

Reactivity of the Bis(dihydrogen) Complex $\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$ toward Small Molecules and Weak Acids

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The reactions of $\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$ (**1**) with N_2 , CO_2 and CS_2 afford respectively $\text{RuH}_2(\text{N}_2)_2(\text{PCy}_3)_2$ (**2**), $\text{RuH}(\text{O}_2\text{-CH})(\text{H}_2)(\text{PCy}_3)_2$ (**3**), and $\text{RuH}_2(\text{S}_2\text{CH}_2)(\text{PCy}_3)_2$ (**4**); the two former reactions are reversible under dihydrogen atmosphere. The reaction of **1** with pyrazole yields $\text{RuH}(\text{H}_2)(\text{NNC}_3\text{H}_3)(\text{NNHC}_3\text{H}_3)(\text{PCy}_3)_2$ (**5**), which shows hydrogen bonding between the pyrazole and pyrazolate groups. The π -bonded phenoxo derivative $\text{RuH}(\eta^5\text{-C}_6\text{H}_5\text{O})(\text{PCy}_3)_2$ (**6**) has been obtained by reaction of **1** with phenol. Complex **6** under H_2 yields $\text{RuH}_2(\eta^6\text{-C}_6\text{H}_5\text{-OH})(\text{PCy}_3)_2$ (**7**) whereas dehydrogenation of cyclohexanone occurs with or without hydrogen acceptor to give $\text{Ru}(\eta^5\text{-C}_6\text{H}_5\text{O})(\text{C}_6\text{H}_{10}\text{PCy}_2)(\text{PCy}_3)$ **8**. Finally, **8** reacts with H_2 to give a mixture of **6** and **7**.

Introduction

Since the original report by Kubas in 1984¹ that dihydrogen could coordinate to a transition metal center without dissociation, numerous examples of dihydrogen complexes have been described in the literature and several recent reviews have indicated the ever growing interest for these compounds.² The reactivity of dihydrogen derivatives has been extensively reviewed by Jessop and Morris.^{2d} It is however not clear yet whether dihydrogen derivatives show a specific reactivity compared to similar dihydride derivatives, except for two reactions, *viz.* exchange with D_2 to give coordinated H-D^1 and transfer of proton, since cationic dihydrogen derivatives are very acidic.^{2,3}

We have been studying for a few years the reactivity of $\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$ (**1**)⁴ which has long been the only thermally stable bis(dihydrogen) complex until the recent preparation in our group of $\text{T}_p\text{RuH}(\text{H}_2)_2$ (T_p = substituted hydridotris(pyrazolyl)-borate) ligand.⁵ Unstable bis(dihydrogen) complexes of iridium and rhenium have been prepared in solution by protonation of polyhydrides precursors⁶ whereas carbonyl bis(dihydrogen) derivatives have been observed in a matrix.⁷ **1** has been shown to give hydrido dihydrogen derivatives upon protonation by carboxylic acids,⁸ and to lead to a series of novel 16 electron dihydrogen derivatives upon reaction with halocarbons and thiols.⁹ Substitution of one dihydrogen ligand by a silane or germane has also been reported.¹⁰

In this paper, we describe the reactivity of **1** with small molecules and hydrocarbons containing weakly acidic protons. The reaction of **1** with N_2 has been mentioned in a preliminary communication.¹⁰

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. Microanalyses were performed at the laboratory's service. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer 1725 FT-IR spectrometer. NMR spectra were recorded on Bruker AC200 (at 200.13 MHz for ^1H , at 50.324 MHz for ^{13}C and at 81.015 MHz for ^{31}P) and AC80 (at 32.44 MHz for ^{31}P) instruments while variable temperature proton spectra were obtained by using a AM250 (250.13 MHz for ^1H and 62.89 MHz for ^{13}C), all these spectrometers operating in the Fourier transform mode. Integration ratios were measured with long repetition times (30–60 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; pyrazole was sublimed and cyclohexanone distilled prior to use.

$\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$ (**1**) was prepared according to published methods.⁴

$\text{RuH}_2(\text{N}_2)_2(\text{PCy}_3)_2$ (**2**). This complex was spectroscopically characterized using the following procedures: (a) bubbling N_2 into a suspension of **1** (100 mg; 0.15 mmol) in 7 mL of pentane results in rapid dissolution and obtention of a very air sensitive pale yellow solution analyzed by IR ($\nu_{\text{N=N}}$ 2163 and 2126 cm^{-1} in pentane solution). Any attempt to isolate the complex failed: (i) after the solvent was slowly removed under a stream of N_2 , an untractable greenish oil was obtained; (ii) under vacuum, the solution turned red yielding a mixture of compounds which were not characterized. (b) **1** was dissolved in C_6D_6 in a NMR tube under an argon atmosphere. After NMR recording showing only **1** (t, -7.8 ppm, $J_{\text{P-H}} = 7$ Hz), N_2 was bubbled during 5 min into the tube resulting in a yellow greenish solution. A NMR spectrum was then recorded and showed only signals attributed to **2** (t, -12.83 ppm, $J_{\text{P-H}} = 22$ Hz). Finally, H_2 was bubbled for 5 min into the solution and **1** was recovered.

$\text{RuH}(\text{O}_2\text{CH})(\text{H}_2)(\text{PCy}_3)_2$ (**3**). CO_2 is bubbled into a suspension of (**1**) (200 mg; 0.3 mmol) in 50 mL of pentane. After 15 min, a pale yellow precipitate is formed, filtered off, washed with pentane (2×5

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Table 1. Selected NMR Data for Compounds 2–7

compound	¹ H NMR hydride region ^a δ _H (ppm)	T ₁ (min) ^b (ms)	³¹ P NMR ^c δ _P (ppm)	selected ¹³ C NMR δ _{CO} or δ _{CS} (ppm)
RuH ₂ (N ₂) ₂ (PCy ₃) ₂ (2)	-12.83 (t, J _{P-H} = 22 Hz)			
RuH(H ₂)(O ₂ CH)(PCy ₃) ₂ (3)	-14.19 (t, J _{P-H} = 13.8 Hz)	34 (243 K)	56.8 ^d	171 (d, J _{C-H} = 196 Hz, O ₂ CH) ^e
RuH ₂ (S ₂ CH ₂)(PCy ₃) ₂ (4)	-10.85 (t, J _{P-H} = 32.9 Hz)	134 (243 K)	75.5	64.6 (t, J _{C-H} = 147 Hz, S ₂ CH ₂) ^f
RuH(H ₂)(NNC ₃ H ₃)(NNHC ₃ H ₃)(PCy ₃) ₂ (5)	-12.04 (t, J _{P-H} = 14 Hz)	26 (243 K)	46.7	
RuH(η ⁵ -C ₆ H ₅ O)(PCy ₃) ₂ (6)	-12.80 (t, J _{P-H} = 38.2 Hz)		53.6 ^d	165.9 (s, C=O) ^f
RuH ₂ (η ⁶ -C ₆ H ₅ OH)(PCy ₃) ₂ (7)	-10.85 (t, J _{P-H} = 33 Hz)			

^a In C₆D₆ at 200 MHz. ^b In C₇D₈ at 250 MHz. ^c In C₆D₆ at 81.01 MHz. ^d In C₆D₆ at 32.44 MHz. ^e In C₆D₆ at 50.32 MHz. ^f In C₆D₆ at 62.89 MHz.

mL), and dried in vacuo. Yield: 84%. Anal. Calcd for RuC₃₇H₇₀P₂O₂: C, 62.6; H, 9.7. Found: C, 62.7; H, 10.3.

RuH₂(S₂CH₂)(PCy₃)₂ (4). CS₂ (17.8 μL; 0.3 mmol) is added to a suspension of **1** (200 mg; 0.3 mmol) in 30 mL of pentane at 0 °C. The red solution formed is stirred for 30 min and allowed to reach room temperature. After concentration to 10 mL, the solution is cooled to -20 °C for several hours. A red brown microcrystalline solid precipitates. It is filtered off, washed with pentane (2 × 5 mL), and dried in vacuo. Yield: 83%. Anal. Calcd for RuC₃₇H₇₀S₂P₂: C, 59.9; H, 9.5; S, 8.6. Found: C, 59.9; H, 9.7; S, 8.6.

RuH(H₂)(NNC₃H₃)(NNHC₃H₃)(PCy₃)₂ (5). A solution of pyrazole (15.3 mg; 0.22 mmol) in 10 mL of toluene is added to a solution of **1** (150 mg; 0.22 mmol) in toluene (30 mL). Evolution of H₂ is observed. The pale yellow solution was stirred for 2 h. The solution was then concentrated to 10 mL and cooled to -20 °C overnight. A white precipitate was formed and filtered off, washed with pentane (2 × 5 mL) and dried in vacuo. Yield: 80% vs pyrazole. Anal. Calcd for RuC₄₂H₇₆N₄P₂: C, 63.0; H, 9.6; N, 7.0. Found: C, 63.0; H, 9.7; N, 6.2.

RuH(η⁵-C₆H₅O)(PCy₃)₂ (6). To a suspension of **1** (300 mg; 0.45 mmol) in 20 mL of acetone is added phenol (45 mg; 0.45 mmol). After 20 h, a pale green precipitate is formed and filtered off, washed with acetone, and dried in vacuo. Yield: 80%. Anal. Calcd for RuC₄₂H₇₂OP₂: C, 66.8; H, 9.5. Found: C, 66.9; H, 9.9.

RuH₂(η⁶-C₆H₅OH)(PCy₃)₂ (7). A solution of **6** (200 mg; 0.26 mmol) in 15 mL of toluene in a Fischer & Porter bottle is pressurized to 1 bar of dihydrogen. The reaction mixture is heated to 80 °C for 20 h and then evaporated to dryness. All our crystallization attempts have failed.

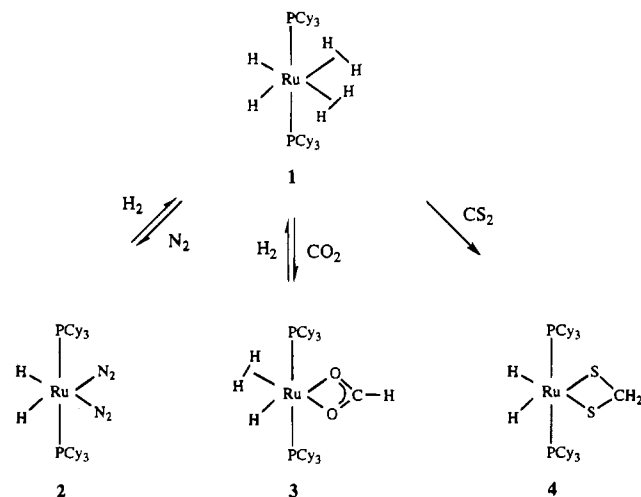
Ru(η⁵-C₆H₅O)(C₆H₁₀PCy₂)(PCy₃) (8). To 170 mg (0.25 mmol) of **1** are successively added 6.6 mL (200 × 0.25 mmol) of *tert*-butylethylene and 0.53 mL (20 × 0.25 mmol) of cyclohexanone. The reaction mixture is heated into a Fischer & Porter bottle at 80 °C for 18 h and then evaporated to dryness. The brown/red solid obtained is dissolved in heptane (5 mL) using ultrasonics and cooled to -20 °C overnight. A beige precipitate is then formed. After filtration, the solid is washed with pentane (2 × 1 mL) and dried in vacuo. Yield: 52%. Anal. Calcd for RuC₄₂H₇₀P₂O: C, 64.4; H, 8.7. Found: C, 63.9; H, 8.6.

Results and Discussion

Reactions of **1** with Small Molecules (See Scheme 1).

Reaction with N₂. The reaction of **1** with N₂ is almost instantaneous in pentane at room temperature. **1**, which is originally insoluble, rapidly dissolves to give a pale yellow solution containing a new bis(dinitrogen) complex, *cis*-RuH₂(N₂)₂(PCy₃)₂ (**2**). **2** is extremely unstable and air-sensitive, it decomposes during work-up and loses N₂ in vacuo which prevented a full characterization. However **2** shows in ¹H NMR a triplet at δ -12.83 ppm (J_{P-H} = 22 Hz) and two ν_{N=N} absorptions in infrared at 2163 and 2126 cm⁻¹ in agreement with the proposed structure. This substitution reaction is similar to that observed with CO which leads to RuH₂(CO)₂(PCy₃)₂ except for the instability of dinitrogen coordination to ruthenium.^{9b} **2** is a rare example of a hydrido bis(dinitrogen) derivative.¹¹ Bubbling H₂ into a pentane solution of **2** regenerates **1**.

Scheme 1



Reaction with CO₂. The reaction of **1** with CO₂ is also rapid in pentane. A solubilization is observed followed by the formation of a yellow precipitate of RuH(H₂)(O₂CH)(PCy₃)₂ (**3**). The infrared spectrum of **3** shows a Ru–H stretch at 2050 cm⁻¹ and ν_{CO} (sym) at 1566 cm⁻¹. The ¹H NMR spectrum shows a high field signal at δ -14.19 (t, J_{P-H} = 13.8 Hz) which broadens at low temperature. The relaxation time T₁ minimum of this signal is 35 ms at 243 K, in agreement with the presence of a coordinated dihydrogen molecule. A low field signal is observed at δ 8.62 (t, J_{P-H} = 1.8 Hz) for the proton of the formate group (relative intensity for these two signals 3:1). The carbon of the formate ligand appears in ¹³C NMR at δ 171.4 (d, J_{C-H} = 196 Hz). Finally a singlet is observed in ³¹P NMR at δ 56.8. These data are very similar to those obtained for a series of hydrido dihydrogen derivatives resulting from the protonation of **1** by carboxylic acids⁸ and indicate the insertion of one CO₂ molecule into one of the hydrides of **1** after substitution of a dihydrogen molecule to give a formate group. In contrast to the preceding reaction, only one dihydrogen molecule is substituted even employing more forcing conditions. A similar reaction with CO₂ has been previously observed by Vol'pin on RuH₂(H₂)(PPh₃)₃ to give RuH(O₂CH)(PPh₃)₃.¹²

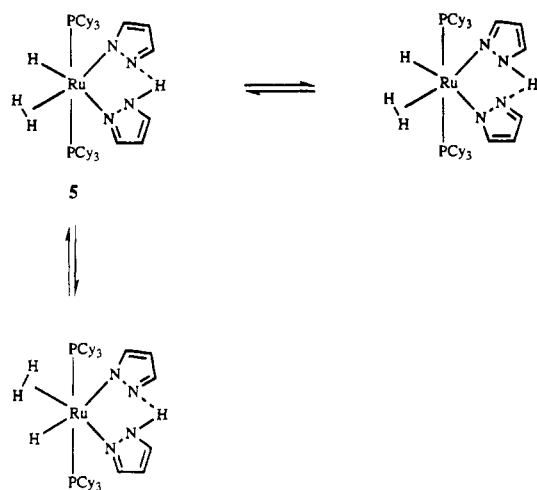
The reaction is reversible since bubbling H₂ in a solution of **3** leads slowly at room temperature to the formation of **1**, but no formic acid is found.

Reaction with CS₂. A rapid reaction occurs between **1** and 1 equiv of CS₂ at 0 °C in pentane. A red complex is obtained which analyzes for RuH₂(S₂CH₂)(PCy₃)₂ (**4**). The most salient features of the ¹H NMR spectrum of **4** are a hydride signal as a triplet at δ -10.85 (J_{P-H} = 32.9 Hz) and a singlet at δ 6.17 (integration ratio compared to hydride signal, 1:1) attributed to the methylene protons of the S₂CH₂ group. The latter value is

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Scheme 2



similar to that recently found for $\text{Ru}(\text{S}_2\text{CH}_2)(\text{Cytpp})$ (δ 6.08).¹³ Cooling **4** to 188 K in C_7D_8 only results in the broadening of the hydride signal. The minimum of the relaxation time T_1 of this signal is 134 ms at 243 K in agreement with a classical dihydride formulation. The presence of the two hydrides is further confirmed by the singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum split into a triplet by selective decoupling of the protons of the cyclohexyl groups ($J_{\text{P-H}} = 33$ Hz). The methylene carbon of the S_2CH_2 group was observed in ^{13}C NMR at δ 64.6 (t, $J_{\text{C-H}} = 147$ Hz). **4** is therefore a 16 electron ruthenium(IV) dihydride that does not react with H_2 . The difference of reactivity between CO_2 and CS_2 is interesting and probably results from the important affinity of ruthenium for sulfur, which could promote the insertion process. Precedents for this type of CS_2 insertion are found with ruthenium and molybdenum, which both show an important affinity for sulfur.

Reactions of 1 with Compounds Containing One Acidic Proton. We have previously studied the reactions of **1** with various carboxylic acids and have shown that they led to a series of new hydrido dihydrogen derivatives. It was therefore of interest to study new chemicals which could either substitute H_2 or protonate a hydride.

Reaction with Pyrazole. The reaction of **1** with 1 equiv. pyrazole is rapid in toluene at room temperature and leads to gas evolution and formation of a yellow solution. After concentration and precipitation, an off white powder is obtained, analyzing for $\text{RuH}(\text{H}_2)(\text{NNC}_3\text{H}_3)(\text{NNHC}_3\text{H}_3)(\text{PCy}_3)_2$ (**5**). The ^1H NMR spectrum shows a high field triplet at δ -12.04 ($J_{\text{P-H}} = 14$ Hz), three singlets for the carbon bound pyrazole protons at δ 6.57, 7.88, and 8.09 and a singlet at δ 21.08. The relative intensity of the peaks is respectively 3:2:2:1. In addition, cyclohexyl protons are visible between δ 1 and 2.3. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at δ 46.7 which splits into a quartet ($J_{\text{P-H}} \approx 14$ Hz) when only the protons of the cyclohexyl groups are irradiated. This is in agreement with the presence of three hydrogen atoms directly linked to ruthenium in **5**. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 50.3 MHz) presents pyrazole carbon resonances at δ 145.2, 131.8 and 105.3.

These results show that two molecules of pyrazole have reacted with **1**. One pyrazole has protonated a hydride of **1** whereas the other has substituted a dihydrogen ligand. However, the apparent symmetry of the structure observed in particular for the carbon-bound pyrazole protons suggest a rapid jump of the nitrogen bound pyrazole proton from one ligand to the other (see Scheme 2). In addition the high field signal of

5 shows a minimum of the relaxation time T_1 of 26 ms at 243 K in agreement with the presence of a dihydrogen molecule. Two fluxional processes are therefore present in the molecule (see Scheme 2). However it was not possible to observe decoalescence at 178 K and as a consequence to gain information on these processes.

Since the formation of **5** is rapid in toluene, we studied the reaction in THF. This allowed to observe by ^1H NMR two transient species showing a high field signal at δ -9.1 and -13.2. The first peak could correspond to a dihydrido dihydrogen complex containing three two electron donor ligands⁴ whereas the second one could be due to a 16 electron species. However, both transform rapidly into **5**. This suggests that pyrazole substitutes a dihydrogen molecule prior to the protonation process. It is interesting to note that the presence of only good σ donor ligands does not induce the formation of a trihydride.

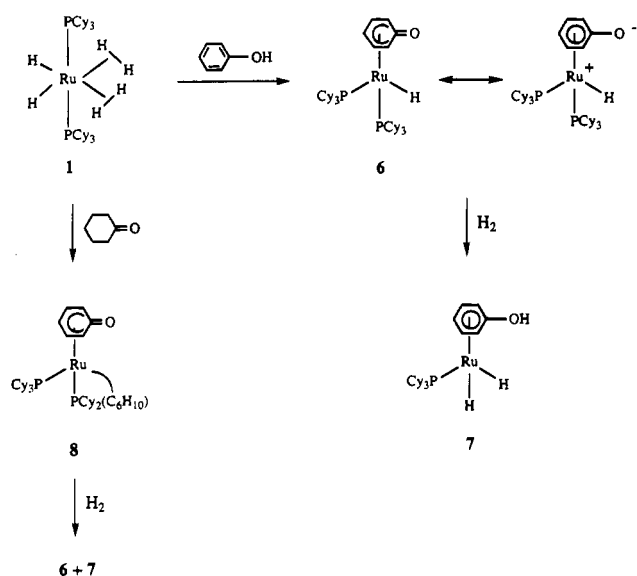
Reactions with Phenol and Cyclohexanone. Phenol contains, like pyrazole, an acidic proton, and it has been shown in the 1970's by Wilkinson *et al.* that it could protonate $\text{RuH}_2(\text{PPh}_3)_4$ to lead after rearrangement to a π phenoxo derivative $\text{RuH}(\eta^5\text{-C}_6\text{H}_5\text{O})(\text{PPh}_3)_2$.¹⁴ However, Yamamoto *et al.* recently showed that a similar reaction between $\text{RuH}_2(\text{PMe}_3)_4$ and phenol led to σ complexes showing hydrogen-bonding with free phenol.¹⁵ PCy_3 being much more bulky and basic than PPh_3 , it was of interest to see whether this reaction would lead to π - or σ -bonded phenoxo. It is noteworthy that terminal alkoxo complexes are rare in ruthenium chemistry.

The reaction between phenol and **1** suspended in acetone is slow at room temperature and leads after 20 h to a yellow analytically pure precipitate of $\text{RuH}(\eta^5\text{-C}_6\text{H}_5\text{O})(\text{PCy}_3)_2$ (**6**). The complex is totally analogous to its PPh_3 congener. Thus, it shows a hydride signal at δ -12.8 (t, $J_{\text{P-H}} = 38.2$ Hz) and peaks attributed to the π coordinated ring at δ 4.34 (t, $J_{\text{P-H}} = 6.6$ Hz, H_p), 5.56 (t, $J_{\text{P-H}} = 6.6$ Hz, H_m) and 5.17 (d, $J_{\text{P-H}} = 6.6$ Hz, H_o). The ^{13}C NMR spectrum has π -coordinated ring carbon resonances at δ 69.60 (C_p , d, $J_{\text{C-H}} = 171.4$ Hz), 96.08 (C_m , d, $J_{\text{C-H}} = 163.8$ Hz), 81.40 (C_o , d, $J_{\text{C-H}} = 164.3$ Hz) and 165.92 (s, $\text{C}=\text{O}$) whereas the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at δ 53.6. It is therefore clear that the reaction of **1** with phenol is similar to that of $\text{RuH}_2(\text{PPh}_3)_4$, and that ruthenium can accommodate two approximately *cis* tricyclohexylphosphines, despite their large cone angle.

Interestingly **6** reacts with H_2 in toluene at 80 °C to give a new monophosphine derivative for which we suggest the formulation $\text{RuH}_2(\eta^6\text{-C}_6\text{H}_5\text{OH})(\text{PCy}_3)$ (**7**). Thus this complex is very similar to π -arene hydride ruthenium complexes studied by Werner *et al.*¹⁶ It shows a doublet at δ -10.57 ($J_{\text{P-H}} = 42.6$ Hz) in ^1H NMR as well as a triplet at δ 5.33 ($J_{\text{H-H}} = 5.7$ Hz, H_m) and a multiplet centered at δ 5.16 due to the overlap of the resonances of the ortho and para hydrogens. The ^{13}C NMR spectrum shows the π -coordinated ring at δ 83.2 (C_o , $J_{\text{C-H}} = 166$ Hz), 85.8 (C_m , $J_{\text{C-H}} = 166$ Hz) and 96.7 (C_p , $J_{\text{C-H}} = 166$ Hz). The resonance of $\text{C}-\text{OH}$ is probably hidden by the solvent peak. It is interesting that this reaction corresponds to a heterolytic activation of H_2 . The π -bonded phenoxo ligand can be viewed as a zwitterionic species (see Scheme 3) which will favor the heterolytic addition of H_2 . This type of reaction is involved in hydrogenation processes but remains very rare. A precedent has been described by Shvo *et*

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Scheme 3



al. upon hydrogenation of [Ru(η^4 -Ph₄C₄CO)(CO)₂]₂.¹⁷ Unfortunately it proved impossible to isolate **7** in a pure form despite several attempts. **7** was always found contaminated with small amounts of **6** and PCy₃.

We have precedently shown that **1** could dehydrogenate alkanes in the presence of ^tBuCH=CH₂ and separately we have shown that the electrophilic fragment "Cp^{*}Ru⁺" would selectively activate C–O bonds in the presence of C–H bonds.¹⁸ For example the reaction of "Cp^{*}Ru⁺" with cyclohexanone leads to [Cp^{*}Ru(η^6 -C₆H₆)]⁺ rather than to [Cp^{*}Ru(η^6 -C₆H₅OH)]⁺. It was therefore of interest, after the isolation of a π -phenoxo complex, to study the reactivity of **1** with cyclohexanone. First we found that in contrast to what is observed with alkanes, the presence of a hydrogen acceptor such as ^tBuCH=CH₂ is not necessary. Thus **1** reacts with excess of cyclohexanone at 80

°C for 20 h to give a new complex analyzing for Ru(η^5 -C₆H₅O)(C₆H₁₀PCy₂)(PCy₃) (**8**) in *ca.* 60% yield. The presence of a π -phenoxo ring coordinated to **8** is demonstrated by peaks at δ 3.82 (t, $J_{\text{H-H}} = 6.0$ Hz, Hp), 4.90 (dd, $J_{\text{H-H}} = 6.0$ and 6.4 Hz, Hm) and 5.37 (d, $J_{\text{H-H}} = 6.4$ Hz, Ho) in ¹H NMR and peaks at δ 61.3 ($J_{\text{C-H}} = 164.2$ Hz, Cp), 79.4 ($J_{\text{C-H}} = 167.1$ Hz, Cm), and 93.2 ppm ($J_{\text{C-H}} = 166.1$ Hz, Co) in ¹³C NMR. The carbon linked to oxygen is observed at δ 162. In addition a multiplet is observed at δ -0.35 in ¹H NMR which could correspond to the proton of a metalated carbon of a cyclohexyl ring. We propose that the reaction of **1** with cyclohexanone leads to the dehydrogenation of the cyclic ketone into a phenoxo ring and that activation of a cyclohexyl ring occurs during the dehydrogenation process. In order to confirm this proposal **8** was reacted with H₂ at 80 °C in toluene. The reaction leads to a mixture of **6** and **7**. If the reaction is carried out at room temperature no reaction occurs. This demonstrates unambiguously the dehydrogenation of cyclohexanone in the absence of hydrogen acceptor and the absence of activation of the C–O bond. No byproduct containing benzene was detected by spectroscopic methods.

In conclusion, this paper further demonstrates the rich chemistry displayed by the bis(dihydrogen) complex **1**. The initial step of all reactions is presumably the substitution of dihydrogen, as previously observed for the reaction of **1** with CO and, in this report, for the reaction of **1** with N₂. This is followed by hydride insertion in the case of CO₂. A second hydride insertion is possible in the case of CS₂. The reason for this difference of behavior is not clear but could be similar to the much higher affinity of ruthenium for the soft thiolato ligand as compared to the alkoxo one. In the case of pyrazole or phenol the substitution is followed by a protonation and a rearrangement of the molecule in the latter case. The uncoordinated nitrogen group of pyrazole is probably very nucleophilic which would explain the formation of the bis(pyrazole) complex. Finally it is interesting to note the dehydrogenation of cyclohexanone without hydrogen acceptor and the heterolytic activation of dihydrogen on a hydridophenoxoruthenium derivative.

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