 8$ Hz); $\text{L} = \text{PCy}_3$, $\delta -7.8$ (t, $J_{\text{PH}} = 18$ Hz)] (see Figure 2). After a few minutes at room temperature, a third signal (C) appears near $\delta -12$. These C signals belong to dinuclear species which are formed in better yield by hydrogenation of $\text{Ru}(\text{COD})(\text{COT})$ in the presence of 2 equiv of phosphine at higher temperature and are described in the next paper. Heating the reaction mixture causes a rapid conversion of the initial complexes RuH_4L_3 into the dinuclear species $\text{Ru}_2\text{H}_6\text{L}_4$. The same evolution has been observed in C_6D_{12} for $\text{RuH}_4(\text{P-}i\text{-P})_3$.

(20) Byrne, J. W.; Blaser, H. V.; Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3781.

(21) Chaudret, B.; Cole Hamilton, D. J.; Wilkinson, G. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 763.

(22) Cole Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chim.* **1977**, *1*, 141.

(23) Felkin, H.; Fillebeen-Kahn, T.; Gault, Y.; Holmes-Smith, R.; Zahrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 1279.

(24) Kelle Zeiher, E. H.; De Wit, D. G.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 7006.

(25) Werner, H.; Kletzin, H. *J. Organomet. Chem.* **1983**, *243*, C59; **1982**, *228*, 289.

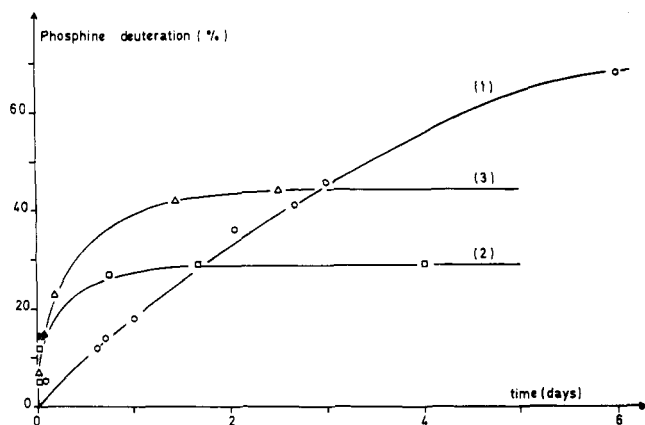


Figure 3. Percentage of deuteration of the phosphine as a function of time (1) P-*i*-Pr₃, (2) PCy₃, (3) P(NEt₂)₃.

Table II. Total Conversion and Approximate Rate of Deuteration as Measured by Integration of the ¹H NMR Spectra

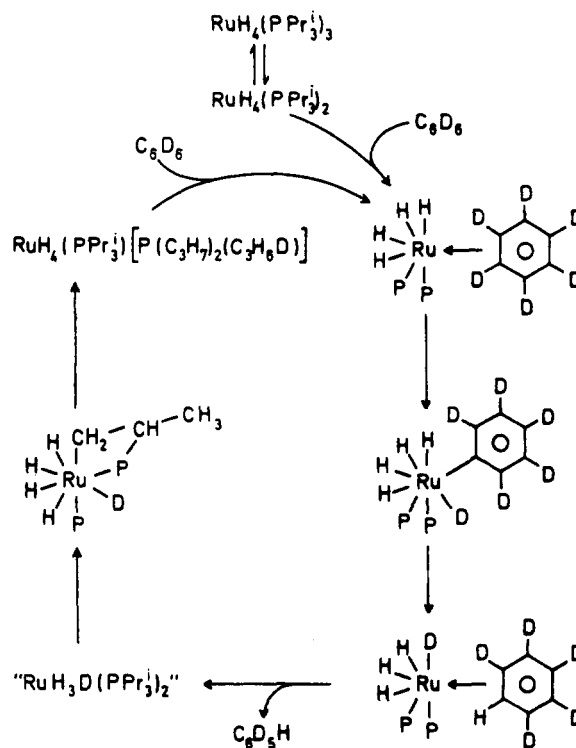
| complex | temp, °C | solv | time, h | conv % | rate, ^a cps |
|---|----------|-------------------------------|---------|--------|------------------------|
| RuH ₄ (P- <i>i</i> -Pr ₃) ₃ | 36 | C ₆ D ₆ | 168 | 70 | 0.26 |
| RuH ₄ (P- <i>i</i> -Pr ₃) ₃ | 36 | C ₇ D ₈ | 96 | 10 | 0.06 |
| RuH ₄ (PCy ₃) ₃ | 36 | C ₆ D ₆ | 12 | 25 | 2.1 |
| RuH ₄ (PCy ₃) ₃ | 36 | C ₇ D ₈ | 24 | 15 | 0.6 |

^a Cycles per second.

precursors for C-H bond activation reactions.²⁶

As quoted above, another reaction occurs in the medium: an H-D exchange (i) between the hydrides and the solvent and (ii) between the hydrides and the phosphine protons. This leads to catalytic deuteration of a phosphine using C₆D₆ as the deuteration source. Although this reaction is well documented,²⁷ the originality of this system is to be spontaneous (e.g., it occurs at room temperature in the dark). Thus in solution, together with the reactions above quoted, we observed a decrease in intensity of all the signals (especially of the hydrides, but also those of the phosphine protons) together with an important increase of the peak of "benzene" (in fact all the possible combinations of C₆H_{6-x}D_x (x = 0-5) or of "toluene". Immediately after dissolution, all hydride signals decrease rapidly in the three systems so that in the case where L = PCy₃ or P(NEt₂)₃, no signal is visible anymore. The peak for the dinuclear complex only does not seem to decrease through exchange with the solvent. We followed the reaction by ¹H NMR spectroscopy by measuring the integration ratio between the partially deuterated solvent peak and that of the phosphine (see Table II). Figure 3 shows the percentage of deuteration of the phosphine in C₆D₆ as a function of time at room temperature. It shows that the P(NEt₂)₃ and the PCy₃ systems are very fast but rapidly reach a limit. These limits (deuteration rate of 40% and 25%, respectively) correspond to about two protons exchanged in an ethyl group and also to two or three protons exchanged of a total of 11 in a cyclohexyl group. The limit was not explained in the case of P(NEt₂)₃ since both the CH₂ and CH₃ groups are shown to be deuterated at the same rate; in the case of PCy₃ it is possible that the axial protons in positions 2 and 6 could be exchanged (the proton in position 1 could also be exchanged). This means that the approach of other C-H bonds of the ligands is not

Scheme II. Proposed Mechanism for the H-D Exchange between C₆D₆ and P-*i*-Pr₃ Catalyzed by RuH₄(P-*i*-Pr₃)₃



possible probably because of steric reasons and that the reaction is intramolecular, the phosphine activated being the one remaining on the complex and not that dissociated in the first step. In both cases, heating the reaction mixture and using longer reaction times yield deuteration rates slightly above the found limit. This can mean that another mechanism for this reaction is possible although difficult and can be related to the increase of the reaction rate observed when the reaction is heated (vide infra).

In toluene-*d*₈, the same reaction takes place but is really slower since after 4 days, only about 10% of the phosphine protons had been exchanged in the case where L = P-*i*-Pr₃ (1 day, 10% for L = PCy₃). Heating the reaction mixture at 110 °C for 1 min leads to ca. 50% deuteration. A similar reaction is observed in the case where L = PCy₃ but again with a less important conversion (ca. 17%).

As these observations are supported by NMR data only, we decided to undertake a study by mass spectroscopy to prove the effective deuteration of the phosphine (in the case where L = P-*i*-Pr₃). Thus, we obtained mass spectra (EI) of RuH₄(P-*i*-Pr₃)₃ before reaction and of the residues after evaporation to dryness of the reaction mixtures of three different experiments (two of RuH₄(P-*i*-Pr₃)₃ in C₆D₆ and one in C₇D₈). The parent ion of RuH₄(P-*i*-Pr₃)₃ is not seen while that of the phosphine is observed at *m/e* 160. The isopropyl groups are further detected at *m/e* 43. After deuteration, these peaks are replaced by a series of peaks in the range *m/e* 160-180 (maximum abundance *m/e* 175-178) and 43-50, respectively. This tends to prove (i) that the phosphine has been deuterated as expected and (ii) that all the positions of the isopropyl group can be deuterated including the isopropyl proton.

The mechanism of this reaction is not clear (see Scheme II for our proposal), but it is reasonable to propose as the first step the dissociation of a phosphine as observed by ¹H NMR spectroscopy. Then, an η²-coordination of the arene seems likely as this would stabilize the structure. The much slower reaction of toluene when compared to benzene could be due to its more important steric bulkiness and is in favor of arene precoordination. There are

(26) Kletzin, H.; Werner, H. *Angew. Chem., Int. Ed. Engl.* 1983, 22, 873.

(27) See, for example: Parshall, G. W. *Acc. Chem. Res.* 1975, 8, 113. Klabunde, U.; Parshall, G. W. *J. Am. Chem. Soc.* 1972, 94, 9081. Grebenick, P. D.; Green, M. L. H.; Izquierdo, A. *J. Chem. Soc., Chem. Commun.* 1981, 186 and references therein.

Table III. Analytical Data for New Ruthenium Complexes

| compd | found | | | | expected | | | |
|---|-------|------|------|------|----------|------|------|------|
| | C | H | P | N | C | H | P | N |
| Ru(COD)(COT)(P(OMe) ₃) | 52.0 | 7.0 | 6.6 | | 51.9 | 7.1 | 7.1 | |
| RuH ₆ (PCy ₃) ₂ PhCH ₃ | 65.9 | 10.6 | 8.7 | | 66.7 | 10.4 | 8.7 | |
| RuH ₄ (PCy ₃) ₃ | 67.8 | 11.5 | 9.6 | | 68.6 | 10.9 | 9.8 | |
| RuH ₄ (P- <i>i</i> -Pr) ₃ | 53.5 | 12.2 | 15.1 | | 55.4 | 11.5 | 15.9 | |
| RuH ₄ (P(NEt ₂) ₃) ₃ | 50.4 | 11.3 | 11.0 | 14.2 | 51.1 | 11.1 | 11.0 | 14.9 |
| [Ru(H ₂ O) ₅ (PCy ₃) ₃](BF ₄) ₂ ·H ₂ O | 32.1 | 6.5 | 4.3 | | 32.6 | 6.8 | 4.7 | |
| RuH[C ₆ H ₁₀ P(C ₆ H ₁₁) ₂][P(C ₆ H ₁₁) ₃](C ₂ H ₄) ₂ | 66.6 | 11.8 | 8.4 | | 66.9 | 10.3 | 8.6 | |

two possibilities for the next step: either oxidative addition of the solvent C–D bond or of the phosphine C–H bond with obtention of a ruthenium(VI) intermediate or reductive elimination of H₂ and reaction of the ruthenium(II) species RuH₂L₂(η²-C₆R₆). We think that the first possibility is the most likely since the NMR signal for RuH₄L₃ is always present throughout the deuteration reaction (H–D and D–H exchange with the solvent and with the phosphine, respectively). The important increase in the reaction rate at 110 °C can be explained by a change in the mechanism of reaction. The presence of colloids is not likely since the same limit of deuteration is observed for L = PCy₃. Elimination of H₂ or of another phosphine could make the approach, and thus the exchange, easier.

The reaction is catalytic since exchange of about 70% of the P-*i*-Pr₃ protons represents about 44 protons exchanged per ruthenium. To our knowledge, this is the first system spontaneously able to catalyze H–D exchange between its ligands and the solvent.

Conclusion

We have found that hydrogenation of the ruthenium(0) olefin complex Ru(COD)(COT) in the presence of bulky phosphines is a convenient method for the preparation of mononuclear polyhydrides of the type RuH₆L₂ and RuH₄L₃. RuH₆L₂ is the first hexahydride of ruthenium prepared and is shown to lose easily hydrogen through a variety of reactions. Like the heptahydride ReH₇P₂, it is easily converted into a dinuclear hydride-bridged complex. Complexes of the type RuH₄L₃, although known for a long time when L = PPh₃, exhibit an interesting reactivity when L is a more bulky phosphine. They are shown to dissociate a phosphine in solution to give "RuH₄L₂", an extremely reactive product which is able to catalyze H–D exchange between the solvent and the phosphine through a series of inter- and intramolecular C–H activations. Although this reaction also is well-known, it is the first case where it is spontaneous (e.g., at room temperature in the dark).

Experimental Section

Microanalyses were performed by the Centre de Microanalyse du CNRS and by Miss Magna in the laboratory. Infrared spectra were obtained as Nujol mulls by using a Perkin-Elmer PE 577 or PE 225 grating diffractometer, and NMR spectra were obtained by using a Bruker WH90 (90 MHz) or WM250 (250 MHz) spectrometer operating in the Fourier transform mode with proton noise decoupling when ³¹P NMR spectra were recorded and a Perkin-Elmer R12 (60 MHz) spectrometer.

All solvents were thoroughly degassed before use, and all operations were carried out in nitrogen or argon atmosphere.

Ru(COD)(COT)¹¹ was prepared according to published methods. RuCl₃·3H₂O was purchased from Johnson Matthey Ltd., and PCy₃, P-*i*-Pr₃, and P(NEt₂)₃ were purchased from Alfa. Analytical data for new complexes are summarized on Table III.

(Cyclooctadiene)(cyclooctatriene)(trimethyl phosphine)ruthenium(0) (1). The best method is adding 1 equiv of phosphite to Ru(COD)(COT) in hexane solution as already published.¹⁶

¹³C NMR: δ 50.94 (CH₃ of P(OMe)₃), J_{PC} = 5.55 Hz; 23.2 (CH₂); 2, 27.4 (CH₂); 3, 30.8 (CH₂); 4, 31.7 (CH₂); 5, 32.1 (CH₂); 6, 33.4 (CH₂); 7, 48.7 (CH); 8, 50.2 (CH); 9, 68.3 (CH), J_{PC} = 9.2 Hz; 10, 69.8 (CH), J_{PC} = 9.2 Hz; 11, 78.4 (CH), J_{PC} = 5.5 Hz; 12, 82.5 (CH), J_{PC} = 5.5 Hz; 13, 89.9 (CH) J_{PC} = 3.7 Hz; 14, 92.5 (CH), J_{PC} = 3.7 Hz; 15, 118.9 (CH), J_{PC} = 3.7 Hz; 16, 137.1 (CH), J_{PC} = 5.5 Hz.

(Cyclooctadiene)(cyclooctatriene)(trimethylphosphine)ruthenium(0) (2): as for 1, with 0.3 g (0.95 mmol) of Ru(COD)(COT) and 0.090 mL (0.95 mmol) of PMe₃ in 10 mL of hexane.

¹³C NMR: δ 20.0 (CH₃ of PMe₃), J_{PC} = 24.0 Hz; 1, 22.5 (CH₂); 2, 27.4 (CH₂); 3, 30.6 (CH₂); 4, 32 (CH₂); 5, 32.1 (CH₂); 6, 34 (CH₂); 7, 47.7 (CH), J_{PC} = 5.5 Hz; 8, 50.3 (CH), J_{PC} = 2 Hz; 9, 66.8 (CH), J_{PC} = 7.4; 10, 68.0 (CH), J_{PC} = 7.4 Hz; 11, 77.6 (CH), J_{PC} = 5.5 Hz; 12, 82.5 (CH), J_{PC} = 3.7 Hz; 13, 88.8 (CH); 14, 91.5 (CH); 15, 117.8 (CH), J_{PC} = 3.7 Hz; 16, 137.9 (CH), J_{PC} = 3.7 Hz.

Hexahydridobis(tricyclohexylphosphine)ruthenium(VI) (3). Ru(COD)(COT) (0.5 g, 1.58 mmol) was added to a solution of 0.89 g (3.18 mmol) of PCy₃ in 30 mL of hexane. The reaction mixture was stirred for 15 min at room temperature, after which hydrogen was bubbled slowly into the reaction mixture for 3 h during which a white precipitate separated. It was then filtered off and found pure by spectroscopic methods (yield ca. 60%).

Recrystallization from 5 mL of toluene and 5 mL of hexane afforded white crystals of RuH₆(PCy₃)₂PhCH₃ in ca. 30% yield. It is essential not to warm the toluene and to avoid concentrating the solution in vacuo since under these conditions hydrogen is evolved and the red dinuclear product Ru₂H₆(PCy₃)₄ is obtained.

Reaction of RuH₆(PCy₃)₂ with HBF₄/H₂O (4). RuH₆(PCy₃)₂ (0.4 g, 0.6 mmol) was dissolved in THF (20 mL), and 1 mL of HBF₄ (35% in H₂O) was added. The solution turned immediately to orange while hydrogen was evolved. After 30 min of stirring, the solution was evaporated to dryness and the resulting oil recrystallized from CH₂Cl₂/Et₂O, thus affording orange crystals of [Ru(H₂O)₅(PCy₃)₃](BF₄)₂ (yield ca. 80%).

Reaction of RuH₆(PCy₃)₂ with Ethylene (5). RuH₆(PCy₃)₂ (300 mg, 0.45 mmol) was suspended in 20 mL of hexane, and ethylene was bubbled slowly through the solution for 15 min after which it was left under ethylene for 2 h. The precipitate dissolved rapidly to give a red solution from which a white precipitate separated. It was found to be the analytically pure complex RuH[C₆H₁₀P(C₆H₁₁)₂][P(C₆H₁₁)₃](C₂H₄)₂ (yield ca. 80%).

Tetrahydridotris(tricyclohexylphosphine)ruthenium(IV) (6). The reaction was performed as described for 3 but with 0.5 g of Ru(COD)(COT) (1.58 mmol) and 1.35 g (4.82 mmol) of PCy₃ in 50 mL of hexane. After 3 h, a pale red solution was obtained (occasionally some white precipitate of RuH₆(PCy₃)₂ was also found in which case the solution was filtered off). The solution was then concentrated in vacuo to about 15 mL and cooled at –78 °C. White crystals of the complex were formed in ca. 40% yield.

Tetrahydridotris(triisopropylphosphine)ruthenium(IV) (7): as for 6, with 0.97 mL (4.85 mmol) of P-*i*-Pr₃. No precipitate is observed (yield ca. 20%).

Tetrahydridotris[tris(diethylamino)phosphine]ruthenium(IV) (8): as for 7 (yield ca. 40%).

Registry No. Ru(COD)(COT)P(OMe)₃, 97570-12-2; Ru(COD)(COT), 42516-72-3; Ru(COD)(COT)PMe₃, 97570-13-3; RuH₆(PCy₃)₂, 85435-92-3; Ru₂H₆(PCy₃)₄, 97570-09-7; [Ru(H₂O)₅(PCy₃)₃](BF₄)₂, 97570-15-5; RuH[C₆H₁₀P(C₆H₁₁)₂][P(C₆H₁₁)₃](C₂H₄)₂, 97570-16-6; RuH₄(PCy₃)₃, 91946-50-8; RuH₄(P-*i*-Pr)₃, 91946-51-9; RuH₄(P(NEt₂)₃)₃, 91986-00-4; Ru₂H₆(P-*i*-Pr)₄, 97570-10-0; RuH₄(PCy₃)₂, 97570-17-7; RuH₄(P-*i*-Pr)₃, 97570-18-8.