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Ruthenium hydrides bearing $SbPh_3$ and $AsPh_3$ ligands: characterization of the bis(dihydrogen) complexes $[Cp^*Ru(H_2)_2(EPh_3)]^+$ ($Cp^* = C_5Me_5$; E = Sb, As)

Halikhedkar Aneetha, Manuel Jiménez Tenorio, M. Carmen Puerta, Pedro Valerga *

Departamento de Ciencia de Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, 11510 Puerto Real, Cádiz, Spain

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This paper is dedicated to Professor Pascual Royo

Abstract

Reaction of $NaBH_4$ with $[Cp^*RuCl_2(EPh_3)]$ (E = Sb **1a**, As **1b**) in THF/EtOH affords the trihydride complexes $[Cp^*RuH_3(EPh_3)]$ (E = Sb **2a**, As **2b**) in good yield. These trihydrides are protonated by $HBF_4 \cdot OEt_2$ in CH_2Cl_2 at −80 °C furnishing the cationic bis(dihydrogen) complexes $[Cp^*Ru(H_2)_2(EPh_3)][BF_4]$ (E = Sb **3a**, As **3b**), which were characterized in solution by T_1 and $^1J_{HD}$ measurements. These species are unstable and decompose at $T > 0$ °C. The reaction of $[Cp^*RuCl(SbPh_3)_2]$ with H_2 and $NaBAr'_4$ in fluorobenzene yields the dihydride $[Cp^*RuH_2(SbPh_3)_2][BAr'_4]$ (**5**). Protonation of the monohydride $[Cp^*RuH(SbPh_3)_2]$ (**6**) by $HBF_4 \cdot OEt_2$ in CH_2Cl_2 at −80 °C generates the dihydrogen complex $[Cp^*Ru(H_2)(SbPh_3)_2]^+$ (**7**), which rearranges to its dihydride tautomer **5** when the temperature is raised.

Keywords: Hydride complexes; Dihydrogen complexes; Ruthenium; Stibine; Arsine

1. Introduction

The number of dihydrogen complexes bearing more than one dihydrogen ligand is very limited. Accordingly only a few bis(dihydrogen) complexes have been characterized [1], and only four of them have been isolated: $[RuH_2(H_2)_2(PCy_3)_2]$ [2], $[Tp^*RuH(H_2)_2]$, $[Tp'RuH(H_2)_2]$ (Tp^* = hydrotris(3,5–dimethylpyrazolyl)borate; Tp' = hydrotris(3-isopropyl-4-bromo-pyrazolyl)borate) [3], and very recently $[RuH_2(H_2)_2(P^iPr_3)_2]$ [4]. Protonation of the trihydride complexes $[Cp^*MH_3(PR_3)]$ (M = Ru, Os) [5–7] is a route that should lead to complexes of general formula $[Cp^*MH_4(PR_3)]^+$. Thus, protonation of $[Cp^*OsH_3(EPh_3)]$ (E = P, As) with $HBF_4 \cdot Et_2O$ yielded the corresponding $[Cp^*OsH_4(EPh_3)][BF_4]$ derivatives. A neutron diffraction study performed on the PPh_3 complex showed it to contain one "elongated" dihydrogen ligand and two hydrides, hence it can be formulated as $[Cp^*OsH_2(H_2)(PPh_3)][BF_4]$ [8]. In the case of ruthenium, attempts to protonate $[Cp^*RuH_3(PR_3)]$ ($PR_3 = PPh_3$, PCy_3) with $HBF_4 \cdot Et_2O$ immediately led to extensive dihydrogen evolution and even dehydrogenation of one cyclohexyl ring of the PCy_3 ligand [9]. It has been previously noted for the derivatives $[Cp^*RuH_3(PR_3)]$, particularly those containing bulky phosphine ligands such as P^iPr_3 or PCy_3, the occurrence of quantum exchange coupling (QEC). The hydride signals in the ^{1}H-NMR spectrum of compounds in which QEC occurs exhibit large, temperature dependent H–H coupling constants [6,10]. These quantum mechanical exchange couplings can be modulated through hydrogen bonding. Thus, addition of various proton donors such as methanol, indole, phenol, or hexafluoroisopropanol to $[Cp^*RuH_3(PCy_3)]$ leads to an increase of the quantum mechanical exchange couplings between the hydride sites. This has been interpreted in terms of a "weak" interaction (hydrogen bonding) between $[Cp^*RuH_3(PCy_3)]$ and the proton donors added, with

* Corresponding author. Fax: +34-956-016-288
E-mail address: pedro.valerga@uca.es (P. Valerga).

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H···H separations of 1.92 Å as inferred from the decrease in the value of the minimum longitudinal relaxation time $(T_1)_{min}$ [11]. More recently, the species $[Cp^*RuH_4(PCy_3)]^+$ has been identified as a result of the protonation of the hydrogen-bonded complex $[Cp^*RuH_3(PCy_3)]\cdots[HOR]$ ($R = CH(CF_3)_2$, $C(CF_3)_3$) by $(CF_3)_2CHOH$ or $(CF_3)_3COH$ in $CDClF_2/CDCF_3$ at 200 K [12]. An analogous complex, $[Cp^*RuH_4(PPh^iPr_2)]^+$, had already been postulated as one of the species involved in the reaction of $[Cp^*RuH_3(PPh^iPr_2)]$ with CF_3CH_2OH [13]. T_1 measurements for $[Cp^*RuH_4(PCy_3)]^+$ are consistent with a dihydrido(dihydrogen) structure $[Cp^*RuH_2(H_2)(PCy_3)]^+$, although a bis(dihydrogen) structure $[Cp^*Ru(H_2)_2(PCy_3)]^+$ cannot be excluded [12].

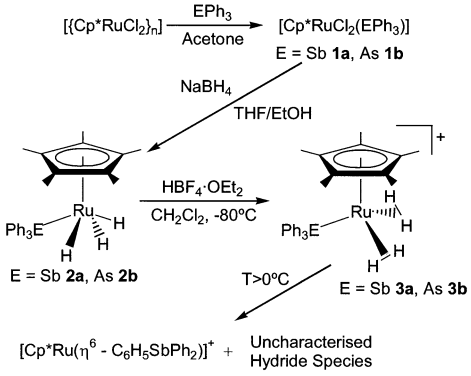
Werner and co-workers have reported the preparation of the ruthenium dihydrido(dihydrogen) complex $[RuH_2(H_2)(Sb^iPr_3)_3]$ [14], as well as a number of other novel organometallic compounds bearing triisopropylstibine as co-ligand [15,16]. It is known that despite the poorer donor properties of stibines compared to phosphine or arsine ligands, they can otherwise form very similar complexes [17], although these tend to adopt higher coordination numbers (i.e. $[RuCl_2(SbPh_3)_4]$ versus $[RuCl_2(PPh_3)_3]$ [18]) as well as a reduced tendency to dissociation in solution in contrast with their phosphine homologues.

We have now shown that at variance with PPh_3, both $SbPh_3$ and $AsPh_3$ are effective co-ligands for the stabilization of the ruthenium–dihydrogen bond in complexes $[Cp^*Ru(H_2)_2(EPh_3)][BF_4]$ (E = Sb, As), which are obtained by protonation of the trihydrides $[Cp^*RuH_3(EPh_3)]$ with $HBF_4\cdot OEt_2$ in CD_2Cl_2 at −80 °C. The synthesis and spectral properties of these species, as well as the study of the relative stability of dihydride and dihydrogen tautomers of $[Cp^*RuH_2(SbPh_3)_2]^+$ are presented in this work.

2. Results and discussion

$[\{Cp^*RuCl_2\}_n]$ reacts with $SbPh_3$ or $AsPh_3$ in dichloromethane or acetone yielding the corresponding derivatives $[Cp^*RuCl_2(EPh_3)]$ (E = Sb **1a**, As **1b**) in good yield. These compounds are homologues of the known phosphine complex $[Cp^*RuCl_2(PPh_3)]$, which is prepared in a similar fashion [5,6]. The derivative $[Cp^*RuCl_2(Sb^iPr_3)]$ has also been synthesized, and unequivocally characterized by X-ray crystallography [15]. Complexes **1a** and **1b** are red–orange paramagnetic materials. Their effective magnetic moment value of 1.7 μ_B for **1a**, and 1.9 μ_B for **1b** in solution suggests the presence of one unpaired electron, as expected.

Both **1a** and **1b** react with $NaBH_4$ in THF–ethanol affording the Ru^{IV} trihydride complexes $[Cp^*RuH_3(SbPh_3)]$ (**2a**) and $[Cp^*RuH_3(AsPh_3)]$ (**2b**), respectively (Scheme 1). Thus, the validity of the synthetic procedure for the preparation of trihydride derivatives of the type $[Cp^*RuH_3(PR_3)]$ is not only restricted to phosphine ligands [5,6], and can be easily adapted for the preparation of stibine and arsine hydride complexes. Complexes **2a** and **2b** display strong ν(RuH) absorption bands near 2000 cm^{-1} in their IR spectra. The hydride ligands in these complexes give rise to one sharp resonance in their ^{1}H-NMR spectra. This resonance does not experiment decoalescence when the temperature is lowered down to −90 °C, remaining relatively sharp even at this temperature. A $(T_1)_{min}$ of 210 ms was measured for the hydride protons of **1a**, the value being 190 ms for **2b** ($CD_3C_6D_5$, 400 MHz, 213 K in both cases). These values point out to a formulation as Ru^{IV} trihydrides like $[Cp^*RuH_3(PR_3)]$ derivatives (PR_3 = PMe_3, PPh_3, P^iPr_3, PCy_3) [5,6], rather than to hydrido(dihydrogen) complexes like $[Tp^*RuH(H_2)(PCy_3)]$ [3] or $[TpRuH(H_2)(PR_3)]$ (Tp = Hydrotris(pyrazolyl)borate, $PR_3 = PPh_3$, PCy_3, PMe^iPr_2) [19–21]. It has been previously noted for the derivatives $[Cp^*RuH_3(PR_3)]$ the occurrence of quantum mechanical exchange coupling (QEC) [6,10–12]. In the case of **1a** or **1b**, there is no evidence for QEC at the lowest temperature measured (183 K). However, QEC cannot be observed in a fluxional spectrum. Since the static spectrum was not observed because the minimum temperature reached was not low enough, the occurrence of QEC in these complexes is therefore still possible. Consistent with their formulation as "classical" Ru^{IV} trihydrides, complexes **1a** and **1b** are quite stable towards thermal reductive elimination of dihydrogen. Thus, they do not react with unsaturated molecules such as ethylene, phenylacetylene or thiophene. However, they react slowly with chlorinated solvents such as dichloromethane, losing the hydride ligands as inferred from NMR studies.



Scheme 1.

Protonation of **2a** and **2b** in CD_2Cl_2 at −80 °C using $HBF_4\cdot OEt_2$ generates in solution the bis(dihydrogen) complexes $[Cp^*Ru(H_2)_2(EPh_3)][BF_4]$ (E = Sb **3a**, As **3b**). Attempts made to prepare the homologous PPh_3

compound $[Cp^*Ru(H_2)_2(PPh_3)]^+$ had been unsuccessful, because this compound is unstable towards loss of H_2 [9]. The dihydrogen ligands in these complexes give rise to one single resonance in their respective ^{1}H-NMR spectra at −7.79 ppm for **3a**, and −7.14 for **3b**. These resonances become broader when the temperature is lowered, but no decoalescence is observed (Fig. 1). The variation of T_1 for the dihydrogen resonance in **3a** and **3b** with the absolute temperature is shown in Fig. 2. From this plot, the corresponding $(T_1)_{min}$ for **3a** (11.2 ms at 210 K) and **3b** (11.0 ms at 221 K) are obtained. Attempts to protonate **2a**–**2b** using HBF_4/D_2O in order to determine the value of $^1J_{HD}$ failed. The dihydrogen complex decomposes and apparently, species containing coordinated D_2O/HDO are generated. Alternatively, we protonated the complexes $[Cp^*RuD_3(EPh_3)]$ with $HBF_4{\cdot}OEt_2$ in CD_2Cl_2 at −80 °C. In this fashion we were able to generate the isotopomers $[Cp^*Ru(HD)(D_2)(EPh_3)]^+$ (E = Sb, As). The high-field NMR resonance (Fig. 3) appears as a non-binomial septet for both **3a** and **3b**, indicating the coupling to three deuterium atoms and therefore confirming the presence of four hydrogen atoms attached to ruthenium. The value of the averaged $^1J_{HD}^{obs}$ coupling constants is 9.3 Hz for **3a**, and 9.9 Hz for **3b**. Assuming that $^2J_{HD} \sim 0$ Hz, these values lead to a $^1J_{HD}$ coupling constant within coordinated H-D of 27.9 Hz for **3a**, and 29.7 Hz for **3b**.

In Table 1 a compilation of NMR data is shown for the known bis(dihydrogen) complexes, plus data for the related complex $[Cp^*OsH_2(H_2)(PPh_3)][BF_4]$. Structural characterization by neutron diffraction of $[Cp^*OsH_2(H_2)(PPh_3)][BF_4]$ showed a dihydride(dihydrogen) structure, with a H–H separation of 1.014(11) Å in the dihydrogen ligand. In this complex rapid scrambling between hydride and dihydrogen sites occurs, and decoalescence of the hydride resonance was only observed for the derivative $[Cp^*OsH_2(H_2)(AsPh_3)][BF_4]$ at −140 °C (in $CDFCl_2$), suggesting a free energy of activation of 6.0 kcal mol^{-1} for the hydride–dihydrogen exchange in this case [8]. Consistent with this, the values of $(T_1)_{min}$ and $^1J_{HD}$ are averaged, as expected. However, this behaviour has not been observed in the case of **3a** and **3b**, which exhibit the shortest $(T_1)_{min}$ values and the largest $^1J_{HD}^{obs}$ coupling constants among the compounds shown in Table 1. Both the variation of T_1 with temperature as well as the $^1J_{HD}$ coupling constants point out to a formulation as bis(dihydrogen) derivatives. If the equilibrium shown in Eq. (1) indeed occurs in our system, it would be most likely shifted to the left.

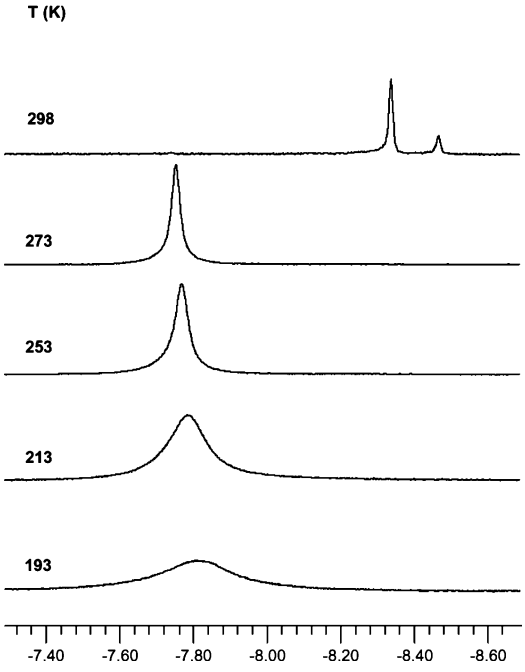


Fig. 1. Variable temperature ^{1}H-NMR spectra (400 MHz) in the high-field region of $[Cp^*Ru(H_2)_2(SbPh_3)][BF_4]$ (**3a**).

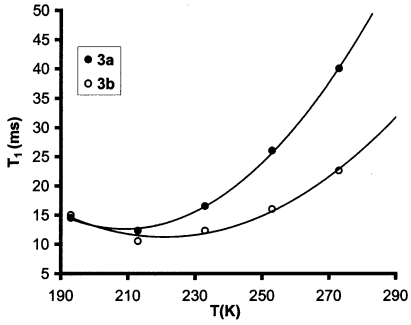


Fig. 2. Plot of the T_1 values for **3a** and **3b** versus temperature (K).

$$[Cp^*Ru(H_2)_2(EPh_3)]^+ \rightleftharpoons [Cp^*RuH_2(H_2)(EPh_3)]^+ \quad (1)$$

The $(T_1)_{min}$ value of 14.4 ms reported for the species $[Cp^*RuH_4(PCy_3)]^+$ is close to ours for **3a** and **3b**, but in that case it was not possible to measure $^1J_{HD}$ [12], leaving doubts on its formulation either as $[Cp^*RuH_2(H_2)(PCy_3)]^+$ or $[Cp^*Ru(H_2)_2(PCy_3)]^+$.

$^1J_{HD}$ and $(T_1)_{min}$ can be used for the determination of the H–H separation in these complexes. Thus using the equation developed by Morris and co-workers [22],

$$r_{HH} = 1.42–0.0167(^1J_{HD}) \quad (2)$$

the calculated values for r_{HH} are 0.95 Å for **3a**, and 0.92 Å for **3b**. r_{HH} can be also estimated using the equation

$$r_{HH} = K[(T_1)_{min}/\nu]^{1/6} \quad (3)$$

$(T_1)_{min}$ is in seconds, ν is the frequency of the spectrometer in MHz, and K is a constant which takes the values 5.815 if no rotation of the dihydrogen ligand is considered, or 4.611 if there is a fast rotation of the dihydrogen ligand [22,23]. In our case, for each of the two possible situations the resulting r_{HH} values are 1.01/0.80 Å for both **3a** and **3b**. The r_{HH} calculated using $(T_1)_{min}$ assuming no rotation of the dihydrogen ligand are closer to the values determined using $^1J_{HD}$. In fact, it

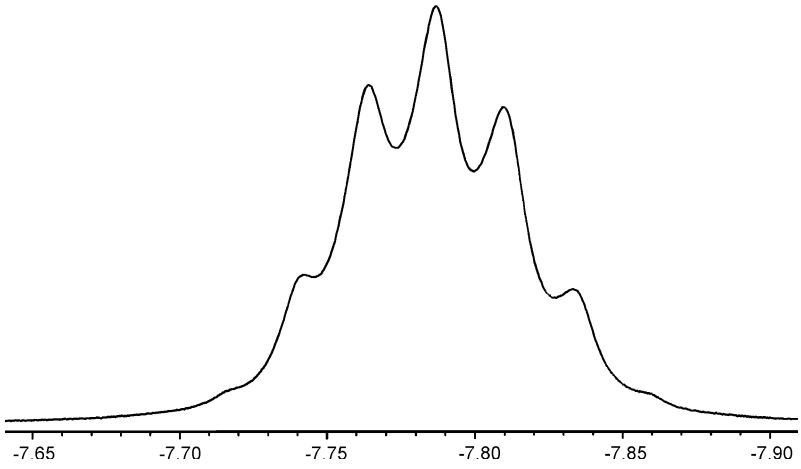


Fig. 3. High field ^{1}H-NMR signal of $[Cp^*RuHD_3(SbPh_3)][BF_4]$ (**3a-*d*$_3$**) showing the expected non-binomial septet pattern (400 MHz, CD_2Cl_2, 263 K).

is recognized that only in a few cases is it necessary to invoke the fast rotation model to produce a reasonable H–H distance in the H_2 ligand, and r_{HH} determination using $(T_1)_{min}$ data should consider static rotation around the M–H_2 axis [24].

The complexes **3a** and **3b** are stable in CD_2Cl_2 solution up to 0 °C. Above this temperature, the dihydrogen resonance disappears, and signals corresponding to at least two new species appear (Fig. 1). Several multiplet resonances between 5.0 and 6.0 ppm are indicative of the formation of a π-arene complex, most likely $[Cp^*Ru(\eta^6\text{-}C_6H_5EPh_2)]^+$, which is consistent with the release of the dihydrogen ligands and subsequent rearrangement of the coordinated EPh_3 from η^1 to η^6 (Scheme 1). Apart from this, new hydride resonances appears near −8.4 ppm for both **3a** and **3b**. It is not clear what these new hydridic species might be, but they seem to be intermediates in the decomposition of the bis(dihydrogen) complexes, since they also disappear on standing, and complex mixtures are obtained at room temperature. We can tentatively think of coordinatively unsaturated hydrides of the type $[Cp^*RuH_2(EPh_3)]^+$, formed upon dihydrogen elimination from **3a**–**3b**, prior to the rearrangement to the sandwich species $[Cp^*Ru(\eta^6\text{-}C_6H_5EPh_2)]^+$, although other possibilities, i.e. products of the reaction with the solvent, species containing coordinated H_2O coming from the acid, etc., cannot be ruled out.

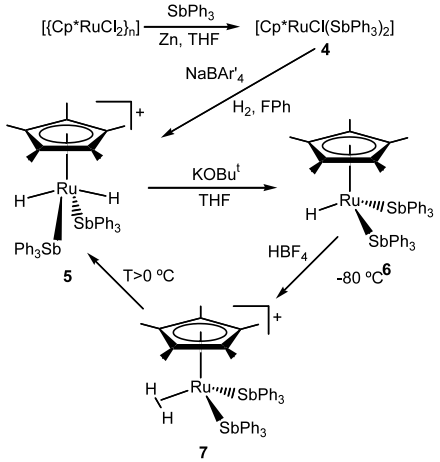
Once it is clear that $SbPh_3$ and $AsPh_3$ ligands can stabilize the ruthenium–dihydrogen bond in a manner similar or even better than PPh_3, it seems logical to assume that species of the type $[Cp^*Ru(H_2)(EPh_3)_2]^+$ (E = Sb, As) might also be accessible, just like their congeners $[Cp^*Ru(H_2)(PR_3)_2]^+$ [25–27]. We carried out the reduction with zinc dust of $[\{Cp^*RuCl_2\}_n]$ in THF in the presence of two equivalents of either $SbPh_3$ or $AsPh_3$, in an attempt to prepare the chloro-complexes $[Cp^*RuCl(EPh_3)_2]$ as starting materials. The reaction with $AsPh_3$ gave a mixture of products, but from the $SbPh_3$ reaction yellow–orange $[Cp^*RuCl(SbPh_3)_2]$ (**4**) was isolated in pure form and in good yield. Halide abstraction using $NaBAr'_4$ (Ar′ = 3,5-$C_6H_3(CF_3)_2$) in

Table 1
Compilation of NMR data for bis(dihydrogen) complexes and related species

Compound	$\delta(H_2)$ (ppm)	$(T_1)_{min}$ (ms) [a]	$^1J_{HD}{}^{obs}$ (Hz)	Ref.
$[RuH_2(H_2)_2(PCy_3)_2]$	−7.9 (C_6D_6, 298 K)	45.0 [b]	–	[1,2]
$[Tp^*RuH(H_2)_2]$	−11.26 (C_6D_6, 298 K)	26	5.4	[1,3]
$[Tp'RuH(H_2)_2]$	−11.82 (C_6D_6, 298 K)	28	5.2	[3]
$[RuH_2(H_2)_2(P^iPr_3)_2]$	−8.31 (THF-d_8, 298 K)	48.0 [c]	4.0	[4]
$[Cp^*OsH_2(H_2)(PPh_3)]^+$	−9.61 (CD_2Cl_2, 296 K)	79.2 [d]	3.6	[8]
$[Cp^*RuH_4(PCy_3)]^+$	−8.4 ($CDClF_2/CDF_3$, 200 K)	14.4 [e]	–	[12]
$[Cp^*Ru(H_2)_2(SbPh_3)]^+$	−7.79 (CD_2Cl_2, 193 K)	11.2	9.3	This work
$[Cp^*Ru(H_2)_2(AsPh_3)]^+$	−7.14 (CD_2Cl_2, 193 K)	11.0	9.9	This work

[a] All data extrapolated at 400 MHz, for comparison purposes.
[b] 60 ms at 500 MHz.
[c] 28 ms at 250 MHz.
[d] 99 ms at 500 MHz.
[e] 18 ms at 500 MHz.

fluorobenzene under hydrogen gave the dihydride complex $[Cp^*RuH_2(SbPh_3)_2][BAr'_4]$ (**5**) (Scheme 2). Complex **5** is characterized by one sharp hydride resonance at −8.51 ppm, with a minimum T_1 of 1052 ms (400 MHz, CD_2Cl_2, 298 K). This compound is homologous of the well-known dihydride derivatives $[CpRuH_2(P)_2]^+$, which have four-legged "piano stool" structures with *transoid* disposition of hydride ligands [25,26]. Exactly as it occurs with its PPh_3 counterpart $[Cp^*RuH_2(PPh_3)_2]^+$, the dihydride is the most stable tautomeric form. However, in the phosphine case the dihydrogen tautomer $[Cp^*Ru(H_2)(PPh_3)_2]^+$ is accessible as the kinetic product of the protonation of the neutral monohydride $[Cp^*RuH(PPh_3)_2]$ [27]. Hence the monohydride complex $[Cp^*RuH(SbPh_3)_2]$ (**6**) was prepared by reaction of the dihydride **5** with a strong base such as $KOBu^t$. This yellow material displays one strong ν(RuH) band at 1852 cm^{-1}, and one sharp hydride signal at −11.33 ppm. Protonation of **6** using $HBF_4 \cdot OEt_2$ in CD_2Cl_2 at −80 °C afforded the dihydrogen complex $[Cp^*Ru(H_2)(SbPh_3)_2][BF_4]$ (**7**) quantitatively. This compound displays one dihydrogen resonance at −8.32 ppm in its ^{1}H-NMR spectrum. This signal has a $(T_1)_{min}$ of 17 ms (243 K, 400 MHz), which leads to H–H separations of 1.08/0.86 Å for the no rotation/fast spinning of the dihydrogen ligand. When temperature is raised the dihydrogen complex **7** undergoes irreversible tautomerization to its dihydride form **5**, the conversion being complete at room temperature (Scheme 2). However, the rate of tautomerization of **7**→**5** is slower than those of analogous phosphine complexes [26,27], the half-life period being ca. 20 min at 273 K ($k_{obs} = (5.7 \pm 0.2) \times 10^{-4}$ s^{-1}). We can therefore conclude that the system $[Cp^*RuH_2(SbPh_3)_2]^+$ behaves very much as its phosphorus counterpart, and that the use of $SbPh_3$ as co-ligand instead of PPh_3 does not alter the observed relative thermal stabilities of the dihydride and dihydrogen tautomers, although the kinetic stability of the dihydrogen tautomer is slightly increased.



Scheme 2.

3. Experimental

All synthetic operations were performed under a dry dinitrogen or Ar atmosphere by following conventional Schlenk techniques. THF, Et_2O and petroleum ether (boiling point range 40–60 °C) were distilled from the appropriate drying agents. Solvents were deoxygenated immediately before use. $\{[Cp^*RuCl_2\}_n]$ and $NaBAr'_4$ were prepared according to reported procedures [28,29]. $SbPh_3$ and $AsPh_3$ were purchased from Aldrich, and used without further purification. IR spectra were recorded in Nujol mulls on Perkin–Elmer FTIR Spectrum 1000 spectrophotometer. NMR spectra were taken on a Varian Unity 400 MHz or Varian Gemini 200 MHz equipment. Chemical shifts are given in parts per million from $SiMe_4$. T_1 measurements were made by the inversion–recovery method. Magnetic moments were measured by the Evans' method [30]. Microanalysis was performed by the Serveis Científico-Tècnics, Universitat de Barcelona.

3.1. $[Cp^*Ru(EPh_3)Cl_2]$ (E = Sb **1a**, As **1b**)

To 0.31 g (1 mmol) of $[\{Cp^*RuCl_2\}_n]$ in 15 ml of CH_2Cl_2 or acetone, 1 mmol of either $SbPh_3$ or $AsPh_3$ was added. The reaction mixture was stirred for 1 h. Solvent was removed to dryness. Addition of 10–15 ml of EtOH gave a bright orange solid which was filtered, washed with petroleum ether and dried. Yield 80–85%. **1a**: Anal. Calc. for $C_{28}H_{30}Cl_2RuSb$: C, 50.9; H, 4.54. Found: C, 50.5; H, 4.62%. $\mu_{eff} = 1.7$ μ_B (CD_2Cl_2 solution). **1b**: Anal. Calc. for $C_{28}H_{30}AsCl_2Ru$: C, 54.8; H, 4.89. Found: C, 54.6; H, 4.77%. $\mu_{eff} = 1.9$ μ_B (CD_2Cl_2 solution).

3.2. $[Cp^*Ru(EPh_3)H_3]$ (E = Sb **2a**, As **2b**)

To $[Cp^*Ru(EPh_3)Cl_2]$ (1 mmol) in THF, a solution containing an excess of $NaBH_4$ in EtOH was added. The reaction mixture was stirred at room temperature for 1 h. The solvent was removed in vacuo and the residue extracted with petroleum ether. Filtration, concentration and cooling to −20 °C gave an off white crystalline solid. It was recrystallized from petroleum ether. Yield: 65%. **2a**: Anal. Calc. for $C_{28}H_{33}RuSb$: C, 56.8; H, 5.57. Found: C, 56.9; H, 5.89%. IR: ν(RuH) 1925 (s), 2000 (w) cm^{-1}. ^{1}H-NMR (400 MHz, $CD_3C_6D_5$): δ −10.12 (s, 3H, RuH_3, $(T_1)_{min}$ 210 ms (400 MHz, 223 K)); 2.05 (s, $C_5(CH_3)_5$); 7.12, 7.82 (m, $Sb(C_6H_5)_3$). $^{13}C\{^1H\}$-NMR (100.58 MHz, C_6D_6): δ 13.1 (s, $C_5(CH_3)_5$); 104.9 (s, $C_5(CH_3)_5$); 129.3, 129.9, 135.9, 137.2 (s, $Sb(C_6H_5)_3$). **2b**: Anal. Calc. for $C_{28}H_{33}AsRu$: C, 61.7;

H, 6.05. Found: C, 61.5; H, 5.95%. IR: ν(RuH) 1939 cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ −9.70 (s, 3 H, RuH_3, $(T_1)_{min}$ 190 ms (400 MHz, 223 K)); 1.88 (s, $C_5(CH_3)_5$); 7.06, 7.66 (m, As(C_6H_5)$_3$). ^{13}C{^{1}H}-NMR (100.58 MHz, C_6D_6): δ 12.1 (s, $C_5(CH_3)_5$); 94.7 (s, $C_5(CH_3)_5$); 128.2, 129.0, 133.1, 140.8 (s, As(C_6H_5)$_3$). The deuterated derivatives [Cp*RuD_3(SbPh$_3$)] (**2a-*d*$_3$**) and [Cp*RuD_3(AsPh$_3$)] (**2b-*d*$_3$**) were obtained following an identical procedure, but using $NaBD_4$ instead of $NaBH_4$.

3.3. [Cp*Ru(H_2)$_2$(EPh$_3$)][BF_4] (E = Sb **3a**, As **3b**)

Both **3a** and **3b** were obtained and characterized in solution by protonation of the corresponding trihydrides **2a** or **2b** in CD_2Cl_2 at −80 °C using a slight excess of $HBF_4 \cdot OEt_2$. The isotopomers [Cp*Ru(HD)-(D_2)(SbPh$_3$)][BF_4] (**3a-*d*$_3$**) and [Cp*Ru(HD)(D_2)(As-Ph$_3$)][BF_4] (**3b-*d*$_3$**) were generated in analogous fashion by protonation of **2a-*d*$_3$** or **2b-*d*$_3$** in CD_2Cl_2 at −80°C using $HBF_4 \cdot OEt_2$. Yield: quantitative. **3a**: NMR (CD_2Cl_2, 193 K) ^{1}H: δ −7.79 (s, br, Ru(H_2), $(T_1)_{min}$ 11.2 ms (400 MHz, 210 K), $^1J_{HD}^{obs} = 9.3$ Hz); 1.89 (s, $C_5(CH_3)_5$); 7.42, 7,49 (m, Sb(C_6H_5)$_3$). **3b**: NMR (CD_2Cl_2, 193 K) ^{1}H: δ −7.14 (s, br, Ru(H_2), $(T_1)_{min}$ 11.0 ms (400 MHz, 221 K), $^1J_{HD}^{obs} = 9.9$ Hz); 1.70 (s, $C_5(CH_3)_5$); 7.29, 7.46 (m As(C_6H_5)$_3$).

3.4. [Cp*RuCl(SbPh$_3$)$_2$] (**4**)

To [{Cp*RuCl_2}$_n$] (0.31 g, 1 mmol) and SbPh$_3$ (0.71 g, 2 mmol) in 30 ml of THF, an excess of zinc dust was added. The reaction mixture was stirred for 1.5 h. It was allowed to settle and then filtered over celite. THF was removed in vacuo. The residue was repeatedly extracted with Et_2O. Filtration and solvent removal afforded a yellow–orange solid. Yield: 70%. Anal. Calc. for $C_{46}H_{45}ClRuSb_2$: C, 56.5; H, 4.60. Found: C, 56.1; H, 4.37%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.40 (s, $C_5(CH_3)_5$); 7.14, 7.47 (m, Sb(C_6H_5)$_3$). ^{13}C{^{1}H}-NMR (100.58 MHz, $CDCl_3$): δ: 10.4 (s, $C_5(CH_3)_5$); 83.3 (s, $C_5(CH_3)_5$); 128.2, 128.6, 136.1 (s, Sb(C_6H_5)$_3$).

3.5. [Cp*RuH_2(SbPh$_3$)$_2$][BAr$'_4$] (**5**)

To a solution of **4** (0.2 g, ca. 0.2 mmol) in fluorobenzene (10 ml) under hydrogen, NaBAr$'_4$ (0.18 g, 0.2 mmol) was added. The pale yellow to colourless reaction mixture was stirred for 30 min under a hydrogen atmosphere. Then, it was filtered through celite. Removal of the solvent gave a glassy solid which became crystalline on cooling. It was recrystallized from Et_2O/petroleum ether. Yield: 60%. Anal. Calc. for $C_{78}H_{59}BF_{24}RuSb_2$: C, 51.8; H, 3.26. Found: C, 51.5; H, 3.46%. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ −8.51 (s, RuH_2, $(T_1)_{min}$ 1052 ms (400 MHz, 298 K)); 1.75 (s, $C_5(CH_3)_5$); 7.33, 7.40 (m, Sb(C_6H_5)$_3$). ^{13}C{^{1}H}-NMR (100.58 MHz, CD_2Cl_2): δ: 11.5 (s, $C_5(CH_3)_5$); 99.8 (s, $C_5(CH_3)_5$); 130.0, 130.3, 131.5, 136.9 (s, Sb(C_6H_5)$_3$).

3.6. [Cp*RuH(SbPh$_3$)$_2$] (**6**)

To a solution of **5** (0.4 g, 0.22 mmol) in 10 ml of THF, an excess of solid KOBu^t was added. The reaction mixture was stirred for 1 h. The solvent was removed in vacuo. The residue was extracted with petroleum ether and filtered through celite. Concentration and cooling gave a pale yellow residue. Yield 63%. Anal. Calc. for $C_{46}H_{46}RuSb_2$: C, 58.6; H, 4.88. Found: C, 58.2; H, 4.50%. IR: ν(RuH) 1852 cm^{-1}. NMR: ^{1}H (400 MHz, C_6D_6): δ −11.33 (s, RuH); 1.79 (s, $C_5(CH_3)_5$); 6.97, 7.65 (m, Sb(C_6H_5)$_3$). ^{13}C{^{1}H}-NMR (100.58 MHz, C_6D_6): δ: 12.7 (s, $C_5(CH_3)_5$); 87.2 (s, $C_5(CH_3)_5$); 128.3, 128.6, 135.7, 138.6 (s, Sb(C_6H_5)$_3$).

3.7. [Cp*Ru(H_2)(SbPh$_3$)$_2$][BF_4] (**7**)

The preparation of **7** is analogous to that for **3a**, using the monohydride **6** as starting material. Yield: quantitative. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ −8.32 (s, RuH_2, $(T_1)_{min}$ 17 ms (400 MHz, 243 K)); 1.75 (s, $C_5(CH_3)_5$); 7.33, 7.40 (m, Sb(C_6H_5)$_3$). ^{13}C{^{1}H}-NMR (100.58 MHz, CD_2Cl_2): δ: 11.5 (s, $C_5(CH_3)_5$); 99.8 (s, $C_5(CH_3)_5$); 130.0, 130.3, 131.5, 136.9 (s, Sb(C_6H_5)$_3$).

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