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Synthesis, Characterization, and Chemistry of 16-Electron Dihydrogen Complexes of Ruthenium

M. Lorraine Christ, Sylviane Sabo-Etienne, and Bruno Chaudret*

Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne,
31077 Toulouse Cedex, France

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The reaction of $RuH_2(H_2)_2(PCy_3)_2$ (**1**) with halocarbons (methyl iodide or dichloromethane) in pentane yields the new 16-electron hydrido dihydrogen derivatives $RuHX(H_2)(PCy_3)_2$ (X = I, **2a**; X = Cl, **2b**) characterized by spectroscopic methods and by X-ray crystallography in the case of **2a**. In the presence of excess dihydrogen, **2a,b** transform into bis(dihydrogen) species $RuHX(H_2)_2(PCy_3)_2$ (X = Cl, **3b**; X = I, **3a**), in which all hydrides exchange rapidly in the whole range of accessible temperatures. Complexes **3a,b** were only observed in solution. **1** reacts with thiols (RSH) to yield 16-electron thiolato species $RuH(SR)(H_2)(PCy_3)_2$ (R = Cy, **2c**; R = Ph, **2d**; R = ^tBu, **2e**). Whereas **2c** shows a slow exchange with H_2, **2e** reacts to give **1** and HS^tBu. Finally compounds **1** and **2a−f** react with carbon monoxide to yield the *cis* dicarbonyl derivatives $RuHX(CO)_2(PCy_3)_2$ (X = H, **4a**; X = I, **4b**; X = Cl, **4c**; X = SCy, **4d**; X = SPh, **4e**; X = S^tBu, **4f**).

Introduction

The discovery by Kubas of dihydrogen coordination without dissociation has opened a whole new field in inorganic chemistry[1−4] and stimulated a renewed interest in polyhydride chemistry. As a consequence of this discovery, several polyhydrides were reformulated as dihydrogen derivatives.[2] For example, the difference in reactivity between $RuH_4(PPh_3)_3$ and $OsH_4(PPh_3)_3$ was explained by the presence of a dihydrogen molecule on the former.[2] It is clear now both from experimental evidence and from calculations[5] that electronic factors play a dominant role in the ability of a transition metal center to coordinate or to oxidatively add dihydrogen.[3] However, more and more systems have now been discovered which lead either to both dihydride and dihydrogen isomers or to a tautomeric equilibrium between the two species.[3,6] Furthermore, NMR data and neutron diffraction have demonstrated that elongated H−H bonds could be present in osmium[7] or rhenium[8] polyhydrides such as $ReH_7(PR_3)_2$. These observations led to the conclusion that σ-bonds such as dihydrogen can be coordinated in a stretched or unstretched mode.[2c]

The reactivity of dihydrogen species has been attracting more and more interest but remains relatively little developed compared to the efforts for characterizing new species. Dihydrogen coordination has been observed in the presence of very different ligands (carbonyls, phosphines, tris(pyrazolyl)borate) and mixed-ligand systems (cyclopentadienyl and carbonyl or phosphine, phosphine and nitrogen or oxygen donors, ...), but most examples of dihydrogen derivatives are found in a d^6 octahedral configuration.[1−4] This is true for the first such complex $W(H_2)(CO)_3(P^iPr_3)_2$[1] and is general throughout ruthenium chemistry. It is important to note that, is all cases reported so far, the electronic configuration of the complex was found saturated (18 electrons). The most unexpected aspect of dihydrogen derivatives is their acidity[3] when they are cationic with pK_a down to −2 in $[Re(H_2)Cp^*(CO)(NO)]^+$.[9] However, in most cases, the chemistry of dihydrogen complexes resembles that of their polyhydride congeners just displaying a considerable increase in reactivity.[3] Some of us reported several years ago the preparation of $RuH_6(PCy_3)_2$,[10] which was later specified as $RuH_2(H_2)_2(PCy_3)_2$ (**1**).[11] To date, **1** represents the only reported thermally stable bis(dihydrogen) complex, but we have recently isolated new bis(dihydrogen) derivatives $LRuH(H_2)_2$ L = HB(3,5Me$_2$-pz), HB(3-^{i}Pr,4-Br-pz) which were fully characterized thanks to selective deuteration.[12] Other bis(dihydrogen) complexes have been either prepared in a matrix[13] or observed in solution.[14] Although no X-ray crystal structure of **1** has yet been obtained, it was proposed to

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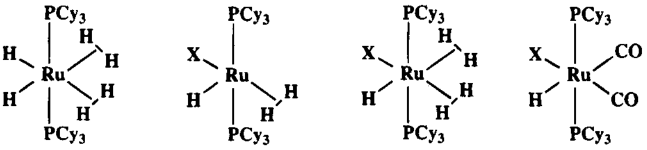
Chart 1



1

2a: X = I
2b: X = Cl
2c: X = SCy
2d: X = SPh
2e: X = StBu

3a: X = I
3b: X = Cl

4a: X = H
4b: X = I
4c: X = Cl
4d: X = SCy
4e: X = SPh
4f: X = StBu

be an octahedral *cis*-dihydride. Its structure would thus be similar to that of $RuH_2(PPh_3)_4$.[15] This last complex readily undergoes substitution reactions, for example with H_2 or N_2, protonation, and reactions with halocarbons and thiols to yield 16-electron hydride derivatives.[16] Similarly, $RuH_2(H_2)_2(PCy_3)_2$ reacts with N_2 leading to $RuH_2(N_2)_2(PCy_3)_2$.[17] The facile substitution of H_2 can allow the approach of reactive molecules able to further react with the ruthenium center, a hydride, or the dihydrogen molecule as observed recently in the reactions of **1** with silanes and germanes.[17] This reactivity also accounts for the protonation of **1** by carboxylic acids which leads to hydrido dihydrogen species.[6f] It was thus of interest to determine whether 16-electron dihydrogen derivatives, no example of which was known prior to this work, could be prepared and to investigate the reactivity of such species.

We describe in this paper the preparation of 16-electron dihydrogen complexes, a study of the mechanism of their formation, and a reactivity study with H_2 and CO. Part of this work has been reported in a preliminary communication.[18] All the characterized substances are listed in Chart 1.

Results

1. Reactions of $RuH_2(H_2)_2(PCy_3)_2$ (1) with Halocarbons. Synthesis and Characterization of 2a,b.

The reaction of $RuH_2(H_2)_2(PCy_3)_2$ (**1**) with CH_3I or PhI leads after dissolution of **1** to the precipitation of $RuHI(H_2)(PCy_3)_2$ (**2a**) as a brown air- and light-sensitive solid. In the case of the reaction with PhI, 1 equiv of benzene was detected by GLC. A similar reaction between **1** and CH_2Cl_2 yields $RuHCl(H_2)(PCy_3)_2$ (**2b**). Both complexes exhibit IR absorption bands attributed to a Ru–H stretch respectively at 2109 and 2059 cm^{-1}. The ^1H NMR spectra of **2a,b** consist of broad peaks arising from the PCy_3 protons between 0.5 and 2.5 ppm and of one common signal for the hydride and dihydrogen ligand at −16.3 ppm when using C_6D_6 and at −16.8 ppm when using CD_2Cl_2 as solvent. The integration ratio of the two signals, using large repetition delays (30 s), is *ca.* 66:3 as expected. The high-field signal consists of a broad singlet in the case of aromatic solvents but of a broadened triplet in CD_2Cl_2, arising from scalar coupling with two equivalent ^{31}P atoms. The coupling constant is $J(\text{av})_{P-H} \sim 11$ Hz. This value represents an average over the hydride and the dihydrogen environments, characterized by the coupling constants J_{PH} and J_{PH2} ($J(\text{av})_{P-H} = {}^1/_3 J_{PH} + {}^2/_3 J_{PH2}$). Since $J_{PH2} \sim 0$ it follows that $J_{PH} \sim 33$ Hz, a reasonable value for *cis* J_{PH} couplings in classical hydrido phosphine complexes. The dihydrogen/hydrido signals of **2a,b** further broaden as temperature is lowered, but the regime of slow exchange between the hydrido and the dihydrogen ligands could not be reached by cooling to 193 K. The relaxation times T_1 exhibit a minimum of 30 ms near 243 K. This value is in agreement with those found for other ruthenium hydrido dihydrogen complexes.[6f] The $^{31}P\{^1H\}$ NMR spectra of **2a,b** were also measured and consist of single lines near 55 ppm.

The crystal structure of **2a** has been described in a preliminary communication.[18] The most salient features of the molecular structure of **2a** are (i) an octahedral geometry with a vacant site of coordination and (ii) the presence of an elongated dihydrogen molecule (H–H = 1.03(7) Å) *cis* to a hydride and *trans* to the iodide group. The Ru–P, Ru–I, and Ru–H distances are normal for such compounds (Ru–H = 1.60(5) and 1.59(4) Å for the dihydrogen ligand and Ru–H = 1.51(5) Å for the hydride ligand; Ru–I = 2.710(1) Å; Ru–P = 2.339(1) and 2.344(1) Å). The nonbonded hydride–hydrogen distance is relatively short (H···H = 1.66(6) Å), and the dihydrogen molecule lies in the plane containing ruthenium, hydride, and iodide. These facts reveal that **2a** is the first characterized 16-electron dihydrogen complex and that a *cis* interaction between the hydride and the hydrogen molecule could be present. The latter point has been discussed in the preliminary communication.[18] The high fluxionality of the molecule which renders all three hydrogens of **2a,b** equivalent at all accessible temperatures in standard solvents could be due to this interaction.

NMR Studies of 1 in CD_2Cl_2. In order to gain insight into the mechanism of the formation of **2a,b** various solutions of **1** were prepared in CD_2Cl_2 and followed by ^1H NMR spectroscopy. Hence, when cold (<10 °C) CD_2Cl_2 is added to solid **1** in a NMR tube, only one triplet signal at −8.4 ppm ($J_{P-H} = 8$ Hz) is observed at high field characteristic for unreacted **1** in which the hydrido and dihydrogen ligands exchange very fast. After some minutes at room temperature, an additional broad line appeared at −14.0 ppm. Lowering the temperature below 243 K led to a splitting of the latter into two exchange-broadened signals at −16.9 and −7.9 ppm characterized by a relative intensity of 3:2. Their longitudinal relaxation times T_1 at 250 MHz and 193 K were found to be 32 and 10 ms. The two signals were assigned to the reaction product **2b** and the new species $RuHCl(H_2)_2(PCy_3)_2$ (**3b**) as follows. When the NMR tube was opened under argon to remove some excess dihydrogen, the concentration of **3b** decreased as detected by a high-field shift of the coalesced line in the room temperature spectrum and by the decrease of the intensity of the signal at −7.9 ppm observed below 243 K. After further dihydrogen loss only **2b** was detected. It should be pointed out that **2b** was the only species present when solutions of **1** in CD_2Cl_2 were prepared at room temperature using Schlenk techniques. Adding gaseous dihydrogen to the samples again led to the formation of **3b** rapidly exchanging with **2b** (see Scheme 1).

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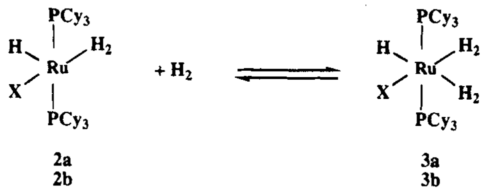
Scheme 1



In a similar way dihydrogen also adds to **2a** dissolved in organic solvents to give $RuHI(H_2)_2(PCy_3)_2$ (**3a**) (see Scheme 1). Again, exchange between **2a** and **3a** is fast at room temperature but slow below 263 K. Under these conditions separate lines are observed at −16.6 and −8.0 ppm when using CD_2Cl_2 as solvent (See Figure 1). The measurements revealed two different T_1 values of 24 and 12 ms at 250 MHz at 223 K for these signals (similar to the case of **2b** and **3b**). At first sight, these values could be interpreted in terms of the intrinsic values not affected by the exchange. However, the T_1 value of **2a** at 223 K is shorter than the minimum intrinsic value of 30 ms obtained in the absence of dihydrogen. Therefore, it seems that the regime of slow exchange with respect to longitudinal relaxation was not yet reached. In principle, the latter should be nonexponential in this regime; however, a detailed analysis was beyond the scope of this study.

The relative signal intensities of **2a** and **3a** at low temperatures and, as a consequence, the position of the coalesced line at room temperature depend strongly on the experimental conditions. Bubbling H_2 through the solutions led to an increase of **3a** which was even more pronounced when increasing the H_2 pressure to 6 bar (see Figure 1). Using toluene-d_8 as solvent, the situation becomes more complex. An averaged signal for **2a**/**3a** appears here between −11 and −7 ppm, depending on the conditions. The slow-exchange regime cannot be reached by lowering the temperature. We ascribe this finding to the higher solubility of H_2 in this solvent and a fast exchange between **3a** and dissolved H_2 which will average their chemical shifts.

2. Reactions of 1 with Thiols. Compounds **2a,b** are the first 16-electron dihydrogen complexes. It has been shown previously that 16-electron hydrido thiolato derivatives could be obtained from $RuH_2(PPh_3)_4$ and thiols in a way similar to the reaction between $RuH_2(PPh_3)_4$ and halocarbons yielding 16-electron $RuHX(PPh_3)_3$ derivatives.[16] Furthermore sulfur has been shown to take part in hydrogen transfer processes.[19] This led us to attempt the reactions of **1** with thiols.

The reaction of **1** with thiol RSH (R = c-C_6H_{11}(Cy), C_6H_5 (Ph), $(C(CH_3)_3$ (^tBu)) at 0 °C or room temperature in pentane yields a yellow brown solution from which yellow brown microcrystals are obtained upon cooling to −20 °C in respectively 95% (R = Cy) or 60% (R = Ph) yield. In the case of R = ^tBu, the complex formed is unstable and could not be recrystallized. All complexes analyze for $RuH(SR)(H_2)(PCy_3)_2$ (R = Cy, **2c**; R = Ph, **2d**; R = ^tBu, **2e**). Complexes **2c**−**e** show a Ru−H stretch in infrared near 2070 cm^{-1} (see Table 1) and a high-field signal near −13 ppm in ^1H NMR. The signal is a triplet at −13.1 ppm (J_{PH} = 14.8 Hz) in the case of **2c** whereas it is broad in the cases of **2d,e**. In addition, the ^1H NMR spectrum of **2c** shows peaks between 0.5 and 2.7 ppm for cyclohexyl protons and a well-defined pseudo triplet at 3.5 ppm (J_{H-H} = 10.7 Hz) attributed to the proton on the carbon α to sulfur of the SCy group (integration ratio compared to the high-field triplet: 1:3). **2d** shows a phenyl group at 7.9 ppm (d, J_{H-H} = 7.3 Hz, ortho protons) and 7.15 ppm (m, meta and para hydrogens, correct integration ratio) whereas the *tert*-butyl resonances in **2e** are obscured by those of the cyclohexyl rings. All complexes show a singlet near 58 ppm (see Table 1) in the ^{31}P NMR spectrum and are highly fluxional since no decoalescence is observed in the high-field signal corresponding to the hydride and dihydrogen group down to 203 K. The observed minimum T_1 values are 36 ms at 243 K for **2c** and 38 ms at 243 K for **2e** comparable to those found for **2a,b**. All these data are in agreement with a structure for **2c**−**e** similar to that of **2a,b**. The only ambiguity could be the nuclearity of complexes **2c**−**e**. However, in view of the increased steric bulk of ligands in **2c**−**e** compared to those on **2a,b** and of the similarity of spectroscopic data, in particular in ^{31}P NMR, we can safely propose a 16 electron mononuclear structure for **2c**−**e** (see Scheme 1).

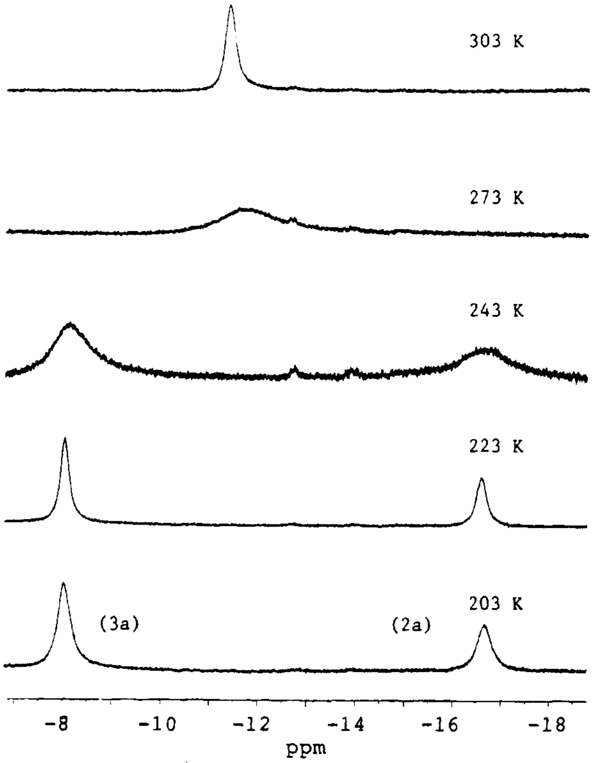


Figure 1. 250 MHz ^1H NMR spectra of **2a** in CD_2Cl_2 under 6 bar H_2 at various temperatures.

3. Reactivity of 16-Electron Dihydrogen Derivatives. Since compounds **2a**−**e** present a novel 16-electron structure for dihydrogen complexes, we investigated some simple reactions to gain some knowledge of their reactivity and stability.

The reactions of **2a,b** with dihydrogen have been previously described in this paper. In contrast **2c,d** show no apparent reaction with H_2 as monitored by ^1H NMR whereas the reaction of **2e** is rapid and yields **1** and HS^tBu. The steric bulk of the *tert*-butyl group on sulfur is probably responsible for the lack of stability of **2e**. However **2c** reacts with D_2 at room temperature and ambient pressure to exchange rapidly all hydrides.

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Table 1. Selected Spectroscopic Data for Compounds 2 and 3

compd	ν_{Ru-H} (cm^{-1})	^{1}H NMR hydride region δ_H (ppm)	T_1 (ms)	^{31}P NMR^c δ_P (ppm)
$RuHI(H_2)(PCy_3)_2$ (**2a**)	2109	−16.8 (t, J_{P-H} = 11 Hz)^a	30 (243 K)	56
$RuHCl(H_2)(PCy_3)_2$ (**2b**)	2059	−16.8 (t, J_{P-H} = 11 Hz)^a	30 (243 K)	54
$RuH(SCy)(H_2)(PCy_3)_2$ (**2c**)	2064	−13.1 (t, J_{P-H} = 14.8 Hz)^b	36 (243 K)	59.8
$RuH(SPh)(H_2)(PCy_3)_2$ (**2d**)	2080	−13.6 (br)^b		57.7
$RuH(S^tBu)(H_2)(PCy_3)_2$ (**2e**)	2069	−13.1 (br)^b	38 (243 K)	58.9
$RuHI(H_2)_2(PCy_3)_2$ (**3a**)		−8.0 (br)^a	12 (223 K)	
$RuHCl(H_2)_2(PCy_3)_2$ (**3b**)		−7.9 (br)^a	10 (193 K)	

^{a} In CD_2Cl_2 (250 MHz). ^{b} In $C_6D_5CD_3$ (250 MHz). ^{c} In toluene/C_6D_6 (32.44 MHz).

Table 2. Selected Spectroscopic Data for Compounds 4

				^{13}C NMR^a (ppm)	
compd	ν_{CO} (cm^{-1})	^{1}H NMR hydride region^a δ_H (ppm)	^{31}P NMR^b δ_P (ppm)	δ_{CO}	δ_{CS}
$RuH_2(CO)_2(PCy_3)_2$ (**4a**)	2004, 1994	−7.9 (t, J_{P-H} = 23 Hz)	68.3	206.2	
$RuHI(CO)_2(PCy_3)_2$ (**4b**)	2025, 1949	−6.3 (t, J_{P-H} = 21.7 Hz)	43.5	199.6, 199.8	
$RuHCl(CO)_2(PCy_3)_2$ (**4c**)	2021, 1947	−4.9 (t, J_{P-H} = 20.1 Hz)	49.8		
$RuH(SCy)(CO)_2(PCy_3)_2$ (**4d**)	2004, 1943	−5.6 (t, J_{P-H} = 21.6 Hz)	45.4	205.2, 199.8	43.5
$RuH(SPh)(CO)_2(PCy_3)_2$ (**4e**)	2015, 1959	−5.4 (t, J_{P-H} = 20.3 Hz)	45.1	205.9, 201.5	149.9
$RuH(S^tBu)(CO)_2(PCy_3)_2$ (**4f**)	2003, 1942	−5.5 (t, J_{P-H} = 21.3 Hz)	44.9		

^{a} In C_6D_6. ^{b} In toluene/C_6D_6 (32.44 MHz).

This behavior is similar to that of **2a** and suggests that a reaction does occur between **2c,d** and excess dihydrogen but that binding of H_2 to these metal centers is very weak. The reason for the unstability of the bis(dihydrogen) thiolato adducts toward dissociation of H_2 could be the steric bulk around the metal center.

In contrast to **1**, none of the 16-electron dihydrogen complexes **2a–e** reacts with N_2 or CO_2 at room temperature under 1 atm of gas whereas reaction of **2a** with pyridine leads to mixtures not containing hydrides. However all compounds **1** and **2a–e** react instantaneously with carbon monoxide to give dicarbonyl species: $RuH_2(CO)_2(PCy_3)_2$ (**4a**) and a series of compounds of general formulation $RuHX(CO)_2(PCy_3)_2$ (X = I, **4b**; X = Cl, **4c**; X = SCy, **4d**; X = SPh, **4e**; X = S^{t}Bu, **4f**). All these compounds show two carbonyl stretches in the infrared spectra, a high-field triplet near −6 ppm (J_{PH} ~ 21 Hz), and a singlet in ^{31}P NMR near 45 ppm (see Table 2). Slight variations in the infrared frequencies suggest that complexes **4d,f** are the most electron rich in agreement with the good σ-donor ability of the alkyl fragments. All these compounds show a similar mononuclear octahedral structure in agreement with the mononuclear formulation for **2c–e**. It has not been possible to isolate intermediates from these reactions, but prolonged reaction of **1** or **2e** with CO generates $Ru(CO)_3(PCy_3)_2$ as deduced from spectroscopic observations.

Discussion

The results described above first demonstrate that 16-electron dihydrogen complexes are stable and isolable. As shown in Scheme 1, the 16-electron species **2** is able to bind in a reversible way excess dissolved H_2 to give a new species **3** which is probably an unstable hydrido bis(dihydrogen) species $RuH(H_2)_2X(PCy_3)_2$, X = Cl and I. Similar additions of dihydrogen to 16-electron hydride complexes have been reported by different authors.[20,21] In particular, Jensen et al. have observed a similar behavior characterized by a mean peak of chemical shift varying as a function of dihydrogen concentration.[21] It is however interesting to note that a rapid exchange occurs between **2b** and **3b** even at very low concentration of dissolved free H_2. The hydride and the dihydrogen molecules in **3b** rapidly exchange, even at low temperature as in **2b**.

It should be pointed out that **3a,b** are new examples of bis(dihydrogen)ruthenium complexes, which, in contrast to **1**, are unstable toward loss of dihydrogen. In the absence of a theoretical investigation on this system, it is reasonable to propose that this behavior could be related to the better σ-donor ability of the hydride ligands compared to the halide ones which stabilizes dihydrogen coordination; however, this seems contradictory to the observation that 16-electron hydrido–halide complexes are stable whereas the corresponding dihydrides are not. The existence of the formally 16-electron derivatives probably results from the additional π-donor ability of halogens and sulfur which stabilizes the unsaturated structure through formation of a partially multiple bond. The high fluxionality of these species could, in our opinion, result from the *cis* interaction between the hydride and dihydrogen molecules already proposed by Eisenstein *et al.* on an iron dihydrido dihydrogen complex[22] and on **2b**.[18]

Finally, these various experiments further demonstrate that **1** contains two dihydrogen ligands. They show the similarity of reactivity between the classical dihydride $RuH_2(PPh_3)_4$ which has been known for a long time and the bis(dihydrogen) complex **1**. $RuH_2(PPh_3)_4$ has been previously shown to react with chloroform or dichloromethane to yield $RuHCl(PPh_3)_3$ and with thiols to give $RuH(SR)(PPh_3)_3$, both derivatives adopting a 16 electron configuration. Dihydrogen behaves in **1** as a standard two electron ligand.

In conclusion, we have described in this paper the preparation of the first 16-electron dihydrogen complexes. Only one of them has been characterized by X-ray diffraction, but the similarity between their spectroscopic properties allows to propose a similar

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structure for all of them. These complexes all exchange with free dihydrogen. In the case of the halides it was possible to observe rare examples of unstable bis(dihydrogen) derivatives, the concentration of which depends on the quantity of H_2 dissolved in the medium, whereas no bis(dihydrogen) complex could be observed in the case of the thiolato complexes. We are now exploring the chemistry of these novel complexes.

Experimental Section

Microanalyses were performed at the laboratory's microanalysis service. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer 1725 FT-IR spectrometer. NMR spectra were recorded on a 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), while variable-temperature proton spectra were obtained by using an AM250 (250 MHz), all these spectrometers operating on the Fourier transform mode. All manipulations were carried out in argon atmosphere by use of Schlenk techniques. Pentane was dried over calcium hydride, while CH_2Cl_2 was dried over P_2O_5; they were distilled under dinitrogen and thoroughly degased under argon before use.

$RuH_2(H_2)_2(PCy_3)_2$ (1) was prepared according to published methods.[10] $RuCl_3{\cdot}3H_2O$ was purchased from Johnson Matthey Ltd; PCy_3, HSCy, HSPh, and HS^tBu were purchased from Aldrich. CH_3I was purchased from Fluka.

$RuHI(H_2)(PCy_3)_2$ (2a). To a suspension of $RuH_2(H_2)_2(PCy_3)_2$ (400 mg; 0.6 mmol) in 20 mL of hexane was added CH_3I (37 μL; 0.6 mmol). The reaction mixture was stirred for 1 h at room temperature, during which a brown precipitate separated. It was filtered off, washed with hexane, and dried in vacuo. Yield: 70%. Recrystallization was from toluene/pentane. Anal. Calcd for $RuC_{36}H_{69}IP_2$: C, 54.60; H, 8.78. Found: C, 54.56; H, 9.16.

$RuHCl(H_2)(PCy_3)_2$ (2b). To a suspension of $RuH_2(H_2)_2(PCy_3)_2$ (400 mg; 0.6 mmol) in 15 mL of hexane was added CH_2Cl_2 (76 μL; 1.2 mmol). The reaction mixture was stirred for 1 h at room temperature, during which a red precipitate separated. It was filtered off, washed with hexane, and dried in vacuo. Yield: 70%. An alternative procedure was used starting with Ru(COD)(COT), the precursor for the synthesis of **1**: To a solution of Ru(COD)(COT) (500 mg; 1.6 mmol) and PCy_3 (890 mg; 3.2 mmol) in 30 mL of pentane was added CH_2Cl_2 (200 μL; 3.2 mmol). Dihydrogen was bubbled slowly into the reaction mixture for 1 h. The brown/red precipitate formed was filtered off, washed with pentane, and dried in vacuo. Yield: 70%. Anal. Calcd for $RuC_{36}H_{69}ClP_2{\cdot}{}^1/_2CH_2Cl_2$: C, 59.01; H, 9.50. Found: C, 59.22; H, 9.75.

$RuH(SCy)(H_2)(PCy_3)_2$ (2c). To a suspension of $RuH_2(H_2)_2(PCy_3)_2$ (200 mg; 0.30 mmol) in 50 mL of pentane was added HSCy (37 μL; 0.3 mmol) at 0 °C. The resulting yellow solution was then allowed to warm to room temperature. After 1 h of stirring, the solution was concentrated to 5 mL and cooled to −20 °C for 2 h. The brown yellow precipitate formed was then filtered off and dried in vacuo. Yield: 95%. Anal. Calcd for $RuC_{42}H_{80}SP_2$: C, 64.66; H, 10.33; S, 4.11. Found: C, 64.49; H, 10.34; S, 4.12.

$RuH(SPh)(H_2)(PCy_3)_2$ (2d) was made according to the same method as for **2c**, using 31 μL (0.3 mmol) of HSPh. The same procedure as before led to a yellow precipitate. Yield: 60%. Anal. Calcd for $RuC_{42}H_{74}SP_2$: C, 65.16; H, 9.63; S, 4.14. Found: C, 64.64; H, 9.69; S, 4.43.

$RuH(S^tBu)(H_2)(PCy_3)_2$ (2e) was made according to the same method as for **2c**, using 34 μL (0.3 mmol) of HS^tBu. The same procedure was followed as before, but as the attempt of recrystallization did not give any precipitate, the solution was evaporated to obtain a brown solid. Anal. Calcd for $RuC_{40}H_{78}SP_2$: C, 63.76; H, 10.35; S, 4.25. Found: C, 62.91; H, 10.31; S, 4.71.

$RuH_2(CO)_2(PCy_3)_2$ (4a). To a suspension of $RuH_2(H_2)_2(PCy_3)_2$ (100 mg, 0.15 mmol) in 10 mL of pentane was bubbled CO during 30 min. The pale yellow solution obtained was then concentrated to 5 mL and cooled to −20 °C overnight to give a white/gray precipitate in 96% yield. Anal. Calcd for $RuC_{38}H_{68}P_2O_2$: C, 63.39; H, 9.52. Found: C, 63.77; H, 9.48.

$RuHI(CO)_2(PCy_3)_2$ (4b) was made according to the same method as for **4a**, using $RuHI(H_2)(PCy_3)_2$ (100 mg, 0.13 mmol). The same procedure gives a white precipitate in 88% yield. Anal. Calcd for $RuC_{38}H_{67}IP_2O_2$: C, 53.96; H, 7.98. Found: C, 53.56; H, 7.86.

$RuHCl(CO)_2(PCy_3)_2$ (4c) was made according to the same method as for **4a**, using $RuHCl(H_2)(PCy_3)_2$ (100 mg, 0.14 mmol). The same procedure gives a white precipitate in 91% yield. Anal. Calcd for $RuC_{38}H_{67}ClP_2O_2$: C, 60.50; H, 8.95. Found: C, 60.83; H, 8.79.

$RuH(SCy)(CO)_2(PCy_3)_2$ (4d) was made according to the same method as for **4a**, using $RuH(SCy)(H_2)(PCy_3)_2$ (100 mg, 0.13 mmol). A white precipitate was obtained in 90% yield. Anal. Calcd for $RuC_{44}H_{78}SP_2O_2$: C, 63.33; H, 9.42; S, 3.84. Found: C, 63.62; H, 9.01; S, 3.42.

$RuH(SPh)(CO)_2(PCy_3)_2$ (4e) was made according to the same method for **4a**, using $RuH(SPh)(H_2)(PCy_3)_2$ (100 mg; 0.13 mmol). A white precipitate was obtained in 83% yield. Anal. Calcd for $RuC_{44}H_{72}SP_2O_2$: C, 63.81; H, 8.76; S, 3.87. Found: C, 64.56; H, 8.72; S, 3.30.

$RuH(S^tBu)(CO)_2(PCy_3)_2$ (4f) was made according to the same method as for **4a**, using $RuH(S^tBu)(H_2)(PCy_3)_2$ (100 mg; 0.13 mmol). A white precipitate was obtained, but the ^1H NMR showed that this is a mixture of **4a** and the expected product as confirmed by the *cis*-dicarbonyl ν_{CO} bands observed in the IR spectrum.

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