A New Class of Dihydrogen Complexes containing Oxygen Donor Ligands. Preparation of $RuH(\eta^2-H_2)(OCOCF_3)[P(C_6H_{11})_3]_2$ and of the Equilibrated Mixture $RuH_2(OCOCF_3)_2[P(C_6H_{11})_3]_2/Ru(\eta^2-H_2)(OCOCF_3)_2[P(C_6H_{11})_3]_2$

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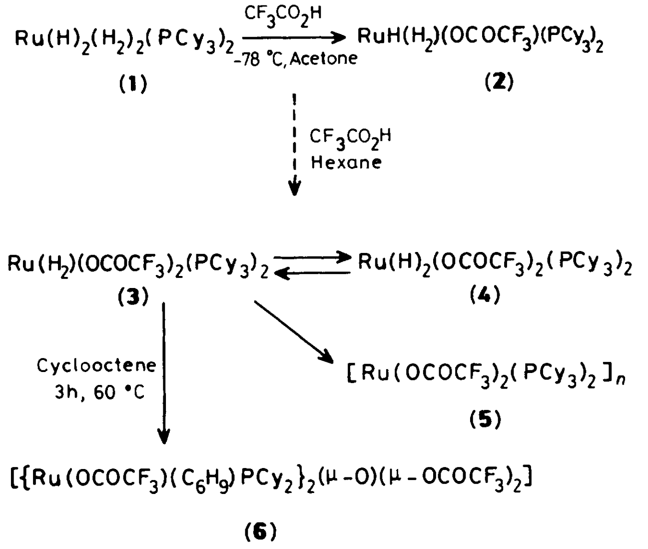
The protonation of $RuH_2(H_2)_2(PCy_3)_2$ (**1**) (Cy = cyclohexyl) with CF_3CO_2H in acetone leads to the hydrido dihydrogen derivative $RuH(H_2)(OCOCF_3)(PCy_3)_2$ (**2**), which reacts further in hexane to yield a very reactive Ru^{IV} dihydride, $RuH_2(OCOCF_3)_2(PCy_3)_2$ (**3**), a species which at room temperature is in equilibrium with the dihydrogen complex $Ru(\eta^2-H_2)(OCOCF_3)_2(PCy_3)_2$ (**4**); (**3**) [or (**4**)] loses H_2 in solution and reacts with cyclo-octene to give $\{Ru(C_6H_9PCy_2)(OCOCF_3)\}_2(\mu-O)(\mu-OCOCF_3)_2$ (**6**).

The chemistry of polyhydrido transition metal derivatives has attracted renewed interest since it has been discovered that many of these species contain co-ordinated dihydrogen.[1] We have developed in recent years the chemistry of polyhydrido ruthenium complexes[2] which were shown recently to be octahedral ruthenium(II) dihydride derivatives.[3] The complexes also contain co-ordinated dihydrogen like the unusual 'hexahydride' $RuH_6(PCy_3)_2$ (Cy = cyclohexyl) reformulated as $[RuH_2(H_2)_2(PCy_3)_2]$.[3] Examples of higher oxidation state ruthenium hydride complexes are rare. However, the carbaborane compounds 2,1,7- and 3,1,2-$[RuH_2(C_2B_9H_{11})(PPh_3)_2]$[4] and $[RuH_3(SiR_3)(PPh_3)_3]$[5] are recognized as genuine Ru^{IV} derivatives. More recently, Davies *et al.* have reported $RuH_3(C_5H_5)PPh_3$[6] and different authors $RuH_3(C_5Me_5)PR_3$ (including us).[2c,7] In all cases, these complexes were considered as seven-co-ordinate ruthenium(IV) trihydrides. However, we have shown that if these complexes are likely to contain ruthenium(IV) in the solid state or at low



Scheme 1. Reactions of $RuH_2(H_2)_2(PCy_3)_2$ with CF_3CO_2H.

temperature in solution, they should be considered at room temperature as ruthenium(II) derivatives containing a novel trihydrogen ligand.[8]

The protonation of ruthenium(II) hydrido complexes has been shown by Simpson *et al.*[9] and Heinekey *et al.*[10] to produce either ruthenium(II) dihydrogen or ruthenium(IV) dihydride compounds according mainly to the steric bulk of the ligand. In some cases, a dihydride–dihydrogen equilibrium was found which demonstrated the small difference of energy between the two forms. A similar protonation of $RuH_3(C_5Me_5)(PCy_3)$ leads to the spontaneous and rapid dehydrogenation of the tricyclohexylphosphine ligand probably because of the existence of unstable intermediates containing co-ordinated dihydrogen.[11]

This led us to reinvestigate more thoroughly the protonation of our 'polyhydro' ruthenium complexes and in particular that of $RuH_2(H_2)_2(PCy_3)_2$.

We reported a few years ago the reaction of $RuH_2(H_2)_2(PCy_3)_2$ (**1**) with $HBF_4{\cdot}H_2O$ which led to the dication $[Ru(H_2O)_5(PCy_3)]^{2+}$.[2a] The same reaction with $HBF_4{\cdot}Et_2O$ yielded a mixture of compounds. However with CF_3CO_2H in acetone, the reaction is smoother producing a yellow complex analysing for $RuH_3(OCOCF_3)(PCy_3)_2$† (**2**) in 60% isolated yield. The i.r. spectrum shows a hydride at 2095 cm^{-1} (m) and a chelating carboxylato group at 1620 and 1440 cm^{-1} (ms) whereas the ^1H n.m.r. spectrum shows a high-field triplet signal at δ −14.8 (*J* 14.3 Hz). The number of hydrogen atoms is deduced both from the integration of the ^1H n.m.r. spectrum and from the observation of a quartet in a partially decoupled ^{31}P n.m.r. spectrum. The complex is fluxional at all temperatures; only a broadening of the signal is observed at low temperature. The variations with temperature of the relaxation time T_1 of the 'hydrides' has been studied and a minimum of about 20 ms was found near 230 K.† This is typical for a dihydrogen complex and (**2**) can thus be considered as a new example of a fluxional hydrido dihydrogen derivative,[1b,1c,2,3] $RuH(H_2)(OCOCF_3)(PCy_3)_2$. The observed $J_{H\text{-}P}$ for the 'hydride' signal is the mean value between what is expected for a typical hydride (34 Hz) and what is assumed for molecular hydrogen (~4 Hz).[10] This complex is air-sensitive but thermally very stable and for example remains largely unchanged after a 15 h reaction with neohexene at 100 °C in cyclohexane or cyclopentane. Similarly, exposure to u.v. irradiation (high pressure mercury vapour lamp) does not cause H_2 evolution.

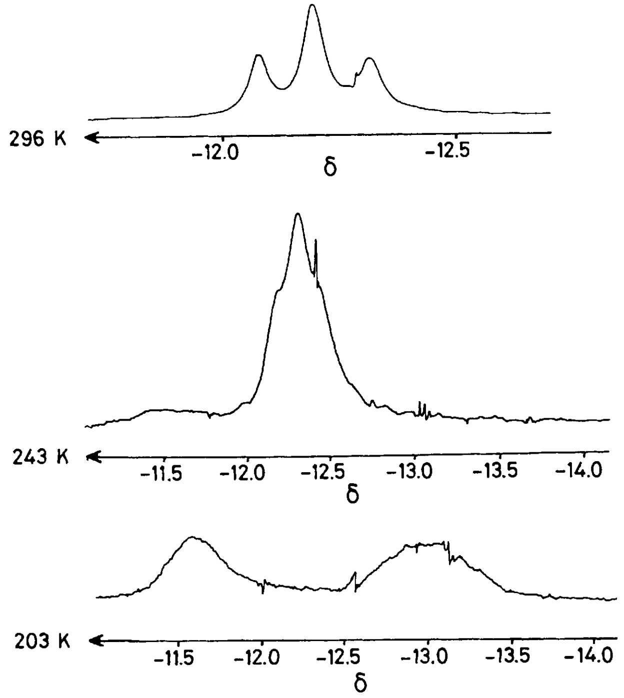


Figure 1. High field ^1H n.m.r. spectrum of the (**3**)/(**4**) mixture at various temperatures (250 MHz).

Complex (**2**) does not react with excess of CF_3CO_2H in acetone but does react instantly in hexane to give after H_2 evolution a quantitative yield of a product analysing for $RuH_2(OCOCF_3)_2(PCy_3)_2$ (**3**).‡ Two ν(Ru–H) i.r. bands are observed as well as a band for a chelating and for a monodentate carboxylato group. The ^1H n.m.r. spectrum shows a hydride signal as a triplet ($J_{P\text{-}H}$ 30 Hz) at room temperature which splits into two broad peaks at 193 K whereas the ^{31}P n.m.r. spectrum shows at room temperature a singlet splitting into two broad peaks of equal intensity at 193 K. These data are clearly in favour of the formulation of the complex as a seven-co-ordinate ruthenium(IV) dihydride. However, a careful study of the ^{31}P n.m.r. spectra demonstrates that a third peak of much smaller intensity is taking part in the exchange (Figure 2), Similarly, a broad peak appears at 243 K in the ^1H n.m.r. spectrum on the side of the hydride peak (Figure 1). It then disappears at lower temperature

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† Spectroscopic data for (**2**): i.r. (Nujol): ν(Ru–H) 2095 cm^{-1}, ν(CO) 1620, 1440 cm^{-1}. ^1H n.m.r. (250 MHz) δ −14.8 (t, *J* 14.3 Hz, 3H), 1—2 (m, 66H); ^{31}P n.m.r. δ 56.12 (s). T_1 values for the high field signal: 296 K, 56 ms; 273 K, 34; 243 K, 23; 213 K, 27; 193 K, 72. Estimated T_1 minimum 15 ms at 226 K.

‡ $RuH_2(OCOCF_3)_2(PCy_3)_2$: i.r. (Nujol) ν(Ru–H) 2160, 2080 cm^{-1}; ν(CO) (bidentate acetate) 1620 (ms), 1440 cm^{-1}; ν(CO) (terminal acetate) 1700 (vs), 1400 cm^{-1}. ^1H n.m.r. (250 MHz) (C_7D_8, 293 K) δ −12.2 (t, *J* 30 Hz, 2H), δ 1—2 (m, 66 H); (C_7D_8, 193 K) δ −11.57 (br.), −12.92 (br.); ^{31}P n.m.r. (C_7D_8, 293 K): 78.52 (s); 193 K: 92.84 (s), 67.61 (s) and 80.37 (s) [peak of (**4**), see text and Figure 2].

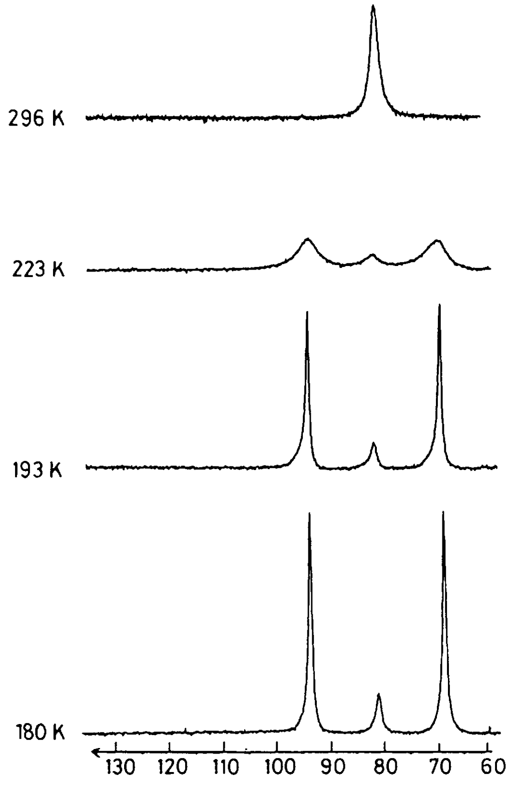
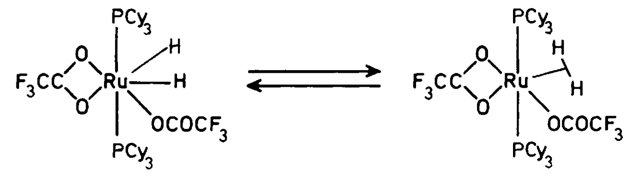


Figure 2. ^{31}P ^{1}H n.m.r. spectrum of the (**3**)/(**4**) mixture at various temperatures (101.2 MHz).

probably because of broadening. The determination of the relaxation time of the hydride signals gives 432 ± 10 ms at 193 K for the two peaks of (**3**) and 45 ± 5 ms at 293 K for the average signal. These values cannot arise from a normal variation as a function of the temperature since, as (**2**) and (**3**) have similar steric bulk, the temperature of the minimum will not be very different.[1c] However a rapid equilibrium at room temperature, between a dihydride complex (**3**) and a dihydrogen complex, Ru(H$_2$)(OCOCF$_3$)$_2$(PCy$_3$)$_2$ (**4**) would fit all the data (Scheme 2). When the temperature is lowered, the exchange becomes slow and it is then best observed by ^{31}P n.m.r. spectroscopy at 193 K. The high field ^{1}H n.m.r. signal for (**4**) is probably so broad at 193 K that it is not observed.

Complex (**3**) or (**4**) is very reactive, losing H$_2$ slowly in solution to give a species characterized by spectroscopic methods and tentatively formulated as [Ru(OCOCF$_3$)$_2$(PCy$_3$)$_2$]$_n$ (**5**); with O$_2$ a blue species unidentified so far is obtained and with cyclo-octene a dehydrogenation of tricyclohexylphosphine is observed to give cyclo-octene and a 50% isolated yield of [{Ru(C$_6$H$_9$PCy$_2$)(OCOCF$_3$)}$_2$(μ-O)(μ-OCOCF$_3$)$_2$] (**6**) characterized by an *X*-ray structure determination. The mechanism of formation and the magnetic properties of this diruthenium(III) species are currently being studied.

In summary, we have described a new example of a fluxional hydrido dihydrogen derivative and to the best of our knowledge, the first dihydride of $\mathrm{Ru^{IV}}$ containing oxygen donor ligands, which furthermore shows a dihydride–dihydrogen equilibrium.[12] The interesting point is the instability of (**4**) which readily loses H$_2$. This can be deduced from the replacement of a good σ donor ligand (H$^-$) by an electron-withdrawing ligand, (-OCOCF).[13]§ However, this electronic factor should prevent the formation of a dihydride. The existence of the dihydride (**3**) then results most probably from steric factors: the increase of ligand bulk when replacing H$^-$ by OCOCF$_3$$^-$. Another possibility would be the unusual stabilization of the dihydrogen ligand in (**2**) through interaction with the hydride ligand. Such an interaction has been proposed to account for the anomalous n.m.r. properties of some trihydride–trihydrogen derivatives.[8,14] A hydride–dihydrogen interaction has been demonstrated for the first time in an iron dihydrido dihydrogen complex.[15]



Scheme 2. Proposed structure for the equilibrated mixture (**3**) ⇌ (**4**).

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§ A referee pointed out that carboxylato groups are good π-donor ligands. However, if the existence of (**3**) is due to electronic factors, then the instability of (**4**) is unexpected.