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Chemistry of bis(dihydrogen) ruthenium complexes and of their derivatives

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Contents

Abstract

This review is devoted to the chemistry of bis(dihydrogen) complexes. Only a few bis(dihydrogen) complexes have been characterized, among which the three that have been isolated

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in our group, namely $RuH_2(H_2)_2(PCy_3)_2$ **1** and $LRuH(H_2)_2$ (L = hydridotris(3,5-dimethylpyrazolyl) borate, Tp*, **65**; L = hydridotris(3-isopropyl-4-bromo-pyrazolyl)borate, Tp′, **66**). The first part will present in detail the synthesis and characterization of $RuH_2(H_2)_2(PCy_3)_2$. Its reactivity, as well as its use as catalyst precursor, will be extensively reviewed. The second part of this review deals with the chemistry of the hydridotris(pyrazolyl)borato ruthenium complexes. The different reactivity of these two classes of compounds is dominated by the nature of the η^2-H_2 coordination. The nucleophilic character of the hydride and dihydrogen ligands in **1** allows substitution and hydrogen transfer reactions, whereas the reactivity of **65** and **66** is dominated by the electrophilic character of the hydride and dihydrogen ligands. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Dihydrogen compounds; Ruthenium

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1. Introduction

The chemistry of dihydrogen complexes has developed considerably since the first discovery of dihydrogen coordination without dissociation in 1984 [1]. Many different compounds have now been isolated and characterized [2–6]. The coordination of dihydrogen can be achieved on both electrophilic and nucleophilic metal centers. The (M–η^2–H_2) coordination results from a subtle balance between σ donation from H_2 to an empty *d* orbital of the metal and back-donation from a filled *d* metal orbital to H_2 (see Fig. 1). Thus, the choice of ligands around the metals will strongly influence the nature of the (M–η^2–H_2) bond. The two extreme situations are the following: when the metal is highly electrophilic, σ donation is predominant and the coordinated dihydrogen becomes a strong Brønsted acid whereas when the metal center is nucleophilic, the bonding is primarily a result of back-bonding from the electron rich metal center leading to an important lengthening of the H–H bond and to a deactivation of the coordinated dihydrogen ligand. All possible intermediate situations can be found, in particular one in which neither the σ-donation nor the π-back donation will be very efficient which will favour H_2 dissociation and hydrogen transfer [2–6].

Complexes MH_xL_n containing a high number of hydride ligands ($x > 4$) are common, the most hydride-rich complex being K_2ReH_9 which has been known for a long time [7]. The number of complexes containing more than one dihydrogen

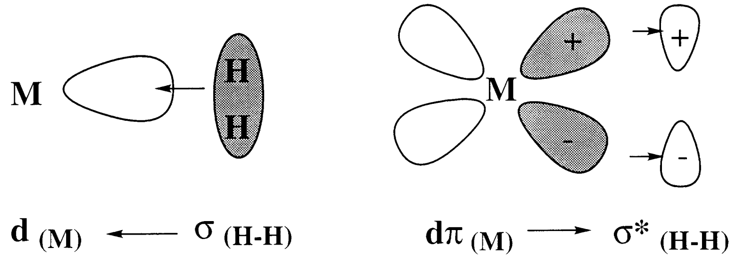


Fig. 1. The bonding picture for an η^2–H_2 complex.

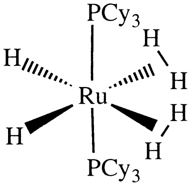
molecule coordinated is, however, very limited. No tris(dihydrogen) complex is known and only a few bis(dihydrogen) complexes have been characterized [8–18]. The first bis(dihydrogen) complex $[IrH_2(H_2)_2(PCy_3)_2]^+$ has been characterized in solution in 1985 by Crabtree and Lavin [13]upon protonation of the neutral precursor $IrH_5(PCy_3)_2$ [13,14]. In our group, we have described the three so far isolated bis dihydrogen complexes, namely $RuH_2(H_2)_2(PCy_3)_2$ and $LRuH(H_2)_2$ (L= hydridotris(3,5-dimethylpyrazolyl) borate, Tp*; L=hydridotris(3-isopropyl-4-bromo-pyrazolyl)borate, Tp′) [8–12]. $Cr(CO)_4(H_2)_2$ has been observed in an argon matrix or in liquid xenon. It has been characterized by infrared spectroscopy [15,16]. In the osmium chemistry the complex $OsH_4Cl_2(P^iPr_3)_2$, obtained by addition of H_2 on $OsH_2Cl_2(P^iPr_3)_2$, exists in solution as a mixture of $Os(H_2)_2Cl_2(P^iPr_3)_2$ and $OsH_2(H_2)Cl_2(P^iPr_3)_2$, and the dicationic complex $[Os(H_2)_2(NCMe)_2(P^iPr_3)_2]^{2+}$ was characterized after protonation of $[OsH_3(NCMe)_2(P^iPr_3)_2]^+$ [17,18]. A number of unstable bis(dihydrogen) ruthenium complexes have also been prepared when studying the reactivity of $RuH_2(H_2)_2(PCy_3)_2$; they will be described hereafter.

We will present in this review the synthesis of the three thermally stable bis(dihydrogen) complexes, all involving ruthenium and prepared in our group. Their characterization by different spectroscopic techniques, their reactivity and some catalytic applications will be described.

2. $RuH_2(H_2)_2(PCy_3)_2$

2.1. Synthesis

The use of tricyclohexylphosphine was crucial in order to synthesize the bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$ (**1**). Steric and electronic properties (cone angle: 170°, pK_a: 9.7) allow the stabilization of the octahedral ruthenium (II) complex. In addition, we will also see (Section 2.3.7Section 2.3.8) that this phosphine plays an important role in hydrogen transfer reactions and very active species result from the partial dehydrogenation of one or more cyclohexyl rings of the starting phosphine.



1

Complex **1** was first reported in 1982 as the result of the hydrogenation of Ru(COD)(COT) in the presence of 2 equiv of PCy_3. The reaction is carried out at room temperature, in pentane and in the presence of bubbling dihydrogen. This procedure leads to the precipitation of the pure complex as a white powder which could be recrystallized from toluene/pentane to give colourless crystals [8–10]. This reaction was attempted with several other phosphine ligands. Spectroscopic evidence for the presence of a similar bis(dihydrogen) complex was obtained when using PPh_3 and P^iPr_3 but the complexes rapidly lose dihydrogen and transform into the dinuclear derivatives $Ru_2H_4(H_2)(PR_3)_4$ (R = Ph, ^{i}Pr) [19]. Upon carrying out the reaction under 3 bar H_2, the complex $RuH_2(H_2)_2(PCy_3)_2$ could be isolated within 1 h. in 89% yield [20]. This preparation from Ru(COD)(COT) is very smooth and leads directly to a pure complex. However, alternative synthesis have been recently proposed by Beatty and Paciello [21] and Belderrain and Grubbs [22] which avoid the intermediacy of Ru(COD)(COT). In each case, they obtained a yellow powder characterized as $RuH_2(H_2)_2(PCy_3)_2$.

2.2. Characterization

Complex **1** was first formulated as $RuH_6(PCy_3)_2$ since at that time the discovery of Kubas had not yet been reported. It was reformulated in 1988 as a bis(dihydrogen) dihydride, the first thermally stable bis(dihydrogen) complex [8–10]. The infrared spectrum of the complex shows two strong Ru–H bands of equal intensity at 1927 and 1890 cm^{-1}. This feature seemed first anomalous for a hexahydride but is coherent with a *cis*-dihydride formulation. The intensity of these bands is also astonishing but can be probably understood in terms of coupling between the Ru–H, Ru–H_2 and perhaps H–H modes as in $LRuH(H_2)_2$ (vide infra). The ^1H NMR spectrum shows a single signal at high field for the hydride and dihydrogen ligands in rapid exchange, down to 173 K in toluene d_8 and 130 K in a freon mixture. This signal displays at room temperature a triplet pattern at δ -7.9(C_6D_6; $J_{P\text{-}H} = 7$ Hz) and a minimum T_1 relaxation time of 28 ms at 203 K (250 MHz) in agreement with the proposed formulation. The two phosphorus are equivalent as evidenced by the single line observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 76.5 (C_6D_6). Unfortunately no X-ray or neutron structure of this compound is available. Several attempts at characterization by X-ray crystallography led to the refinement of the ruthenium and of the two *trans* tricyclohexylphosphine groups but not to the location of the disordered hydride and dihydrogen ligands. This can result from the presence of dynamic processes, even in the solid state. An inelastic neutron scattering spectrum obtained at 1.5 K shows the presence of the characteristic pair of bands at ± 4.7 cm^{-1} compared with the elastic peak [23]. This is a signature of the presence of the dihydrogen ligands and can be interpreted in terms of planar rotation of dihydrogen in a double minimum well with a rotation barrier of 1.1 kcal mol^{-1}. In this complex, a structure is observed in the inelastic peaks, the interpretation of which is not yet certain but could be due to the presence of the two dihydrogen ligands. The presence of a quasielastic line appearing at higher temperature can result from the rapid hydride/dihydrogen fluxionality. DFT/B3LYP calculations carried out on the model compound $RuH_2(H_2)_2(PH_3)_2$ suggest a *cis*-dihydride, *cis*-dihydrogen structure with the two dihydrogen ligands lying in the equatorial plane, an H–H distance of ca. 0.85 Å and a rotation barrier of dihydrogen of ca.

1 kcal mol^{-1}. These calculations are in agreement with the NMR and INS results [23].

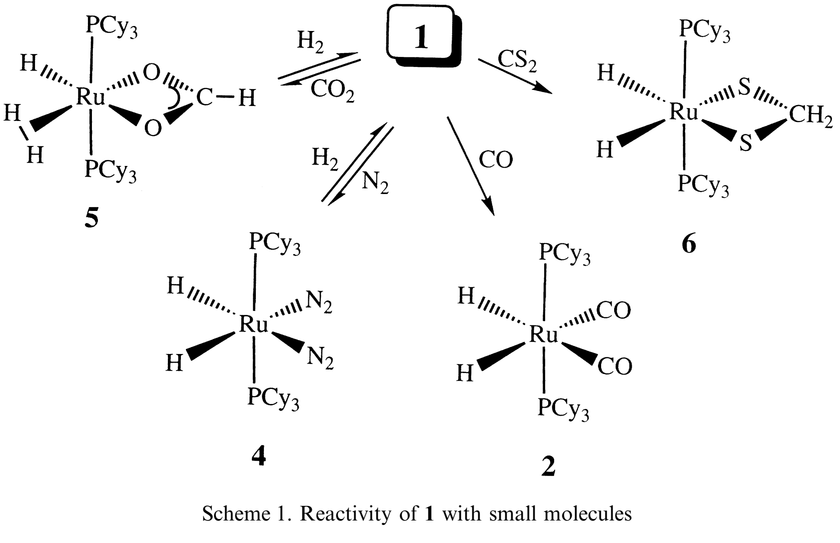
2.3. Reactivity

2.3.1. Small molecules

In order to characterize more precisely the coordination of dihydrogen in $RuH_2(H_2)_2(PCy_3)_2$ (**1**), we have attempted several reactions with small molecules (see Scheme 1). CO reacts easily with **1**, as expected, to give the new *cis* dihydrido *cis* dicarbonyl complex $RuH_2(CO)_2(PCy_3)_2$ (**2**) [24]. Prolonged reaction leads to the formation of the ruthenium (0) complex $Ru(CO)_3(PCy_3)_2$ (**3**).

A similar reaction occurs with dinitrogen leading to the bis(dinitrogen) complex $RuH_2(N_2)_2(PCy_3)_2$ (**4**) [25,26]. The complex is characterized by two N–N stretching frequencies at 2163 and 2126 cm^{-1} in agreement with a *cis*-bis(dinitrogen) configuration. Morris has proposed an analogy between dihydrogen and dinitrogen coordination to a transition metal, estimating that dihydrogen complexes could exist when the corresponding dinitrogen derivatives display N–N stretches between 2150 and 2060 cm^{-1} [27]. This is in agreement with the values found for **4**. The reaction is reversible and bubbling H_2 into a solution of **4** rapidly regenerates **1**.

1 also reacts rapidly with carbon dioxide to give the insertion product $RuH(H_2)(CO_2H)(PCy_3)_2$ (**5**) which contains a hydride and a dihydrogen ligand [26]. A single resonance is observed for the hydride and dihydrogen ligands down to 173 K. This absence of decoalescence is characteristic of *cis* hydrido dihydrogen compounds and only a few static spectra have been reported [13,14,28]. The dihydrogen ligand in this complex is stretched as deduced from the relatively high value of T_1 minimum (35 ms at 243 K). This is again typical for this kind of hydrido dihydrogen complexes (vide infra). This insertion is reversible and bubbling H_2 into



Scheme 1. Reactivity of **1** with small molecules

a solution of **5** regenerates **1**. The reaction is, however, much slower than the **4**→**1** conversion.

The reaction of **1** with CS_2 leads after a double insertion to $RuH_2(S_2CH_2)(PCy_3)_2$ (**6**). In contrast with the previous complex, **6** is a dihydride of ruthenium (IV). This is deduced from the large $J_{H\text{-}P}$ coupling constant for the hydrides (33 Hz), the high T_1 minimum value (134 ms) and the observation of the methylene group linked to sulfur (^1H NMR: δ 6.17; ^{13}C NMR: δ 64.6 (*t*, $J_{C\text{-}H}$ 147 Hz). The reaction is not reversible in this case. The difference in reactivity between CO_2 and CS_2 probably results from the greater affinity of ruthenium for sulfur [26].

2.3.2. Halogenated compounds

$RuH_2(H_2)_2(PCy_3)_2$ reacts with halogenated compounds (1 equiv of CH_3I or 2 equiv of CH_2Cl_2) to give, through a sequence of substitution/addition, the hydrido dihydrogen derivatives $RuH(H_2)X(PCy_3)_2$ (X = I, **7**; X = Cl; **8**) [29,24]. Complexes **7** and **8** were the first characterized 16 electron dihydrogen complexes. The X-ray crystal structure of **7** (see Fig. 2) carried out at low temperature shows the presence of a long H–H bonding distance [1.03 (7) Å] in agreement with the T_1 minimum value of 28 ms at 218 K (250 MHz). Complexes **7** and **8** are characterized by a single signal for the hydride and dihydrogen ligand at δ −16.8 ($J_{P\text{-}H}$ ca. 11 Hz). No decoalescence is observed down to 130 K. Addition of dihydrogen to the solution leads to a broadening and a downfield shift of the hydride signal. Fig. 3 shows a ^1H NMR spectrum of **7** carried out in CD_2Cl_2 under a pressure of 6 bar H_2. A mean peak is observed at room temperature near δ −12. This signal decoalesces at

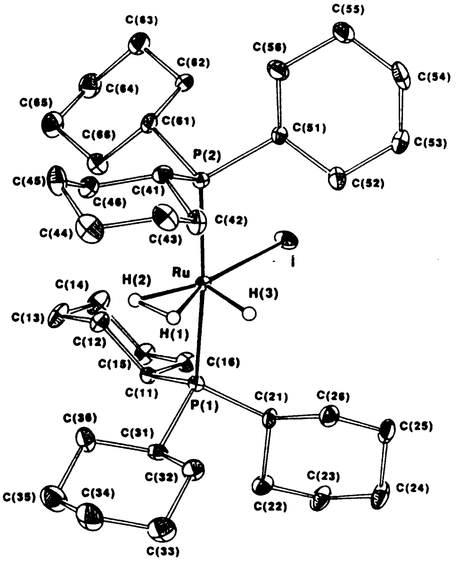


Fig. 2. The structure of the first 16 electron dihydrogen complex **7**.

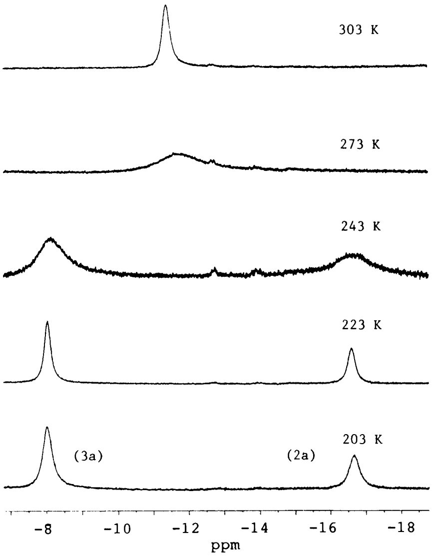
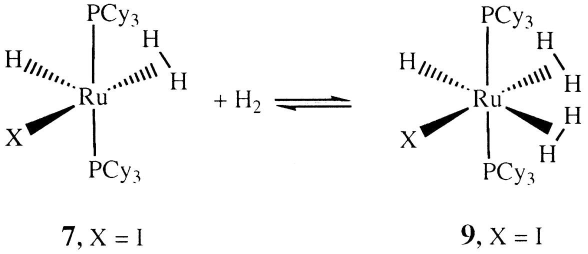


Fig. 3. ^1H NMR spectra of **7** in CD_2Cl_2 under 6 bar H_2 at various temperatures.

low temperature and at 203 K two signals are observed, respectively, at δ −16.9 for **7** and at δ −7.9 for a new compound $RuHI(H_2)_2(PCy_3)_2$ (**9**). When releasing the pressure in the NMR tube the signal for **9** decreases in intensity to give back eventually pure **7**. This phenomenon is due to a rapid equilibrium between $RuHI(H_2)(PCy_3)_2$ and the unstable bis(dihydrogen) complex $RuHI(H_2)_2(PCy_3)_2$. The same observation can be made using **8** (see Scheme 2). It is interesting to note that the replacement of the very good σ-donor hydride ligand by a π-donor chloride or iodide leads to the destabilization of dihydrogen coordination and a preference for a 16 electron configuration. This could be due to the presence of "partially multiple bonding" between the halide and the metal as proposed in another system by Eisenstein [30].

The corresponding P^iPr_3 complexes, namely $RuHI(H_2)(P^iPr_3)_2$ (**10**) and $RuHCl(H_2)(P^iPr_3)_2$ (**11**), were prepared through a one pot reaction from



7, X = I
8, X = Cl

9, X = I
9', X = Cl

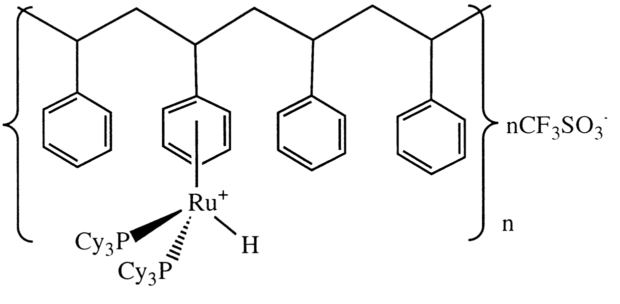
Scheme 2. Equilibrium between 16 and 18 electron dihydrogen complexes

Ru(COD)(COT) and P^iPr_3 in the presence of CH_3I or CH_2Cl_2 under 4 bar H_2 [19]. The reason for this study was to obtain good NMR data using complexes displaying a shorter correlation time than **7** or **8** and therefore to determine whether in solution the complexes adopt the same hydrido(dihydrogen) structure. Also to determine whether the steric effect of the phosphine would play a role. Calculation of the coordinated H–H bond distance, using T_1 data and taking into account the effects of the other ligands, produced a value of 1.02 (3) Å in **10** close to the value of 1.03 (7) Å found for **7**. A H–D coupling of 13.5 Hz could be calculated within the dihydrogen molecule in agreement with the proposed structure. No significant difference is therefore present between **7** and **10**.

Caulton [31] recently found that further reaction between **1** and CH_2Cl_2 occurs in pentane to lead to the carbene complex $RuCl_2(=CH_2)(PCy_3)_2$ (**12**) originally prepared by Grubbs and coworkers [32]. This route does not, however, provide a pure complex (contamination with **8**). We have found that in freons ($CDCl_3$: $CDFCl_2$: $CDF_2Cl = 1:5:5$), **1** transformed into a mixture containing **8** and a new complex of ruthenium IV: $RuH_2Cl_2(PCy_3)_2$ (**13**). This latter complex can be isolated in 60% yield by addition of 2 equiv of HCl to **1** [23]. A similar complex containing triisopropylphosphine has recently been reported by Werner et al. [33]. Complex **13** contains a non-linear P–Ru–P arrangement and exists as a mixture of rapidly interconverting isomers which were identified by low temperature NMR studies.

2.3.3. Strong acids and carboxylic acids

Protonation of **1** by strong acids leads to extensive evolution of dihydrogen and formation of $[Ru(H_2O)_5(PCy_3)](BF_4)_2$ (**14**), $[RuH(PCy_3)_2(\eta^6\text{-}C_6H_5CH_3)](BF_4)$ (**15**) and $Ru[(HO)_2PO_2]_2(PCy_3)_2$ (**16**) when using, respectively, $HBF_4 \cdot H_2O$, $HBF_4 \cdot Et_2O$ in toluene and H_3PO_4 [8,34,35]. No complex could be isolated when protonating **1** with $HBF_4 \cdot Et_2O$ in other organic solvents, even at very low temperature. As an extension of the toluene reaction, the possibility of arene coordination to the metal center was used to prepare a soluble polystyrene–ruthenium complex (**17**) in which 25% of the phenyl rings are attached to a "$[RuH(PCy_3)_2]^+$" moiety [36].



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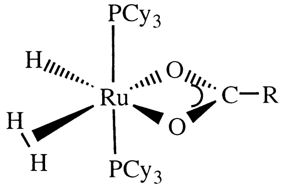
When carboxylic acids are employed, a series of hydrido dihydrogen derivatives could be isolated: $RuH(H_2)(OCOR)(PCy_3)_2$ ($R = CH_3$, **18**; $R = C_6H_5$, **19**;

R = CF_3, **20**) [34,35]. The analogous propionate complex, namely $RuH(H_2)(OCOEt)(PCy_3)_2$ (**21**) has been obtained by addition of 2 equiv of methyl acrylate to **1** [20].



18, R = Me; **19**, R = Ph; **20**, R = CF_3; **21**, R = Et

Complexes **18**, **19** and **21** display a long T_1 minimum of ca. 35 ms near 243 K (250 MHz) in agreement with the presence of an elongated H–H distance of ca. 1.1–1.2 Å. The X-ray crystal structure of **21** is also in agreement with the elongation of the H–H bond (see Fig. 4) [20]. Complex **20** on the other hand shows a more reduced T_1 minimum, 15 ms at 230 K. This is indicative of the presence of a less elongated H–H bond as a result of a decrease of the electron density on the ruthenium center. Complex **20** can give rise to a second addition of CF_3COOH to give $RuH_2(OCOCF_3)_2(PCy_3)_2$ (**22**) which adopts a ruthenium IV dihydride structure in the ground state but for which NMR studies suggest an equilibrium with a dihydrogen isomer [34,35]. It is interesting to mention that complexes **18**–**21** are very stable and little reactive. **18** can for example be heated at 100 °C for one day in the presence of an olefin without noticeable changes. This probably results from deactivation of the dihydrogen ligand through back-donation from the metal center.

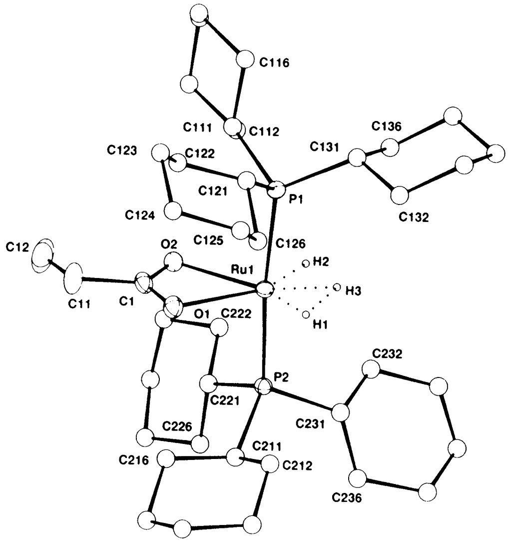
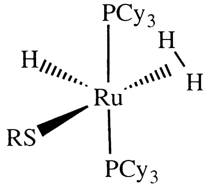


Fig. 4. The structure of the hydrido dihydrogen propionato complex **21**.

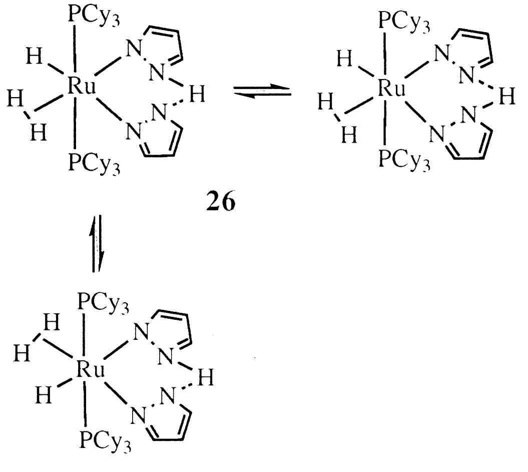
2.3.4. Weak acids

Weak acids such as thiols, pyrazol and phenol react with **1** to give a protonation reaction followed by loss of H_2. The reaction with thiols leads to a new series of 16 electron dihydrogen derivatives $RuH(H_2)(SR)(PCy_3)_2$ (R = Cy, **23**, R = Ph, **24**; R = ^{t}Bu, **25**) similar to **7** and **8** [24]. Relaxation NMR data indicate a further lengthening of the coordinated dihydrogen ligand but in contrast to **7** and **8**, **23** and **24** do not show any apparent reaction with dihydrogen besides H/D exchange. However, addition of H_2 to **25** rapidly regenerates **1**.



23, R = Cy; **24**, R = Ph; **25**, R = ^{t}Bu

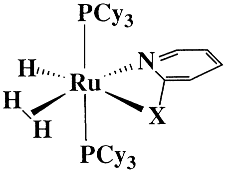
A similar reaction proceeds with pyrazol but an additional pyrazol molecule binds to the ruthenium center to yield $RuH(H_2)(NNC_3H_3)(NNHC_3H_3)(PCy_3)_2$ (**26**) [26]. In this complex, two fluxional processes coexist involving proton and hydride transfer which have both low energy barriers (see). In the case of phenol, the protonation is followed by coordination of the ruthenium center to the π-system of the ring to give $RuH(\eta^5\text{-}C_6H_5O)(PCy_3)_2$ (**27**) similar to complexes prepared in the 70s by Wilkinson and colleagues. This complex adds dihydrogen (1 bar) at 80 °C to give $RuH_2(\eta^6\text{-}C_6H_5OH)(PCy_3)$ (**28**). This is a rare case of heterolytic splitting of dihydrogen involving an oxygen group [26].



Scheme 3. Fluxional processes within **26**

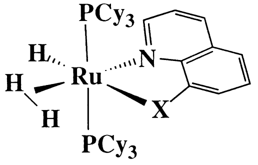
2.3.5. Activation of C–H, N–H and O–H bonds in bidentate systems

The reaction of **1** with the bidentate ligands L-XH yields the hydrido dihydrogen derivatives $RuH(H_2)(L\text{-}X)(PCy_3)_2$ ($L = py = C_5H_4N$: $X = O$, **29**; $X = NH$, **30**. $L = quin = C_9H_6XH$: $X = O$, **31**; $X = NH$, **32**) in which the good σ-donating properties of the amino or hydroxo pyridine and quinoline ligands induce a further important elongation of the H–H bond [37].



29, X = O

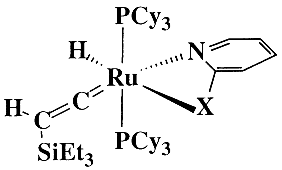
30, X = NH



31, X = O

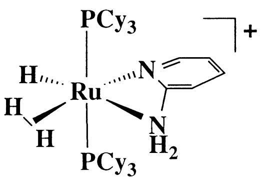
32, X = NH

We were interested in obtaining complexes with very long H–H bonds, in particular for studying their spectroscopic properties. Thus, elongation of the H–H bond is a result of a strong back-bonding from the metal which will also lead to a large rotation barrier for coordinated dihydrogen. This barrier could lead to the observation of quantum mechanical exchange coupling between the hydrogen atoms of the dihydrogen molecule. T_1 data (minimum of 36 ms at 240 K) and the H–D coupling constant (9 Hz) suggest an H–H distance of ca. 1.27 Å for **30**. This is one of the longest H–H distance determined for dihydrogen complexes. Distances of 1.357 and 1.34 Å have been accurately determined by neutron diffraction in $ReH_7[P(p\text{-}C_6H_4CH_3)_3]_2$ [38] and $[Os(H_2)(OAc)(en)_2]^+$ ($en = H_2NC_2H_4NH_2$) [39]. It is difficult to imagine what kind of H–H bonding is present in such species. Nevertheless, the complexes were fluxional down to 170 K and we did not find any evidence for the presence of exchange couplings. **29** and **30** are not highly reactive but do react slowly at room temperature with $CH_2{=}CH(SiEt_3)$ to give the hydrido vinylidene species $RuH({=}C{=}CHSiEt_3)(py\text{-}X)(PCy_3)_2$ ($X = O$, **33**; $X = NH$, **34**). The formation of such vinylidene derivatives in this process is unusual and could re sult from α–C–H activation. Protonation of **30** occurs on nitrogen to give $[RuH(H_2)(py\text{-}NH_2)(PCy_3)_2][B(C_6F_5)_4]$ (**35**) whereas protonation of **29** occurs on the hydrides, but is followed by extensive evolution of dihydrogen and decomposition [40].



33, X = O

34, X = NH



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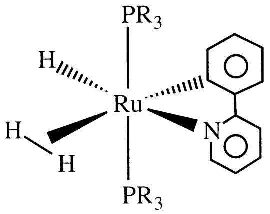
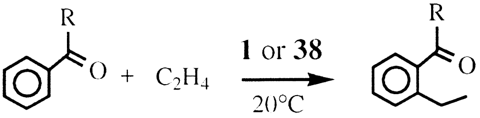
The same type of reaction is possible with phenylpyridine yielding a poorly soluble compound $RuH(H_2)(C_6H_4\text{-py})(PCy_3)_2$ (**36**). The analogous and more soluble complex $RuH(H_2)(C_6H_4\text{-py})(P^iPr_3)_2$ (**37**) was prepared directly from Ru(COD)(COT), P^iPr_3, H_2 and phenylpyridine [41]. This complex is specially interesting due to both the presence of its hydrido dihydrogen ligands and the orthometallated phenylpyridine group.



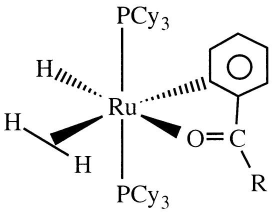
36, R = PCy_3
37, R = P^iPr_3

Indeed, **37** presents a rather common H–H bond distance value, 1.08 Å, as deduced from spectroscopic data, but it is, however, the first one in the series of hydrido dihydrogen complexes presented in this review, on which it was possible to observe a decoalescence between the hydride and the dihydrogen signal. The broad triplet observed at room temperature at δ −8.59 ($J_{P\text{-}H} = 12$ Hz) decoalesces into an AB_2 system at δ −12.1 and δ −6.1. Furthermore, the complex displays, below the coalescence temperature, quantum exchange couplings between the hydride and the dihydrogen group ($J_{H\text{-}H} = 308$ Hz at 218 K). This is the first observation of such a phenomenon and its origin is so far unclear. It could result from the presence of two rotation barriers in the complex, one being 40 kJ mol^{-1} as determined by lineshape analysis and the other much lower (see Fig. 5). In addition, complex **37** contains an orthometallated phenylpyridine as evidenced in particular by the triplet observed in the ^{13}C NMR spectrum at δ 197, ($J_{P\text{-}C} = 10.6$ Hz) [41]. Complexes of this type have been proposed by Murai to be intermediates in the reaction of insertion of olefins into aromatic C–H bonds catalysed by ruthenium complexes [42,43]. These reactions occur in α-position relative to a functional group, generally a ketone. This led us to prepare the new complexes $RuH(H_2)(C_6H_4\text{-COR})(PCy_3)_2$ (R = Me, **38**; R = Ph, **39**) containing orthometallated ketones by reacting **1** with PhCOR.

These compounds also show a decoalescence of the hydride signal and quantum exchange couplings at low temperature. The most salient feature of these compounds is, however, that they catalyse at room temperature the alkylation of aromatic C–H



Scheme 4. Catalytic C–C bond coupling



38, R = Me
39, R = Ph

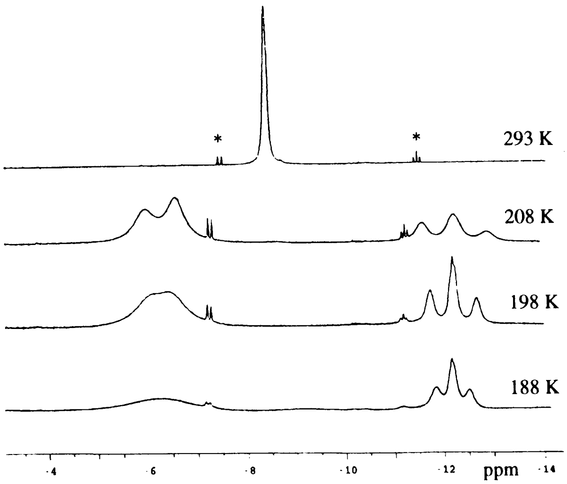


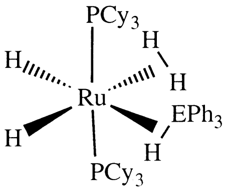
Fig. 5. ^{1}H NMR spectra at various temperatures of **37** in C_7D_8, showing exchange couplings between the hydride and the dihydrogen ligands.

bonds by ethylene or vinyltriethoxysilane (see Scheme 4) [41]. This reaction can be of great synthetic interest and its scope is presently studied.

2.3.6. *Activation of Si–H, Ge–H and B–H bonds*

2.3.6.1. Silanes (germanes) and disilanes. The ease of dihydrogen elimination from **1** can drive substitution reaction and promote coordination of substrates which are weakly coordinating ligands. This strategy was used to coordinate silanes, as Si–H activation is an obligatory step in many transition-metal-mediated transformations of organosilanes. One or two dihydrogen ligands can be substituted depending on the nature of the added substrate and we will see that σ E–H bonds (E = Si, Ge) are highly favored over the formation of Ru–E bonds. In the case of monosilanes, monosubstitution is generally achieved. Thus, addition of 1 equiv of

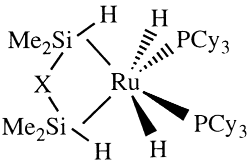
$HSiPh_3$ leads rapidly to the formation of the substitution complex $RuH_2(\eta^2-H_2)(\eta^2-H-SiPh_3)(PCy_3)_2$ (**40**). When starting with the germane $HGePh_3$, the analogous complex $RuH_2(\eta^2-H_2)(\eta^2-H-GePh_3)(PCy_3)_2$ (**41**) was isolated [25].



40, E = Si; **41**, E = Ge

The five different ruthenium bound hydrogens exchange rapidly in the NMR time scale in the case of **40**. No decoalescence of the "hydride" signal was observed down to 173 K. In the case of **41** the germanium bound hydride is found at δ −3.5 whereas the four other hydrogen resonate at δ −8.4 (T_1 min: 17 ms at 263 K). The difference of stability between **40** and **41** can be illustrated by their reactivity towards dinitrogen. Whereas **40** reacts rapidly to give $RuH_2(N_2)_2(PCy_3)_2$ (**4**), **41** exchanges its dihydrogen ligand first to give $RuH_2(N_2)(HGePh_3)(PCy_3)_2$ (**42**). In the case of monosilanes, substitution of the two dihydrogen ligands is observed when using triethoxysilane instead of triphenylsilane, and the new complex $RuH_2[HSi(OEt)_3]_2(PCy_3)_2$ (**43**) can be characterized [44].

When disilanes are used, substitution of the two dihydrogen ligands is easily achieved and we could isolate the first examples of a transition metal complex, where two H–Si bonds are η^2-coordinated to the metal [45].Thus, **1** reacts with the disilanes $(HSiMe_2)_2X$ ($X{=}O$, C_2H_4, C_6H_4) to give $RuH_2[(\eta^2-HSiMe_2)_2X](PCy_3)_2$ ($X{=}O$, **44**; $X{=}C_2H_4$, **45**; $X{=}C_6H_4$, **46**). The chelating effect is responsible for the stabilization of these compounds.



44, X = O; **45**, X = C_2H_4; **46**, X = C_6H_4

This is even more important in the case of the rigid $(HSiMe_2)_2C_6H_4$ compared with the disiloxane $(HSiMe_2)_2O$ as evidenced by the reactivity studies (see below). Complexes **45** and **46** were characterized by X-ray crystallography [44,45]. As can be seen on Fig. 6, the two phosphines are in the plane perpendicular to the bis(silane) ligand. They are now in a *cis* configuration which is quite rare for the bulky PCy_3. As expected the Si(1)–H(1) and Si(2)–H(2) bond lengths [1.88(3) and 1.83(3) Å,

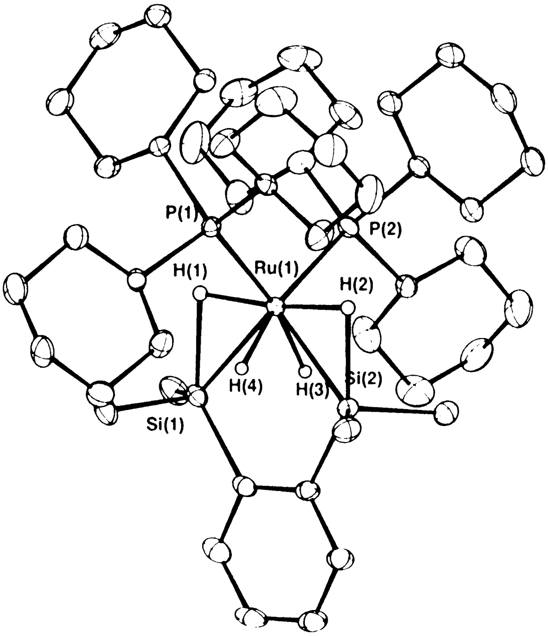
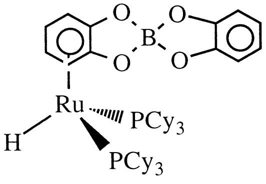


Fig. 6. The structure of **46**, the first complex with two σ Si–H bonds.

respectively] indicate significant Si–H bond lengthening which suggests substantial Ru (dπ) to Si–H (σ*) back-donation. The η^2–H–Si coordination is further confirmed by NMR and IR data. For example, in the case of **46**, the ^{29}Si {^{31}P} INEPT ^{1}H spectrum at 288 K shows a doublet at δ 4.8 with a $J_{\text{Si-H}}$ value of 63 Hz: this value is highly reduced compared with the $^1J_{\text{Si}-\text{H}}$ (190 Hz) in the free disilane and is thus the signature for an η^2–H–Si interaction. The IR spectrum (Nujol mulls) displays one broad Ru–(η^2–H–Si) band at 1778 cm^{-1} (2125 cm^{-1} in the free disilane). In the case of **44**, the stretching of the H–Si bond is even more pronounced as evidenced by the $J_{\text{Si-H}}$ value of 22 Hz and the $\nu_{\text{Ru}-(\eta^2-\text{H}-\text{Si})}$ band at 1699 cm^{-1}. In addition, these compounds present interesting exchange processes. For example, the ^{1}H NMR spectrum of **46** shows at 296 K in the hydride region a triplet at δ −7.74 for the two η^2-bound Si–H protons with $J_{\text{P-H}} = 13$ Hz and an AA′XX′ multiplet at δ −12.03 for the two hydrides. On warming, these two signals coalesce at 355 K, leading to one broad signal at δ −9.9. This exchange is characterized by a 64.5 kJ/mol barrier. In the case of **44** the exchange process between the classical hydrides and the two η^2 H–Si is characterized by a $\Delta G^{\ddagger}$ of 47.5 kJ/mol, thus much lower than that for **46**. Reactivity studies confirm that in **44** the disiloxane ligand is weakly bonded to the ruthenium: the less rigid disiloxane ligand favors substitution reactions. For example, substitution of the (η^2-HSiMe$_2$)$_2$O ligand in **44** is easily achieved by bubbling H_2 or CO: free disiloxane is recovered and **1** or RuH$_2$(CO)$_2$(PCy$_3$)$_2$ are respectively isolated in quantitative yield. But, no substitution of the rigid bis(silane) ligand could be achieved when bubbling H_2 or CO to **46** [45].

The study of this new family of compounds is at its early stage and further investigations on Si–H activation are currently underway in our group. Future efforts will be directed toward the synthesis of new species using functionalized polysilanes, with new catalytic applications in mind. Preliminary catalytic results have already been obtained and are described in Section 2.3.8.

2.3.6.2. Boranes. We have attempted to activate B–H bonds by studying the reactivity of **1** towards two boron compounds [46]. In the case of $HBO_2C_6H_4$ (HBcat), the zwitterionic derivative $RuH(\eta^6\text{-}C_6H_4O_2BO_2C_6H_4)(PCy_3)_2$ (**47**) was obtained. It results from redistribution of substituents at boron and contains a π-coordinated catechol ring. The reaction of **1** with 9-borabicyclo [3.3.1] nonane (HBBN) yields the first example of a 16 electron borohydride complex $RuH(H_2BBN)(PCy_3)_2$ (**48**). It reacts with excess dihydrogen to give back **1**, but the intermediate hydrido borohydride dihydrogen complex $RuH(H_2BBN)(H_2)(PCy_3)_2$ (**49**) could be characterized.



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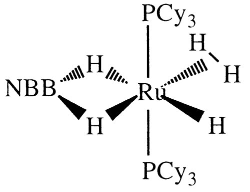

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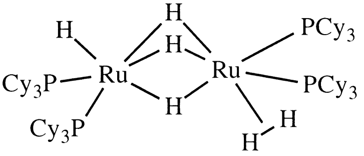
Oxidative addition of water to ruthenium could be promoted by adding HBBN in the presence of H_2O to **1**. The hydrido hydroxo complex $RuH(OH)(PCy_3)_2(H_2O)$ (**50**) was obtained which in turn reacts with H_2 to give first $RuH(OH)(H_2)(PCy_3)_2(H_2O)$ (**51**), a complex incorporating an elongated H–H bond, and ultimately **1**. This indicates the thermodynamic preference for the ruthenium dihydrides to bind dihydrogen rather than water and is in agreement with the lack of reactivity of **1** with water.

2.3.7. Thermal reactions and reactions with olefins

$RuH_2(H_2)_2(PCy_3)_2$ is not very stable thermally and slowly looses H_2 in solution in aromatic solvents to give the bright red dimer $Ru_2H(\mu\text{-}H)_3(H_2)(PCy_3)_4$ (**52**).

The analogous derivative $Ru_2H(\mu\text{-}H)_3(H_2)(PPh_3)_4$ has been reported. It reacts



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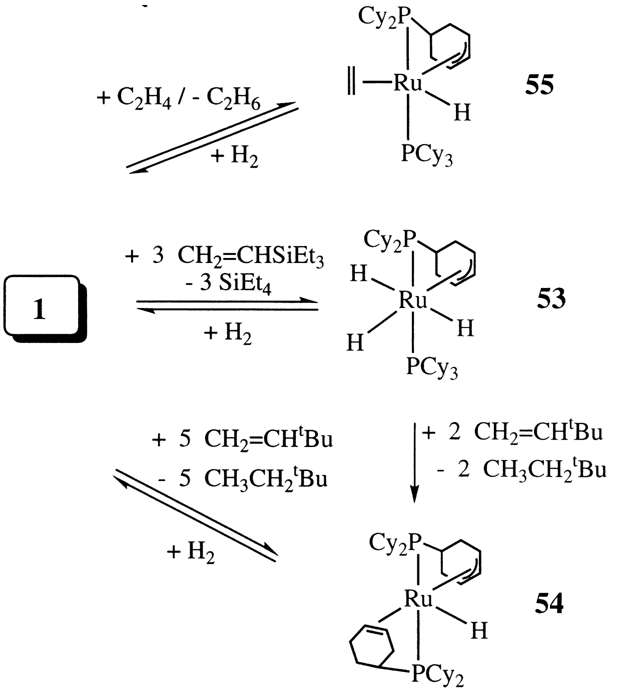
with dinitrogen to yield $Ru_2H(\mu\text{-}H)_3(N_2)(PPh_3)_4$, the X-ray crystal structure of which has been determined [47]. If, however, complex **1** is heated in the solid state under a stream of helium, evolution of H_2 starts at ca. 70 °C with two maxima at 110 and 140 °C corresponding to the loss of six hydrogen atoms followed by the loss of five further hydrogen atoms. Analysis of the hydrocarbons evolved during the thermolysis process evidenced an onset of the decomposition process slightly above 100 °C to give essentially a mixture of cyclohexene and benzene [48]. Analysis of the products remaining after the first loss revealed the presence of two complexes resulting from the dehydrogenation of PCy_3, namely $RuH_3[(\eta^3\text{-}C_6H_8)PCy_2](PCy_3)$ (**53**) and $RuH[(\eta^3\text{-}C_6H_8)PCy_2][(\eta^2\text{-}C_6H_9)PCy_2]$ (**54**). Both **53** and **54** had been previously obtained in solution upon reacting **1** with olefines (vide infra and). Interestingly the first step of the dehydrogenation reaction is reversible in the solid state, since exposing the system to gaseous dihydrogen leads to the reformation of **1** [48].



Scheme 5. Hydrogen transfer reaction.

Dehydrogenation can be achieved in solution upon reacting **1** with various olefines [20]. Thus, the reaction of **1** with ethylene yields the ethylene complex $RuH(C_2H_4)[(\eta^3\text{-}C_6H_8)PCy_2](PCy_3)$ (**55**) in which one cyclohexyl has been dehydrogenated to give rise to an allyl ligand (see Scheme 5) [49]. This new $(\eta^3\text{-}C_6H_8)PCy_2$ ligand is isoelectronic with the well-known cyclopentadienyl ligand. It is, however, much more electron rich and much more bulky which will confere to the transition metal center a very high reactivity. Similar reactions are possible with more bulky olefins such as ${}^{t}BuCH=CH_2$ and $Et_3SiCH=CH_2$ (see Scheme 5). In that case, the reaction depends on the stoichiometry of the added olefin [20]. In the presence of three equiv of a bulky olefin, the ruthenium IV trihydride $RuH_3[(\eta^3\text{-}C_6H_8)PCy_2](PCy_3)$ (**53**) is obtained whereas in the presence of 5 or more equiv of olefin a complex in which both PCy_3 ligands are dehydrogenated, namely $RuH[(\eta^3\text{-}C_6H_8)PCy_2][(\eta^2\text{-}C_6H_9)PCy_2]$ (**54**), is formed, thus demonstrating the ability of **1** to transfer up to 5 mols of dihydrogen to organic substrates. The reaction can be cycled several times without decomposition. Support for structures **53–55** is provided by NMR data and in the case of **54** by an X-ray determination (see Fig. 7) [50]. **53** and **54** undergo very rapid H–D exchange in deuterated solvents and addition of H_2 at room temperature and ambient pressure to **53–55** immediatly yields back **1**, hence making this complex "dihydrogen sponge" [20]. **53, 54** illustrate the versatile structures which can be elaborated starting with tricyclohexylphosphine. Further studies show that a wide range of compounds can be obtained with for example two $(\eta^3\text{-}C_6H_8)PCy_2$ or two $(\eta^2\text{-}C_6H_9)PCy_2$ ligands within the same molecule [50].

Functionalized alkenes also react with **1**, but according to a different pathway. Thus, methyl acrylate and dimethyl fumarate yield the products resulting from the demethylation of an ester function namely $RuH(H_2)(OCOEt)(PCy_3)_2$ (**21**), characterized by X-ray crystallography as already mentioned (see Fig. 4) and

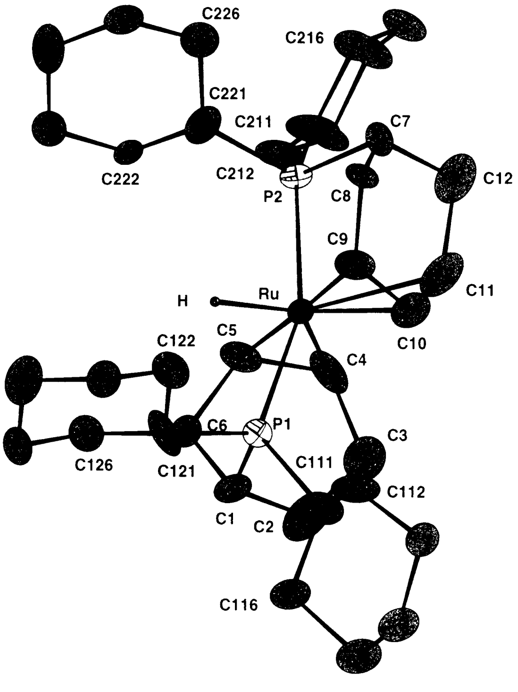
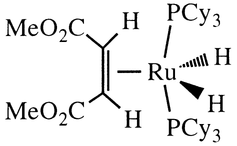


Fig. 7. The structure of **54**, showing the $(\eta^3\text{-}C_6H_8)PCy_2$ and the $(\eta^2\text{-}C_6H_9)PCy_2$ ligands.

$RuH(H_2)(OCOCH_2CH_2CO_2Me)(PCy_3)_2$ (**56**). However, the reaction with dimethyl maleate (the *cis*-isomer of dimethyl fumarate) produces the fluxional dihydride $RuH_2(MeOCOCH{=}CHCO_2Me)(PCy_3)_2$ (**57**). Fast rotation of the alkene is observed at room temperature, but at low temperature, the rotation is blocked which allows coordination to ruthenium of one oxygen of the CO group of an ester function. The rotation barrier for this process is ca. 10 kcal/mol. **57** catalyses both the hydrogenation of dimethylmaleate and the isomerization of dimethyl maleate into dimethyl fumarate in mild conditions [20].



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1 has been shown to react with excess cyclopentene to give the hydrido cyclopentadienyl complex $RuH(C_5H_5)(PCy_3)_2$ (**58**) through hydrogen transfer [51]. Dehydrogenation of cyclopentane by **1** in the presence of $^tBuCH{=}CH_2$ was also attempted at 110 °C. The reaction leads to some cyclopentadienyl derivatives, but is not clean. However, we found during these studies that cyclohexanone could be dehydrogenated by **1**, in the presence or, more interestingly, in the absence of an hydrogen acceptor such as $^tBuCH{=}CH_2$ yielding $Ru(\eta^5\text{-}C_6H_5O)[(C_6H_{10})PCy_2](PCy_3)$ (**59**). The reaction of **59** with H_2 produces a mixture of $RuH(\eta^5\text{-}C_6H_5O)(PCy_3)_2$ (**27**) and $RuH_2(\eta^6\text{-}C_6H_5OH)(PCy_3)$ (**28**) [26].

2.3.8. *Catalytic reactions involving $RuH_2(H_2)_2(PCy_3)_2$ (**1**)*

2.3.8.1. Dehydrogenative silylation versus hydrosilylation. The rich reactivity displayed by **1** towards silanes prompted us to study the catalytic properties of this complex in hydrosilylation. The first attempts were carried out at room temperature in the presence of 100 equiv $HSiEt_3$ per complex **1**, under 1 bar C_2H_4. We discovered that in this system, the competitive dehydrogenative silylation is favored over hydrosilylation and after total conversion of the silane within 105 min, the vinylsilane $CH_2{=}CHSiEt_3$ was obtained in 78% yield. The results were found to depend highly upon the reaction conditions (see Fig. 8) [49]. Thus, adding ethylene to **1** before the introduction of $HSiEt_3$ leads to $CH_2{=}CHSiEt_3$ in 97%. A mechanistic study led us to demonstrate the role of the dihydrogen complex in the catalytic reaction. The bis(dihydrogen) complex **1** serves as a precursor to generate the ethylene complex $RuH(C_2H_4)[(\eta^3\text{-}C_6H_8)PCy_2](PCy_3)$ (**55**) which is the catalyst resting state (see Section 2.3.7.). Then, oxidative addition of the silane occurs and the dihydrido silyl ruthenium (IV) complex $RuH_2(SiEt_3)[(\eta^3\text{-}C_6H_8)PCy_2](PCy_3)$ (**60**) is obtained. Finally, upon exposure of **60** to ethylene, **55** is regenerated (see). Carrying out the reaction directly with **55** as catalyst precursor, produces an efficient long-lived catalyst system. For example, using a $HSiEt_3$/**55** ratio of 1000: 1 at 17 °C under

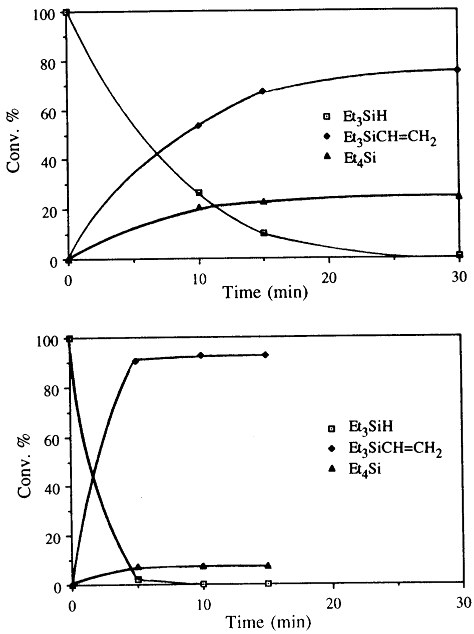
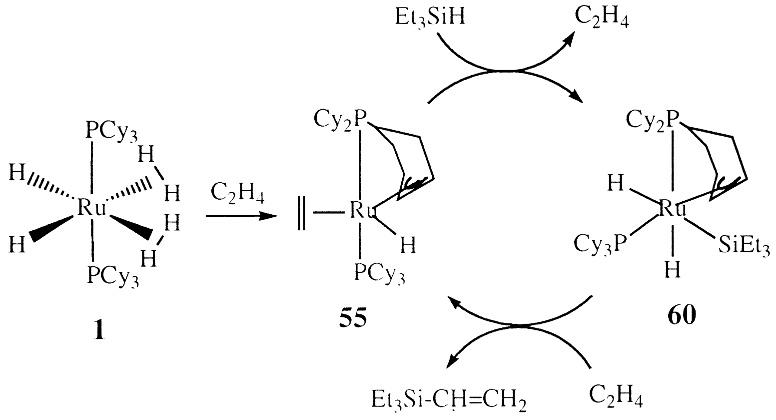


Fig. 8. Hydrosilylation versus dehydrogenative silylation of ethylene (20 bar) catalyzed by **1** (top) or **55** (bottom) with a catalyst: $HSiEt_3$ ratio of 1:1000.



Scheme 6. Catalytic intermediates involved in the synthesis of Et_3 Si–CH=CH_2

20 bar of C_2H_4, total conversion was achieved within 15 min and CH_2=$CHSiEt_3$ was obtained in 93% yield. The reaction can also be run at higher temperatures without loss of selectivity. It should be pointed out that the role of the partially dehydrogenated phosphine ligand is crucial in this system: it allows to combine reactivity and stability by an easy access to intermediate unsaturated species without decoordination of the phosphine.

We are presently exploring the scope of this reaction in parallel with the stoichiometric studies on the reactivity of **1** with disilanes described in Section 2.3.6. For example, preliminary experiments show that we can still favor the catalytic dehydrogenative silylation of ethylene in the presence of polysilanes such as $HR_2Si(CH_2)_4SiR_2H$ or $HR_2SiOSiR_2H$ [44]. In the case of the allylsilane $(CH_2{=}CHCH_2)SiMe_2H$, we can either obtain $(CH_2{=}CHCH_2)SiMe_2(CH_2{=}CH_2)$ or favor the formation of redistribution products such as $SiMe_2(CH_2{=}CH_2)_2$, a reaction which had no precedent in such homogeneous conditions [52].

2.3.8.2. Hydrogenation. Recently, three patents from Beatty and Paciello concerning the use of ruthenium compounds as hydrogenation catalysts have been deposited. Among the various precursors they used, **1** seems one of the best for the hydrogenation of nitriles. For example, adiponitrile was converted into hexamethylenediamine in 97% yield using a **1**: adiponitrile ratio of 1:50 at 90 °C under 70 atm of H_2. The authors lay emphasis on the fact that the process can be conducted in a biphasic medium, **1** being recycled with success in these conditions [21,53].

In our group, we are interested in the hydrogenation of arenes as many of our compounds proved to be active for H–D exchange and hydrogen transfer. We successfully converted anthracene into 1,2,3,4-tetrahydroanthracene in 4 h using **1** as precursor at 80 °C and under 3 bar of H_2. Benzene was, as expected, more reluctantly hydrogenated in the same conditions, but 4% of cyclohexane (30 turnovers) was obtained when using a **1**:C_6H_6 ratio of 1:750 in the same conditions [54]. Future studies are aimed at broadening the scope of all these reactions and providing additional mechanistic informations.

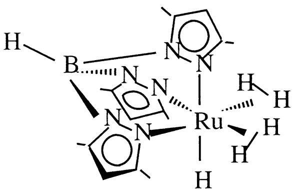
3. $LRuH(H_2)_2$

(L = hydridotris(3,5-dimethylpyrazolyl)borate, Tp*; hydridotris(3-isopropyl-4-bromo-pyrazolyl)borate, Tp′). Besides our interest for the properties of the first bis(dihydrogen) complex **1** described earlier, we have studied the properties of [Cp*Ru] compounds and found two important results: the complexes $Cp^*RuH_3(PR_3)$ were the first reported compounds to present hydrogen exchange couplings, a phenomenom specially studied in our group [55–58], and we reported several applications for the use of the electrophilic "Cp^*Ru^+" fragment [59]. In this respect, the search for analogous hydridotris(pyrazolyl)borate (Tp) ruthenium compounds was tempting. The Tp ligands are normally compared with the Cp one but the resulting compounds very often turned to be quite different. In addition, they offer numerous possibilities of substituents and thus, one can tune both steric and electronic properties and even use chiral ligands [60–63].

3.1. Synthesis

The synthesis of ruthenium hydrido and dihydrogen complexes containing hydridotris(pyrazolyl)borate ligands has been first attempted by reacting

$RuH(H_2)I(PCy_3)_2$ (**7**) with KL (L = hydridotris(pyrazolyl)borate, Tp; hydridotris (3,5-dimethylpyrazolyl) borate, Tp*) to yield $LRuH(H_2)(PCy_3)$ (L = Tp, **61**; L = Tp*, **62**). However, the yields were very low [64]. An alternative and more satisfactory synthesis of such compounds involves first the addition of KL (L = Tp*; L = hydridotris(3-isopropyl-4-bromo-pyrazolyl)borate, Tp′) to RuHCl(COD)(bpzm) (bpzm = bis(pyrazolyl)methane), a complex prepared by Jalon et al. [65]. Interestingly, the reaction does not work with $RuCl_2$(COD)(bpzm) thus demonstrating the need for a hydride to labilize the chloride group. This reaction produces LRuH(COD) (L = Tp*, **63**; L = Tp′, **64**) which is then dissolved in pentane and reacted in a Fischer–Porter bottle with dihydrogen (3 bar) for 15 h to yield $LRuH(H_2)_2$ (L = Tp*, **65**; L = Tp′, **66**), the second examples of a thermally stable bis(dihydrogen) derivative. The procedure is not direct, but each individual step gives a high yield [11,12].



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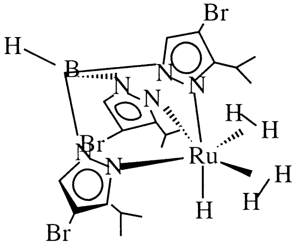

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3.2. Characterization

Complexes **65** and **66** were characterized by different spectroscopic techniques, essentially IR and NMR. For example, **65** displays at high field a signal at δ −11.26 with a T_1 minimum value of 26 ms at 163 K (400 MHz, THF-d_8-C_7D_8). Upon deuteration, it was possible to observe all isotopomers from $LRuH(H_2)_2$ to $LRuD(D_2)_2$ by ^1H and ^2H NMR. Interestingly, Tp^*RuHD_4 (**65-*d*₄**) shows a non-binomal nonet pattern (1:4:10:16:19:16:10:4:1) in ^1H NMR which demonstrates the presence of five ruthenium bound hydrogens (see Fig. 9). The magnitude of the H–D coupling was used to determine the real structure of the complex. The experimental value (5.4 Hz) is indicative of an individual H–D coupling of 27 Hz within a coordinated H–D molecule assuming the structure $Tp^*RuH(H_2)_2$. The other structures (Tp^*RuH_5 and $Tp^*RuH_3(H_2)$) were ruled out on the basis of T_1 and $J_{H\text{-}D}$ data. The NMR data obtained for **65** and **66**, when compared with those measured for corresponding monohydrides such as $Tp^*RuH(THT)_2$ (THT = tetrahydrothiophene) allowed the calculation of the H–H distance within a coordinated dihydrogen molecule. The values found, namely 0.90 Å for **65** and 0.89 Å for **66** are in agreement with a slight elongation of the H–H bond. In contrast to the phosphine complexes described in Section 2, the H–H stretch of coordinated dihydrogen could be localized by infrared spectroscopy in **65** and **66** as broad absorptions, respectively,

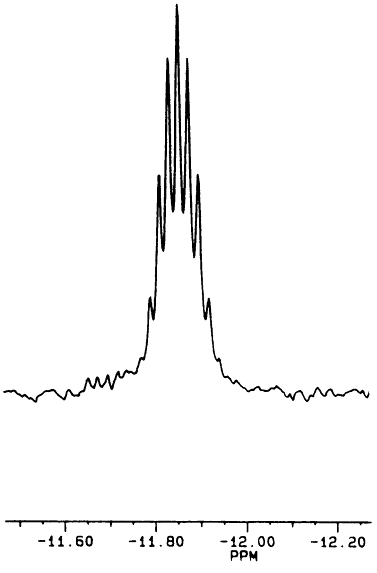


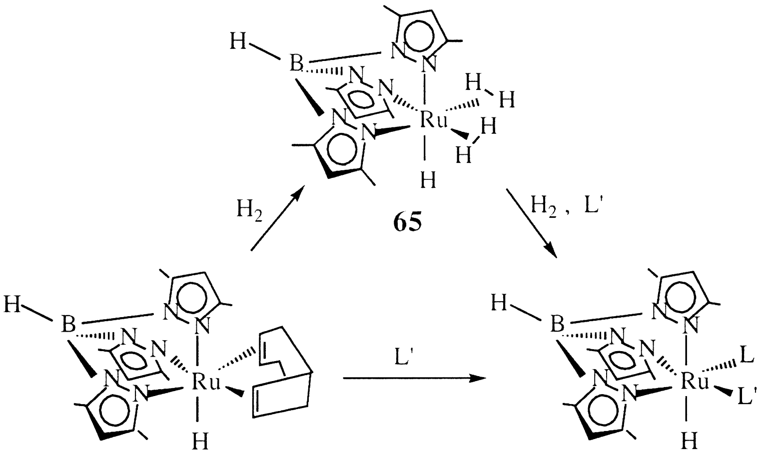
Fig. 9. High field ^1H NMR spectrum of **65**-d_4.

at 2361 and 2250 cm^{-1}. Upon deuteration, these bands shift to ca. 1705 and 1620 instead of the expected 1670 and 1591 cm^{-1} for a $\nu_{H\text{-}H}$ to $\nu_{D\text{-}D}$ shift. It is noteworthy that the H–H elongation mode has been very rarely observed and only for complexes containing unstretched dihydrogen molecules. The discrepancy between calculated and observed isotopic shifts probably results from a coupling between the $\nu_{H\text{-}H}$, $\nu_{Ru\text{-}H}$ and ν_{s-Ru-H_2} modes. The latter modes are localized, respectively, at 1950 and 1948 cm^{-1} ($\nu_{Ru\text{-}H}$) and as shoulders respectively at ca. 1970 and ca. 1980 cm^{-1} (ν_{s-Ru-H_2}). INS experiments have also been carried out on **65**. Preliminary results indicate the presence of a relatively high rotation barrier for the H_2 ligands (ca. 3 kcal mol^{-1}), but also of a fluxional process of very low energy ($\Delta G^{\ddagger} < 0.5$ kcal mol^{-1}) which is not yet fully understood (J. Eckert, pers. comm.).

3.3. Reactivity

3.3.1. Stoichiometric reactions

In contrast with **1**, complexes **65** and **66** do not react with small molecules such as N_2, CO_2, H_2O, NH_3 and CH_3I. **65** does, however, react with CO to give the dicarbonyl complex Tp*RuH$(CO)_2$ (**67**). The substitution complexes Tp*RuH$(H_2)(L')$ (L'=PCy_3, **62**; THT, **68**; pyridine, **69**; $NHEt_2$, **70**) and Tp*RuH$(L'')_2$ (L''=THT, **71**; pyridine, **72**) were prepared either by addition of 1 equiv or of an excess of ligands to **65** or by hydrogenation of **63** in the presence of one equiv or of an excess of ligand (see). Interestingly, we could calculate the H–H distance (r_{HH}) in the series of complexes Tp*RuH$(H_2)(L')$. The values found were: 0.90, 0.92, 0.89, 0.90 and 0.90 Å for L'=H_2, PCy_3, THT, py and $NHEt_2$, respectively.



63

62, L = H_2 L' = PCy_3; **68**, L' = THT
69, L' = py ; **70**, L' = $NHEt_2$
67, L = L' = CO; **71**, THT; **72**, py

Scheme 7. Ruthenium complexes containing the Tp* ligand

Given the sensitivity of the H–H bond length to the electron density on the metal center and the very different electron releasing properties of the ligands used, this result illustrates the fact that the dihydrogen ligand receives little back-bonding from the metal. This implies an eletrophilic character of the coordinated dihydrogen ligands. It is also noteworthy that both **65** and **66** undergo rapid H/D exchange in aromatic solutions at room temperature. The mechanism of this reaction is, however, not known [11,12].

After 15 h in THF, **65** does not react with excess CX_3COOH (X = H, F) in agreement with the electrophilic character of the hydride and dihydrogen ligands. It does, however, react with CF_3SO_3H in MeCN to give $[Tp^*Ru(MeCN)_3]CF_3SO_3$ (**73**) [11,12].

3.3.2. *Catalytic reactions*

65 catalyses the reduction of ketones in mild conditions [66]. At 80 °C under 3 bar H_2 with a [substrate]: [Ru] = 100: 1, 93% conversion of cyclohexanone into cyclohexanol is achieved within 2 h. The same reduction is possible with acetone and acetophenone although the reaction is slower. The reaction works similarly using **63** as catalyst precursor. In contrast to most catalytic systems, the increase in H_2 pressure decreases the reaction rate, probably as a result of the stabilization of **65**. The steric bulk of the Tp* ligand proved to be important for achieving good catalytic conversions since when using TpRuH(COD) (**74**) which contains the unsubstituted hydrido tris(pyrazolyl)borate ligand, hydrogenation of ketones was only achieved at higher temperature (120 °C). The catalytic system was not efficient for aldehydes because of rapid decarbonylation. Interestingly, when the hydrogenation reactions were carried out in the presence of a mixture of olefins and ketone, a net selectivity for the ketone reduction was observed. Furthermore, we could show evidence for a promoting effect of the presence of the olefin for the reduction of ketones [66].

4. Conclusion

The reactivities of both types of bis(dihydrogen) complexes described in this review are very high yet very different. Both complexes present novel spectroscopic features, in particular intriguing fluxional processes which will necessitate further characterization by INS. The chemistry of $LRuH(H_2)_2$, **65** and **66** is dominated by the electrophilic character of their hydride and dihydrogen ligands. This can be illustrated by the rapid H/D exchange occurring in deuterated aromatic solvents or by the absence of protonation by acids with the exception of very strong acids. The search for even more electrophilic compounds, suitable for C–H activation, is still under investigation in our group.

In contrast, the reactivity of complex $RuH_2(H_2)_2(PCy_3)_2$, **1**, is dominated by substitution and hydrogen transfer reactions. Substitutions can give rise to unusual complexes such as the bis(dinitrogen) derivative $RuH_2(N_2)_2(PCy_3)_2$ or the bis(silane) complexes $RuH_2[(\eta^2\text{-}HSiMe_2)_2X](PCy_3)_2$ presently under investigation in the group. Rapid hydrogen transfer of up to five dihydrogen molecules from **1** to an organic substrate can be achieved at room temperature to give $RuH[(\eta^3\text{-}C_6H_8)PCy_2][(\eta^2\text{-}C_6H_9)PCy_2]$ (**54**). The reversibility of the reaction upon bubbling dihydrogen into a solution of **54** leads us to consider complex **1** as a "hydrogen sponge". Complex **1** is also a source of a large series of hydrido dihydrogen derivatives containing stretched H–H bonds. Among these compounds, we can mention the first 16 electron dihydrogen derivatives, complexes containing a very long H–H bond and the first observation of quantum mechanical exchange couplings between a hydride and a coordinated dihydrogen molecule. These properties make **1** a very good catalyst precursor for hydrogenation reactions. The hydrogenation of olefins has been mentioned, but **1** is also a very good catalyst for the hydrogenation of nitriles and a catalyst precursor for arene hydrogenation. Perhaps more unexpectedly, **1** is also a very active and selective catalyst precursor for the dehydrogenative silylation of alkenes, an important industrial reaction still under investigation in our group. Finally we have recently found that **1** is a unique catalyst precursor for the room temperature functionalization of aromatic C–H bonds. The reaction is so far limited to C–H bonds in the ortho position to a function such as a ketone, an amine, etc. but further work is in progress in this field to extend the scope of the reaction.

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