

RuHX(H₂)(PⁱPr₃)₂ (X = Cl, I): 16 Electron Dihydrogen–Hydride or Trihydride Complexes?

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Introduction

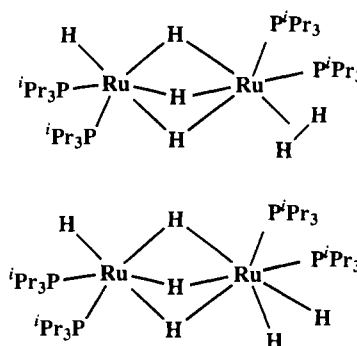
Despite an ever-growing interest for the chemistry of transition metal derivatives containing the dihydrogen ligand,¹ only very few 16 electron dihydrogen complexes are known. All complexes reported so far are of the type RuHX(H₂)(PCy₃)₂, where X is I, Br, Cl, or SR, and have been prepared in our group.² It was recently shown that the osmium analogs to these ruthenium complexes were classical trihydride complexes³ with unusually small H–Os–H angles and unusually large *J*_{HH} values attributed to the presence of exchange couplings.⁴ These osmium derivatives contain the ligand PⁱPr₃. Since the characteristics of the phosphine ligand and in particular the steric properties of PCy₃ could influence the nature of the “polyhydride” complex formed (trihydride or hydrido dihydrogen), we set out to determine if the ruthenium analogs of the osmium complexes were classical or nonclassical complexes. In any case, the replacement of PCy₃ by PⁱPr₃ was anticipated to lead to complexes showing in NMR a minimum of the relaxation time *T*₁ at lower temperature therefore leading to longer *T*₁ at room temperature and hence to sharper peaks and better resolution. This is important if one wants to observe the H–D couplings for partially deuterated complexes, probably the most important diagnostic feature for the presence of undissociated dihydrogen.¹ The H–D couplings were not observed for the corresponding ruthenium polyhydrides containing the PCy₃ ligand. A new, more general, route to complexes of the type RuH₃X(PR₃)₂ was also sought.

Herein we report the synthesis and characterization of the new unsaturated complexes RuHX(H₂)(PⁱPr₃)₂ (X = I, 1; X = Cl, 2).

Results and Discussion

The tricyclohexylphosphine derivatives RuHX(H₂)(PCy₃)₂ were prepared from the bis dihydrogen complex RuH₂(H₂)₂(PCy₃)₂.² However the corresponding bis dihydrogen derivative is not stable when using PⁱPr₃. Thus the reaction of Ru(COD)-

Chart 1



(COT)⁵ (COD = 1,5 cyclooctadiene; COT = 1,3,5 cyclooctatriene) with 2 equiv of PⁱPr₃ in pentane under dihydrogen (4 bar) in a Fischer & Porter bottle yields a mixture of RuH₆(PⁱPr₃)₂ (3) and Ru₂H₆(PⁱPr₃)₄ (4). The former complex was not isolated but detected in solution by NMR by a signal at –7.9 ppm (t, *J*_{P–H} 8 Hz) and is probably RuH₂(H₂)₂(PⁱPr₃)₂, analogous to RuH₂(H₂)₂(PCy₃)₂.^{6,7} It slowly transforms in solution and rapidly *in vacuo* into complex 4, which can be isolated in low yield (20%). The ³¹P NMR spectrum of 4 shows only a singlet at 95.3 ppm at room temperature which splits at 183K into 2 doublet of doublets at 101.9 ppm (*J*_{P–P} = 21 and 15 Hz) and 87.9 ppm (*J*_{P–P} = 19 and 15 Hz) and 2 doublets at 98.75 (*J*_{P–P} = 21 Hz) and 93.5 (*J*_{P–P} = 19 Hz); the pseudo trans phosphorus nuclei couple to each other across the Ru–Ru bond with a coupling constant of about 20 Hz and to their partners on the ruthenium atom with a similar coupling constant. At room temperature, only a single peak is observed in the hydride region of the ¹H NMR spectrum at –12.76 ppm. When the sample is cooled to 243 K, the hydride peak separates into a broad peak at –10.8 ppm (*ν*_{1/2} = 140 Hz) and a very broad peak at ca. –21 ppm (*ν*_{1/2} = 500 Hz) with intensities 5:1. The latter peak corresponds to the terminal hydride while the former to an average of the terminal dihydride (or dihydrogen) and bridging hydride ligands. At 183 K, peaks are observed at –10.2 ppm (1H, t, *J*_{P–H} = 22 Hz), –11.9 ppm (1H, t, *J*_{P–H} = 25 Hz) and –10.6 ppm (3H, s) which correspond to the terminal dihydride and to the bridging hydride ligands while the peak at –21.1 ppm (1H, t, *J*_{P–H} = 21 Hz) can be assigned to the terminal hydride ligand. The lowest *T*₁ value was found to be 110 (5) ms at 243 K (250 MHz) for both signals which indicated that the different hydrides are still in a slow exchange mode at this temperature. Thus, due to broadening of the signal as a consequence of the coalescence process, it was not possible to measure accurately the intrinsic minimum *T*₁ of the system. The value of 110 ms suggests a short contact between two hydrogen atoms but does not allow one to conclude the presence of dihydrogen in this complex. It is therefore possible that 4 is a classical hexahydride complex, namely Ru₂(H)₃(μ–H)₃(PⁱPr₃)₄ or a dihydrogen containing complex like Ru₂H(H₂)(μ–H)₃(PCy₃)₄^{6,8} and Ru₂H(H₂)(μ–H)(μ–Cl)₂(Ptol₃)₄⁹ (Chart 1).

A solution of Ru(COD)(COT) in the presence of 2 equiv of PⁱPr₃ is reacted with CH₃I or CHCl₃ for 30 min under 4 atm of dihydrogen. The new complexes RuHX(H₂)(PⁱPr₃)₂ (X = I, 1;

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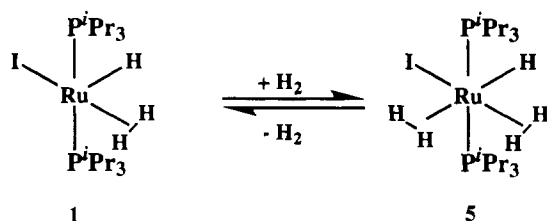
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Scheme 1



X = Cl, 2) are formed in 50–75% isolated yield. In contrast to 4, the complexes 1 and 2 were determined to be dihydrogen complexes from their ^1H NMR spectral data. For 1, the proton spectrum in toluene- d_8 at 250 MHz consists of a broad triplet at -16.70 ppm with $J_{\text{P-H}} = 13.7$ Hz, which broadens as the temperature is lowered but does not show decoalescence like most *cis*-hydrido-dihydrogen derivatives. The minimum T_1 was found to be 32(2) ms at 213 K. This value is similar to that obtained for $\text{RuHX}(\text{H}_2)(\text{PCy}_3)_2$ and suggests that 1 is a dihydrogen complex (see Scheme 1). The T_1 minimum value allowed us to calculate an approximative value of the H–H distance within the dihydrogen molecule. Thus, the observed relaxation R_{obs} is the sum of the relaxation due to hydride–ligand interaction ($R_{\text{H-L}}$) and of that due to hydride–hydride interaction ($R_{\text{H-H}}$). $R_{\text{H-L}}$ has been previously estimated in a similar osmium complex³ to be 6 s^{-1} (250 MHz). Furthermore, $R_{\text{H-H}}$ is the weighted sum of the relaxation due to the hydride (R_{H}) and that due to the dihydrogen ligands (R_{H_2}): $3R_{\text{H-H}} = R_{\text{H}} + 2R_{\text{H}_2}$; R_{H} has also been estimated in $\text{OsH}_3\text{X}(\text{P}^i\text{Pr}_3)_2$ to be 9 s^{-1} .³ Assuming both rapid conversion between hydride and dihydrogen groups and rapid rotation of dihydrogen, we find using approximate equations¹⁰ a H–H distance of 1.02(3) Å within the coordinated dihydrogen molecule which is similar to the value of 1.03(7) Å found in the X-ray structure of $\text{RuHI}(\text{H}_2)(\text{PCy}_3)_2$.^{2b} The structure of 1 is expected to be a square pyramid with the hydride ligand at the apex as was found for the PCy_3 analog. Deuterium incorporation was achieved by placing a sample of 1 under a D_2 atmosphere allowing us to find a J_{HD} value of 4.5 Hz; therefore assuming H_2 –H coupling is zero, the H–D coupling in the dihydrogen unit is 13.5 Hz. This is an acceptable value for an H–D complex with ca. 1 Å separation.^{1f}

The infrared spectra of 1 were recorded before and after deuterium exposure. The spectrum of the non-deuterated species exhibited weak peaks at 1930 and 1880 cm^{-1} in the hydride region; after deuteration these peaks disappeared and a new peak appeared at 1383 cm^{-1} ; this could correspond to a Ru–D stretch (in this case the corresponding Ru–H stretch would appear at 1927 cm^{-1}). In addition, new weak peaks were found at 2173 and 2067 cm^{-1} , the attribution of which is not clear. The peaks near 2100 cm^{-1} could correspond to ν_{CD} vibrations since the corresponding C–H stretches are expected near 2900–3000 cm^{-1} , where such vibrations are indeed observed. No conclusive attribution of absorptions related to the presence of dihydrogen could be made.

In the case of 2 in toluene- d_8 at 250 MHz, the hydride region consists of a broad singlet (-16.3 ppm) at room temperature, which becomes a triplet ($J_{\text{P-H}} = 13.1$ Hz) at 243 K, then broadening at lower temperatures. The minimum T_1 value was found at 213 K to be 33.5(1.4) ms, giving an H–H distance calculated as precedently of 1.04(3) Å similar to the values found for 2.

Like $\text{RuHI}(\text{H}_2)(\text{PCy}_3)_2$,^{2a} 1 reacts with excess dihydrogen to give an unstable bis(dihydrogen) derivative $\text{RuHI}(\text{H}_2)_2(\text{P}^i\text{Pr}_3)_2$ (5). When a solution of 1 in toluene- d_8 is saturated with H_2 , a new single signal is observed for the “hydrides” at -12.9 ppm which decoalesces at 203 K into the signal of 1 at -16.9 and a new signal at -7.5 ppm attributed to the bis(dihydrogen) complex 5. This complex immediately loses H_2 like the corresponding $\text{RuHI}(\text{H}_2)_2(\text{PCy}_3)_2$ in the absence of excess dihydrogen.

In conclusion, we describe in this note a new and probably general method for preparing unsaturated ruthenium polyhydrides. The complexes $\text{RuHX}(\text{H}_2)(\text{P}^i\text{Pr}_3)_2$ (X = I, 1; X = Cl, 2) were shown to be dihydrogen complexes and to adopt in solution a structure similar to that demonstrated for $\text{RuHI}(\text{H}_2)(\text{PCy}_3)_2$ in both solution and solid state. In particular, the H–H distance within the dihydrogen molecule was found to be slightly larger than 1 Å from T_1 measurements. This is in agreement with the observed $J_{\text{H-D}}$ value hence revealing the “stretching” of this molecule. Therefore it is clear that the difference in the steric properties of the phosphine ligands when changing PCy_3 for P^iPr_3 does not appreciably modify the mode of coordination of dihydrogen in these 16 electron complexes.

Experimental Section

All manipulations were carried out in an argon atmosphere by use of Schlenk techniques. The solvents were dried and distilled under nitrogen and thoroughly degassed under argon before use. Microanalysis were performed at this laboratory's service. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer 1725 FT-IR spectrometer. NMR spectra were recorded on a Bruker AC200 (at 200.13 MHz for ^1H and at 81.015 MHz for ^{31}P) while variable temperature proton spectra and all T_1 measurements were obtained by using AM250 (250.13 MHz for ^1H), all these spectrometers operating on the Fourier transform mode. Integration ratios were measured with long repetition times (40–60 s) to avoid relaxation problems. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Johnson Matthey Ltd. and the other reagents from Aldrich; $\text{Ru}(\text{COD})(\text{COT})^5$ was prepared according to a published method.

Preparation of $\text{RuHI}(\text{H}_2)(\text{P}^i\text{Pr}_3)_2$ (1). A Fischer & Porter bottle was charged with $\text{Ru}(\text{COD})(\text{COT})$ (451 mg; 1.44 mmol) then 20 mL of pentane were added to give a clear yellow solution to which P^iPr_3 (0.56 mL, 2.9 mmol, 2 equiv) was added. The bottle was pressurized to 4 atm of H_2 and left stirring vigorously for 0.5 h. The bottle was then recharged to 4 atm of H_2 ; the solution at this time was red-brown. After 3 h, the solution was transferred by cannula to a Schlenk flask, and MeI (90 μL ; 1.44 mmol) was added, inducing bubbling. After 0.5 h, a white precipitate had formed. After another 0.5 h, the cloudy solution was filtered, giving a brown solution. The volume of the solution was reduced to about 3 mL, and it was left at -30 °C for 16 h. After the mother liquors were filtered, a dark microcrystalline precipitate was dried under vacuum. Yield: 56%. $^{31}\text{P}\{^1\text{H}\}$ NMR at 81.0 MHz in C_6D_6 : 68.5 (s). ^1H NMR at 200 MHz in C_6D_6 : -16.75 (br singlet, 3H, RuH), 1.2 (overlapping doublets, 36H, $\text{P}(\text{CHMe}_2)_3$), 2.3 (overlapping septets, 6H, $\text{P}(\text{CHMe}_2)_3$). ^1H NMR at 250 MHz in $\text{C}_6\text{D}_5\text{CD}_3$: -16.70 (t, $J_{\text{P-H}} = 13.6$ Hz). IR (KBr, cm^{-1}): 1930 (m), 1880 (m). Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{P}_2\text{IRu}$: C, 39.2; H, 8.2. Found: C, 39.3; H, 7.9.

Preparation of $\text{RuHCl}(\text{H}_2)(\text{P}^i\text{Pr}_3)_2$ (2). 2 was prepared as for 1 using (389 mg; 1.24 mmol) $\text{Ru}(\text{COD})(\text{COT})$ (389 mg, 1.24 mmol) and 0.50 mL of P^iPr_3 (2.6 mmol, 2.1 equiv.). After 6 h, the reddish solution was transferred to a Schlenk flask by cannula, and CHCl_3 (99 μL ; 1.2 mmol) was added, inducing bubbling. After 0.5 h, a light brown precipitate had formed; the cloudy solution was then filtered and washed three times with 10 mL of pentanes, giving a red-orange solution. The solvent was removed by vacuum to give a red-brown gum, which was left under vacuum for 16 h. Yield: 0.412 g, 72% $^{31}\text{P}\{^1\text{H}\}$ NMR at 81.0 MHz in CD_2Cl_2 : 66.5 (s). ^1H NMR at 200 MHz in CD_2Cl_2 : -17.1 (br triplet, RuH), 1.2 (overlapping doublets, $\text{P}(\text{CHMe}_2)_3$), 2.3 (overlapping septets, $\text{P}(\text{CHMe}_2)_3$). IR (KBr, cm^{-1}): 1929, 1901. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{P}_2\text{ClRu}$: C, 47.0; H, 9.7. Found: C, 47.7; H, 9.5.

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Preparation of $(\text{Pr}^i_3\text{P})_2\text{RuH}(\mu\text{-H})_3\text{Ru}(\text{H}_2)(\text{P}^i\text{Pr}_3)_2$ (4). 4 was prepared as for 1 using 397 mg (1.27 mmol) of $\text{Ru}(\text{COD})(\text{COT})$ and 0.50 mL (2.6 mmol) of P^iPr_3 . The solution was transferred to a Schenk flask by cannula, and 1 equiv of AlCl_3 was added. After 4 h, the solution was filtered, washing with 10 mL of pentanes three times. The solvent was removed under reduced pressure and left under vacuum for 16 h, after which the remaining red gum was taken up in 20 mL of pentanes. The volume of this solution was reduced to about 10 mL, and the red solution was left at $-25\text{ }^\circ\text{C}$ for 16 h. The solution was filtered, leaving dark red crystals which were then dried under vacuum. Phosphorus NMR of the filtrate showed only a trace of $\text{RuH}_3\text{Cl}(\text{P}^i\text{-}$

$\text{Pr}_3)_2$. Yield: 0.124 g, 20%. $^3\text{P}\{^1\text{H}\}$ NMR at 81.0 MHz in $\text{C}_6\text{D}_5\text{CD}_3$: 95.3 (s). $\mu^1\text{H}$ NMR at 200 MHz in $\text{C}_6\text{D}_5\text{CD}_3$: -12.8 (br, 6H, RuH), 1.2 (overlapping doublets, $\text{P}(\text{CHMe}_2)_3$), 2.3 (overlapping septets, $\text{P}(\text{CHMe}_2)_3$). IR (KBr, cm^{-1}): 2057 (w), 2010 (m), 1975 (m), 1540 (w). Anal. Calcd for $\text{C}_{36}\text{H}_{90}\text{P}_4\text{Ru}_2$: C, 50.9; H, 10.7. Found: C, 50.7; H, 11.3.

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