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Reactions of $RuHCl(CO)[P(i\text{-}Pr)_3]_2$ with H_2 in Solution. New Molecular Hydrogen Complexes of Ruthenium: $RuH(H_2)Cl(CO)[P(i\text{-}Pr)_3]_2$ and $Ru(H)_2(H_2)(CO)[P(i\text{-}Pr)_3]_2$

Reactions of dihydrogen with coordinatively unsaturated transition-metal hydride complexes containing Cl ligands lead, in some cases, to new classical and nonclassical hydrides. In solution, $RuHCl(PPh_3)_3$,[1] $OsHCl(CO)[P(i\text{-}Pr)_3]_2$,[2] and $IrHCl_2L_2$ ($L = P(i\text{-}Pr)_3$, PCy_3)[3,4a] add H_2, probably in an η^2-fashion. The reactions of H_2 with the monohydrides $MHCl_2L_2$ (M = Rh, Ir) give also the dihydrides MH_2ClL_2,[4] and IrH_2ClL_2 coordinates H_2 to give $Ir(H)_2(H_2)ClL_2$.[4a,5] The polyhydrides $RuH_4(PPh_3)_3$ and IrH_5L_2 are formed upon reaction of $RuHCl(PPh_3)_3$ and $IrHCl_2L_2$ with dihydrogen in the presence of NaOH.[6] In continuation of these studies we have now found that $RuHCl(CO)[P(i\text{-}Pr)_3]_2$ (**1**)[7] also reacts with H_2 to form the new dihydrogen complexes $RuH(H_2)Cl(CO)[P(i\text{-}Pr)_3]_2$ and $Ru(H)_2(H_2)(CO)[P(i\text{-}Pr)_3]_2$.

The ^1H NMR spectra[8] of **1** in toluene under argon show the H ligand resonance at δ −24.4 in the temperature range 180–290 K. However, in the spectra of this solution under H_2, the chemical shifts of the hydride and dissolved H_2 resonances are temperature dependent, as if a rapid equilibrium exists in the sample. Thus, on cooling a solution of **1** with a slight excess of dissolved dihydrogen ($[\mathbf{1}] = 2.8 \pm 0.4$ mmol/L; $[H_2]/[\mathbf{1}] = 1.3$), the signals of RuH and H_2 shift gradually from δ −23.9 (290 K) to δ −8.5 (180 K) and from δ 4.38 (290 K) to δ 2.41 (223 K), respectively. At the same time, the T_1 value of the H_2 resonance rapidly shortens (from 1.2 s at 308 K to 0.016 s at 234 K) and this signal is not observed below 223 K due to strong broadening. However, in the temperature range between 180 and 200 K a characteristic triplet assigned to η^2-HD (with $J(H,D) = 34.5$ Hz) is clearly observed at δ −0.43 and −0.86 in the ^1H NMR spectra of solutions of **1** ([**1**] is ca. 10 mmol/L) in toluene and dichloromethane (under an atmosphere of HD), respectively. Furthermore, at 200 K in the ^2H NMR spectrum of **1** and HD in CH_2Cl_2 a doublet at δ −0.75 due to the η^2-HD resonance is also detected, which becomes a singlet with ^1H CW-decoupling.

The above observations can be rationalized in terms of an equilibrium (eq 1) between monohydride **1** and dihydrogen complex **2**, which strongly shifts to the right at low temperatures.

$$\underset{\mathbf{1}}{RuHCl(CO)[P(i\text{-}Pr)_3]_2} + H_2 \rightleftarrows \underset{\mathbf{2}}{RuH(H_2)Cl(CO)[P(i\text{-}Pr)_3]_2} \tag{1}$$

The equilibrium 1 becomes slow (on the NMR time scale) below 190 K, and at 180 K separate resonances of **1** and **2** are simultaneously observed at δ −24.4 and −8.5, respectively, if the initial concentration of **1** exceeds that of the dissolved dihydrogen. ΔH° and $\Delta S^\ddagger$ values of -7.7 ± 0.2 kcal/mol and -23.2 ± 1 eu were calculated for the formation of **2** from **1** in toluene from the variable-temperature ^1H NMR spectra.

The solutions of **1** in toluene under an atmosphere of H_2 remained unchanged during 3 months, and the equilibrium was completely reversible. However, in the presence of KOH, **1** reacts with H_2 in toluene (or dichloromethane) affording a new complex **3**.[9] The $^{31}P\{^1H\}$ NMR spectra of this toluene solution exhibit only one signal at δ 81.7 at 290 K and on cooling the sample down to the freezing point. At 290 K, a single broad resonance (δ −7.50) is also observed in the high-field region of the ^1H NMR spectrum of the solution, and at 270 K, it appears as a well-resolved triplet ($^2J(H,P) = 10.8$ Hz). The phosphine protons of **3** give rise to resonances at δ 1.88 (CH) and 1.16 (CH_3) with relative intensities very close to 36:6:4 for CH_3:CH:RuH. The $^{13}C\{^1H\}$ NMR spectrum of **3** shows resonances at δ 28.8 (CH) and 21.1 (CH_3) and a one at δ 205.4 (triplet, $^2J(C,P) = 8.5$ Hz) due to a CO ligand which is cisoid to two $P(i\text{-}Pr)_3$ ligands.[10] These data allow us to formulate **3** as $RuH_4(CO)[P(i\text{-}Pr)_3]_2$.[11] The number of hydrides was also reliably confirmed by an observation of a quintet in the ^{31}P NMR spectrum of **3** with selective decoupling of the phosphine protons at 260 K.

In solutions of **3** under 1 atm of H_2 an exchange exists between the metal-bonded hydrogens and dissolved dihydrogen. At 260

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(8) The ^1H, ^2H, and ^{31}P NMR spectra were obtained on a Bruker WP-200 SY spectrometer. The ^{13}C NMR spectrum was recorded on a Bruker AMX-400 spectrometer. Relaxation time (T_1) experiments employed the inversion recovery method (180°–τ–90° pulse sequence) at 200 MHz. All temperatures were carefully calibrated by using the ^1H chemical shifts of methanol.

(9) The complex **3** was prepared like the related $RuH_4(PPh_3)_3$.[6] In a typical preparation, a mixture of $RuHCl(CO)[P(i\text{-}Pr)_3]_2$ (0.02 g, 0.04 mmol), 18-crown-6 (0.01 g), and solid KOH (0.1 g) in 1 mL of toluene-d_8 (or CH_2Cl_2) was stirred under H_2 (1 atm) at 20 °C in a 50-mL Schlenk flask with attached NMR tube. After 30 min the obtained solution of **3** was transferred into the NMR tube (where the atmosphere was the same as that in the flask) and the tube was then flame-sealed. The samples of the deuterated complex **3** were prepared in a similar way under HD or D_2. A significant deuteration (65%) also took place during the preparation of **3** in CD_2Cl_2 under H_2.

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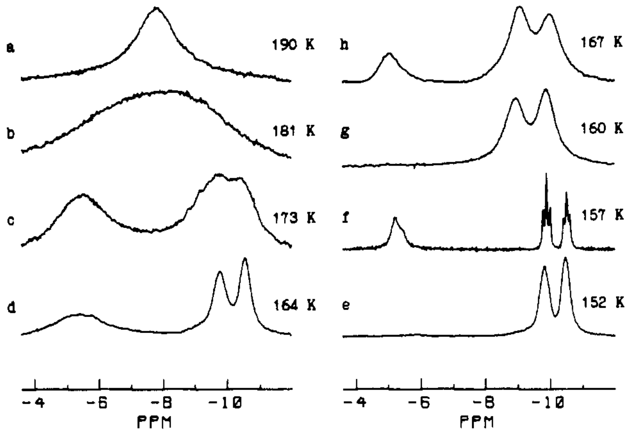


Figure 1. (a–e) Variable-temperature ^{1}H NMR spectra of the hydride region of $Ru(H)_2(H_2)(CO)[P(i\text{-}Pr)_3]_2$ dissolved in a mixture of CH_2Cl_2 and toluene-d_8 (5%) under an atmosphere of H_2 and (f–h) the hydride region of the ^{1}H NMR spectra at lowest attainable temperature of the following samples: (f) partially deuterated **3** (65% D) in CD_2Cl_2; (g) complex **3** in toluene-d_8; (h) partially deuterated **3** (50% D) in toluene-d_8. In the cases of the samples for spectra f and h the sources of deuterium were CD_2Cl_2 and HD gas, respectively.[9] The amount of deuteration was determined by integration of the residual resonance in the hydride region against the resonances of the phosphine protons.

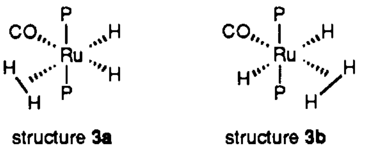
K, irradiating the RuH_4 resonance saturates the resonance of H_2 at δ 4.53. At temperatures above 270 K, this intermolecular exchange destroys $^1H-^{31}P$ spin–spin coupling and the hydride signal is broad. However, at temperatures below 250 K, the width of the RuH_4 resonance increases again due to a fast proton relaxation. The minimum T_1 value of 15 ± 0.5 ms found for this resonance in toluene at 200 K clearly indicates[12] the presence of a dihydrogen ligand in **3**, assuming a rapid intramolecular exchange between the dihydrogen and hydride ligands. The T_1 time of 13.9 ± 0.5 ms is also observed in a dichloromethane solution of **3** at 190 K. According to these data, an H–H bond distance in the η^2-H_2 ligand of $Ru(H)_2(H_2)(CO)[P(i\text{-}Pr)_3]_2$ of 0.86–0.84 Å can be calculated.[13]

At 260 K the ^{1}H NMR spectrum of a deuterated (under a 9:1 D_2:H_2 atmosphere) complex **3** in toluene reveals a pattern at δ −7.64, best described as an AX_2Y_3 spin system ($X = {}^{31}P$, $Y = {}^2H$), with $^2J(H,P) = 10.8$ Hz and $J(H,D) = 5.4$ Hz. The latter is the value expected (if hydrogen and deuterium are distributed statistically) for the HD_3 isotopomer of **3**, where the J(H,D) value for the η^2-HD ligand is actually 32.4 Hz.[14]

A slowing of the exchange between the dihydrogen and hydride ligands of **3** takes place below 190 K (Figure 1a–d). After that, in the ^{1}H NMR spectra separate resonances are observed at δ −5.0, −8.95, and −9.93 in toluene and at δ −5.2, −9.83, and −10.49 in dichloromethane solutions of **3**. In the case of a CD_2Cl_2 solution of a partially deuterated complex **3**, the two signals between −9 and −11 ppm reveal couplings ^2J(H,P) of 21.8 and 19.6 Hz (Figure 1f) as expected for cis hydride and phosphine ligands.

The fact that the width of the signal at δ −5 is substantially reduced by partial deuteration (due to weakening of dipole–dipole interactions) allows us to assign the signal to the dihydrogen ligand. The lack of observable J(H,D) couplings in the spectra of the partially deuterated **3** (Figure 1f,h) can be explained taking into account deuterium relaxation, which results in the scalar relaxation of the second kind of the proton in the HD ligand. Preliminary ^{2}H T_1 data for $Ru(D)_2(D_2)(CO)[P(i\text{-}Pr)_3]_2$ give the T_1 value of ca. 12 ms at 157 K.[15] The relaxation rate ($1/T_1$) of 83 s^{-1} is sufficient to cause the strong broadening of the HD triplet and can preclude observation of the expected 32.4 Hz J(H,D) in **3** at low temperatures.[16]

Chart I



structure **3a**

structure **3b**

There are two possible structures (**3a** and **3b**) for $Ru(H)_2(H_2)(CO)[P(i\text{-}Pr)_3]_2$, which are depicted in Chart I. In the case of the most probable structure **3a**, three hydride signals are expected in the slow-exchange spectra in the ratio 2:1:1 and an averaged resonance must be observed at $\delta = 0.5(\delta(H_2)) + 0.25(\delta_1(H) + \delta_2(H))$. According to the data discussed above, the averaged resonances are expected at δ −7.22 and −7.68 in toluene and dichloromethane solutions of **3**, respectively. These values are in good agreement with the experimental δ of −7.30 and −7.75 at 190 K. The same averaging is valid for the H–P couplings, and the observed $^2J(H,P) = 10.8$ Hz can be obtained if $^2J(H_2\text{–}P) = 0.9$ Hz. Thus, our data are most consistent with the structure **3a** and provide no evidence for the formation of any reliably detectable amounts of **3b** or the classical tautomer, $RuH_4(CO)[P(i\text{-}Pr)_3]_2$.

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Supplementary Material Available: Figures S1 and S2, showing the temperature-dependent behavior of the RuH and H_2 resonances in the ^{1}H NMR spectra of **1** in toluene solution under an atmosphere of H_2 (2 pages). Ordering information is given on any current masthead page.

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Di-*tert*-butylphosphido versus Diphenylphosphido as a Bridging Ligand in Binuclear Iron Carbonyl Complexes: Synthesis and Structural Characterization of $Fe_2(CO)_5(\mu\text{-}P(t\text{-}Bu)_2)_2$ and $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}P(t\text{-}Bu)_2)$

Binuclear iron carbonyls containing two 3-electron bridging ligands, such as phosphido (PR_2), thiolato, amido, certain hydrocarbyls, and several other inorganic and organic groups, represent a numerous class of structurally related complexes.[1,2] The μ-phosphido members of this class are invariably hexacarbonyls,

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