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Reactivity of Ruthenium Trihydrides with BrØnsted and Lewis Acids. X-ray Crystal Structures of $\{Cp^*Ru[C_6H_9P(C_6H_{11})_2]\}BF_4$ and $\{\{Cp^*RuH[P(C_6H_{11})_3]\}(\mu\text{-}H)_2Cu(\mu\text{-}Cl)\}_2$. Evidence for Exchange Coupling between Two Hydrogen Atoms

Thérèse Arliguie and Bruno Chaudret*

Laboratoire de Chimie de Coordination du CNRS, UP 8241 liée par conventions à
l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 route de Narbonne,
31077 Toulouse Cedex, France

Felix A. Jalon and Antonio Otero

Departamento de Quimica, Facultad de Quimica, Universidad de Castilla, La Mancha,
Paseo de la Universidad 4, 13071 Ciudad Real, Spain

José A. Lopez and Fernando J. Lahoz

Departamento de Quimica Inorganica, Instituto de Ciencias de Materiales de Aragon,
Universidad de Zaragoza, CSIC, 50009 Zaragoza, Spain

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The reaction of $Cp^*RuH_3(PPh_3)$ (**1a**; $Cp^* = C_5Me_5$) with $P(OMe)_3$ produces $Cp^*RuH(PPh_3)[P(OMe)_3]$ (**2**), whereas no reaction occurs between **1a** and pyridine. The protonation of **1a** by HBF_4/Et_2O yields $[Cp^*RuH_2(PPh_3)_2]BF_4$ (**3**), but the same reaction with $Cp^*RuH_3[P(c\text{-}C_6H_{11})_3]$ (**1b**) leads to the evolution of 3 mol of H_2 and formation of $\{Cp^*Ru[C_6H_9P(c\text{-}C_6H_{11})_2]\}BF_4$ (**4**). Complex **4** contains a cyclohexenyl group coordinated through the C=C double bond and a strong agostic interaction, as demonstrated by both an X-ray crystal structure determination and ^1H and ^{13}C NMR studies. The protonation of **1b** with CF_3COOH produces $Cp^*Ru(OCOCF_3[P(c\text{-}C_6H_{11})_3]$ (**5**), in which the trifluoroacetato group is bidentate. The reactions of **1b** with the Lewis acids $[CuCl]_n$ and $[Cu(MeCN)_4]BF_6$ lead to $\{[Cp^*Ru[P(c\text{-}C_6H_{11})_3]H(\mu\text{-}H)_2]Cu(\mu\text{-}Cl)\}_2$ (**6**), which was characterized by X-ray crystallography, and to $\{[Cp^*Ru[P(c\text{-}C_6H_{11})_3]H(\mu\text{-}H)_2]_2Cu\}PF_6$ (**7**), respectively. The anomalous ^1H NMR behavior of **1** is retained in **6** (viz. a single signal for the hydrides at room temperature and AB_2 spectra showing large temperature-dependent coupling constants at lower temperature). However, three distinct signals are observed for the hydrides of **7** at low temperature, two of which are coupled with large temperature-dependent coupling constants. These phenomena are discussed in light of the new findings on exchange coupling in trihydride complexes. This is the first observation of exchange coupling between two hydrogen atoms only. Finally, **1b** also reacts with $AlCl_3$ to yield $Cp^*RuCl[P(c\text{-}C_6H_{11})_3]$ but not with BF_3/Et_2O. **4** crystallizes in the monoclinic space group $P2_1$, with $a = 9.305$ (1) Å, $b = 16.101$ (2) Å, $c = 10.621$ (1) Å, $\beta = 97.92$ (1)°, $V = 1576.1$ (3) Å^3, and $Z = 2$. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.043$ for 4052 reflections. In addition to the Cp* ligand and the phosphorus atom of the phosphine, the coordination around the ruthenium atom involves a cyclohexenyl group with three carbon atoms at bond distances from the metal center. Crystals of **6** are monoclinic, space group $P2_1/c$, with $a = 12.2131$ (8) Å, $b = 10.7975$ (8) Å, $c = 22.7072$ (17) Å, $\beta = 104.16$ (1)°, $V = 2903.4$ (4) Å^3, and $Z = 2$. The structure was solved by Patterson methods and refined to $R = 0.040$ for 3916 observed reflections. The molecule is centrosymmetric, with two $\{Cp^*RuH[P(C_6H_{11})_3]\}(\mu\text{-}H)_2Cu$ moieties bridged by two chlorine atoms. The Ru-Cu distance is short (2.651 (2) Å) and is bridged by two μ_2-hydride ligands.

Introduction

The chemistry of "polyhydride" derivatives has recently received fresh impetus due to the high reactivity of these compounds and their possible "nonclassical" structures.[1] Thus, after the discovery by Kubas et al. of a complex containing coordinated dihydrogen, the question arose of the real structure of a number of new or known compounds.[2] A number of polyhydride derivatives were reformulated.[1c,3] For some of these compounds, the reactivity is in good agreement with the new formulation, while for others, for example in the case of ReH_7L_2, the real structure is still open to debate.[3,4] This is especially true since most of these compounds usually show only one ill-resolved resonance in their NMR spectra (first attributed to fluxionality). Furthermore, the groups of Kubas,[2] Simpson,[5] and Heinekey[6] have shown that some compounds could exist in two isomeric (dihydride and dihydrogen) forms and dynamic equilibria have even been demonstrated.[2,7] For example, in our group we have shown the existence of a dynamic $Ru^{IV}(H)_2 \rightleftharpoons Ru^{II}(H_2)$ equilibrium in $RuH_2(OCOCF_3)_2(PCy_3)_2$.[7a] The latter process is especially significant in the study of the specific reactivity of dihydrogen compounds involved in dehydrogenation reactions (one example is given in this paper). A similar process may be invoked to explain the facile H/D exchange reactions occurring with some dihydrido(di-

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hydrogen)ruthenium derivatives.[8]

After the discovery of dihydrogen coordination, another question arose as to whether other polyhydrogen structures could be stabilized by transition metals (H_3^+, H_3^-, H_4, ...). Theoretical calculations by Burdett et al. suggested this possibility.[9] We and others reported at that time the preparation of trihydride derivatives of Ru,[10,11] Ir,[12] and Nb,[13] which were all characterized by anomalous ^{1}H NMR spectra. Thus, AB_2 patterns were observed with large temperature-dependent coupling constants (>100 Hz). The values found for Ru and Nb derivatives were still consistent with the interaction of a hydride with a dihydrogen molecule,[11,13] while a trihydrogen ligand was proposed in the case of Ir and Nb.[12,13]

However, the coupling constants recently found for iridium compounds (>1000 Hz) indicate the presence of a new phenomenon rationalized independently by two groups as exchange coupling between the protons, a heavy-particle quantum-mechanical effect.[14,15]

In the search for a chemical characterization of these derivatives, we attempted some simple insertion and substitution reactions, which proved difficult. The protonation which could lead to bis(dihydrogen) compounds was also attempted, although it is known that the protonation of a classical polyhydride can yield a nonclassical compound (viz. $IrH_5(PCy_3)_2 + H^+ \rightarrow [IrH_2(H_2)_2(PCy_3)_2]^+$).[16] Finally, since after the work of Caulton[17] we had shown that copper(I) salts can coordinate to hydride derivatives to give Lewis base–Lewis acid adducts,[18] we reacted $Cp^*RuH_3PR_3$ with such copper salts in the hope of being able to discriminate the hydride from the coordinated H_2 in a hypothetical hydrido dihydrogen structure. This paper describes our results. Preliminary accounts of parts of this work have been published.[19,20]

Results

Substitution Reactions. The trihydride derivatives $Cp^*RuH_3PR_3$ ($Cp^* = C_5Me_5$, R = Ph (**1a**), c-C_6H_{11} (**1b**), *i*-C_3H_7 (**1c**)) are thermally quite stable since, for example, no reaction is observed between **1a** and neohexene when they are heated in a solution of cyclohexane to 100 °C in a closed vessel. Similarly, no reaction is observed between **1a** and pyridine in refluxing toluene. However, upon reaction with timethyl phosphite in toluene at 90 °C a monohydride species, $Cp^*RuH[P(OMe)_3](PPh_3)$ (**2**), is obtained as a yellow microcrystalline powder. The product is characterized by ^{31}P NMR (two doublets at δ 72.9 (PPh_3) and −0.3 ($P(OMe)_3$ ppm; J_{PP} = 57.3 Hz) and ^{1}H NMR spectroscopy (especially a hydride at δ −12.0 (dd, J_{P_1H} = 3.5 Hz, J_{P_2H} = 17.5 Hz), PPh_3 between 7.03 and 8.04 ppm, a doublet for $P(OMe)_3$ at δ 3.22 ppm (J_{PH} = 11 Hz) and the Cp* ligand at δ 1.90 ppm (t, J_{PH} = 1.5 Hz); all had correct integration ratios). The product presumably adopts a classical piano-stool structure possessing a chiral ruthenium atom.

Reactions with Brønsted Acids. All of the trihydride derivatives **1** react rapidly with acids, as expected for complexes with a strong Lewis base character. **1c** reacts with $HBF_4 \cdot Et_2O$ in acetone at −78 °C, but only [HP-*i*-Pr_3]BF_4 is obtained because of decomposition.

1a reacts with $HBF_4 \cdot Et_2O$ in toluene to give a white precipitate containing a 1:1 mixture of two complexes. The first complex was isolated pure as an orange precipitate and shown to be $[Cp^*RuH_2(PPh_3)_2]BF_4$ (**3**). A Ru–H stretching vibration was observed at 1980 cm^{-1} by infrared spectroscopy. In addition, the ^{1}H NMR spectrum showed the hydrides at δ −6.84 (t, J_{PH} = 30 Hz, 2 H), the Cp* ligand at δ 1.56 (t, $J_{PH} \approx$ 1.5 Hz, 15 H), and phenyl protons (30 H). These data are in good agreement with the proposed structure. The symmetry of the hydride signal together with observations by other groups[5,6] on related compounds led us to propose a trans configuration for the hydrides. The other compound was identified as $[Cp^*Ru(\eta^6\text{-}C_6H_5Me)]BF_4$ by comparison with an authentic sample.[21]

In acetone similar reactions occurred, and again disproportionation of the complex led to **3** and to Cp* derivatives that did not contain any phosphines and were presumably of the type $[Cp^*RuS_3]^+$.

Protonation of **1b** in acetone at −78 °C yielded a yellow-brown solution from which, after appropriate workup with ethanol, we isolated yellow crystals of a complex that was analyzed for $[Cp^*Ru(C_6H_9PCy_2)]BF_4$ (**4**) in low yield. However, the same reaction carried out in hexane at room temperature led to extensive gas evolution and precipitation of **4** in high yield. The ^{1}H NMR spectrum of the compound is complex (see Figure 1 and Scheme I) and shows, together with the Cp* protons at δ 1.85 and cyclohexyl protons between δ 2 and 1, a high-field pseudoquartet at δ −10.5 (H_0, "J" = 11 Hz), a doublet of triplets at δ 4.04 (H_1, J_{HH} = 6.5, 1.2 Hz), a triplet at δ 3.85 (H_2, J_{HH} = 6.5 Hz) and a broad multiplet centered at δ 3.18 (H_3) (Figure 1). Upon phosphorus decoupling, the signal for H_0 became a pseudo-triplet, whereas no change was observed for H_1, H_2, and H_3. Selective ^{1}H decoupling experiments demonstrate the coupling of H_0 to H_3 and of H_1 equally to both H_2 and an alkyl proton of the phosphine (6.5 Hz). H_2 is also coupled to H_3, although with a small coupling constant (1.2 Hz), while H_3 is coupled to H_0, H_1, H_2, and other alkyl protons. The ^{13}C NMR spectra indicate the presence of two olefinic carbons at δ 69.7 and 69.15 ppm (d, J_{CH} = 159 and 174 Hz, respectively) and a relatively broad signal at δ 41.1 ppm (dd, H_2, J_{CH_3} = 159 Hz, J_{CH_0} = 39 Hz) together with peaks between δ 37 and 25 ppm attributed to alkyl carbons of the phosphine and the peaks of Cp* at δ 96.8 (s, C_5Me_5) and δ 10.3 (q, $C_5\mathit{Me}_5$, J_{CH} = 128 Hz). From these data we assume that the

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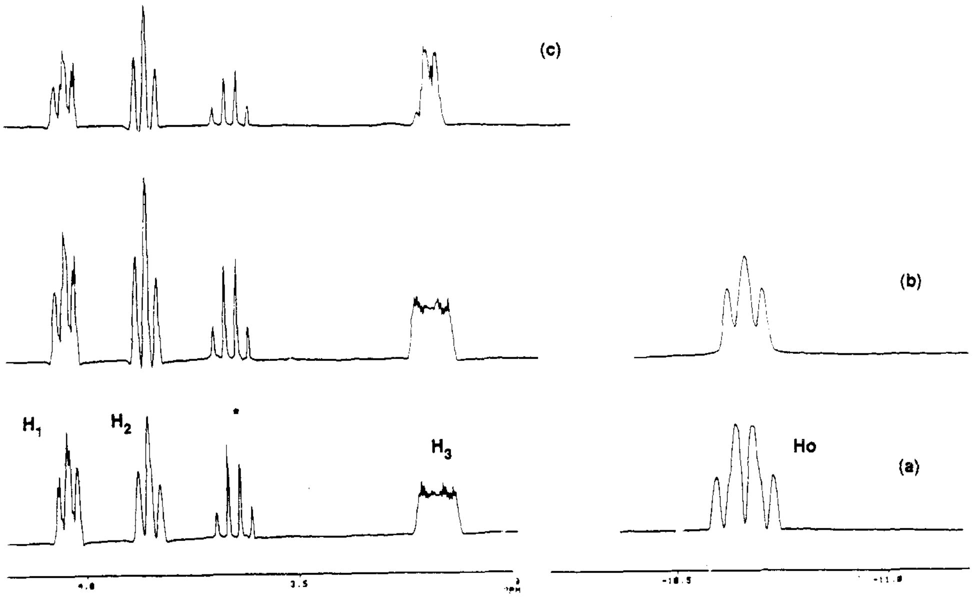

Figure 1. (a) ^1H NMR spectrum of complex 4. (b) ^{31}P-decoupled spectrum. (c) Spectrum with hydride region decoupled. Peaks marked with an asterisk are due to ethanol.

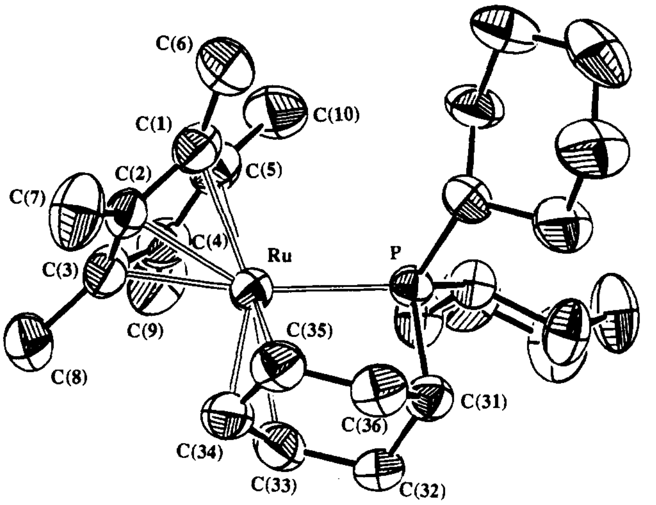

Figure 2. Ortep view of $\{Cp^*Ru[C_6H_9P(C_6H_{11})_2]\}BF_4$ (4) (hydrogen atoms are omitted).

dehydrogenation of a cyclohexyl ligand gives a cyclohexenyl moiety. The two olefinic carbons bearing H_1 and H_2 (C(35) and C(34), respectively, according to crystal structure numbering) and the presence of an agostic interaction between a proton (H_0) of an adjacent carbon (C(33)) and the metal[22] (Scheme I) are consistent with the spectral data.

This dehydrogenation was clearly demonstrated by an X-ray crystal structure determination. Thus, the molecular structure of 4 consists of a mononuclear cation, a BF_4 anion, and an ethanol of crystallization. An ORTEP drawing of the cation with the atomic numbering scheme is given in Figure 2. The coordination around the ruthenium atom involves the C_5Me_5 ligand, the phosphorus atom, and two carbon atoms of the cyclohexenyl group attached to the latter (Ru–C(34) = 2.109 (5) Å and Ru–C(35) = 2.286 (6) Å). The C(34)–C(35) distance (1.403 (8) Å) is significantly shorter than the values expected for a single C–C bond in a cyclohexyl moiety, in agreement with the presence of a coordinated olefinic group. Interestingly, another carbon atom (C(33)) lies in close proximity to the metal. The metal–carbon distance (2.315 (5) Å) is short but still in the range found for carbon atoms bearing an agostic proton.[22] The C(33)–C(34) distance (1.487 (9) Å) is also slightly shortened.

Table I. Selected Bond Lengths (Å) and Angles (deg) for 4[a]

Ru–P	2.327 (1)	Ru–C(1)	2.213 (5)
Ru–G*	1.855 (3)	Ru–C(2)	2.200 (6)
Ru–C(33)	2.315 (5)	Ru–C(3)	2.212 (6)
Ru–C(34)	2.109 (5)	Ru–C(4)	2.236 (6)
Ru–C(35)	2.286 (6)	Ru–C(5)	2.237 (6)
C(31)–C(32)	1.498 (7)	C(33)–C(34)	1.487 (9)
C(31)–C(36)	1.545 (8)	C(34)–C(35)	1.403 (8)
C(32)–C(33)	1.503 (9)	C(35)–C(36)	1.514 (9)
P–Ru–G*	134.0 (1)	G*–Ru–C(34)	125.7 (2)
P–Ru–C(33)	81.4 (2)	G*–Ru–C(35)	133.0 (2)
P–Ru–C(34)	99.9 (2)	C(33)–Ru–C(34)	38.9 (2)
P–Ru–C(35)	80.0 (2)	C(33)–Ru–C(35)	64.7 (2)
G*–Ru–C(33)	137.0 (2)	C(34)–Ru–C(35)	37.0 (2)
Ru–C(33)–C(32)	112.3 (3)	C(32)–C(31)–C(36)	108.9 (4)
Ru–C(33)–C(34)	63.0 (3)	C(31)–C(32)–C(33)	112.5 (4)
Ru–C(34)–C(33)	78.1 (3)	C(32)–C(33)–C(34)	115.5 (5)
Ru–C(34)–C(35)	78.4 (3)	C(33)–C(34)–C(35)	116.8 (5)
Ru–C(35)–C(34)	64.6 (3)	C(34)–C(35)–C(36)	119.2 (5)
Ru–C(35)–C(36)	114.2 (4)	C(31)–C(36)–C(35)	109.3 (5)

[a] G* represents the midpoint of the pentamethylcyclopentadienyl ligand.

All the data presented above are consistent with the dehydrogenation of a cyclohexyl group and the existence of a strong agostic interaction. Unfortunately, the disorder of the anion and solvent molecule prevented a direct location of the agostic proton in the X-ray analysis. However, molecular mechanic positioning of this proton gives a Ru–H distance of 1.786 (6) Å, also in the range found for such interactions. The low value of J_{CH} (39 Hz) and, correspondingly, the relatively high value of J_{HP} (11 Hz) are in agreement with a strong agostic interaction, i.e. a substantial transfer of σ-electron density from the carbon to the metal.[22]

The mechanism of this reaction probably involves protonation of a coordinated hydride and formation of an unstable bis(dihydrogen) derivative due to the reduction of electron density at the metal. Activation of a C–H bond

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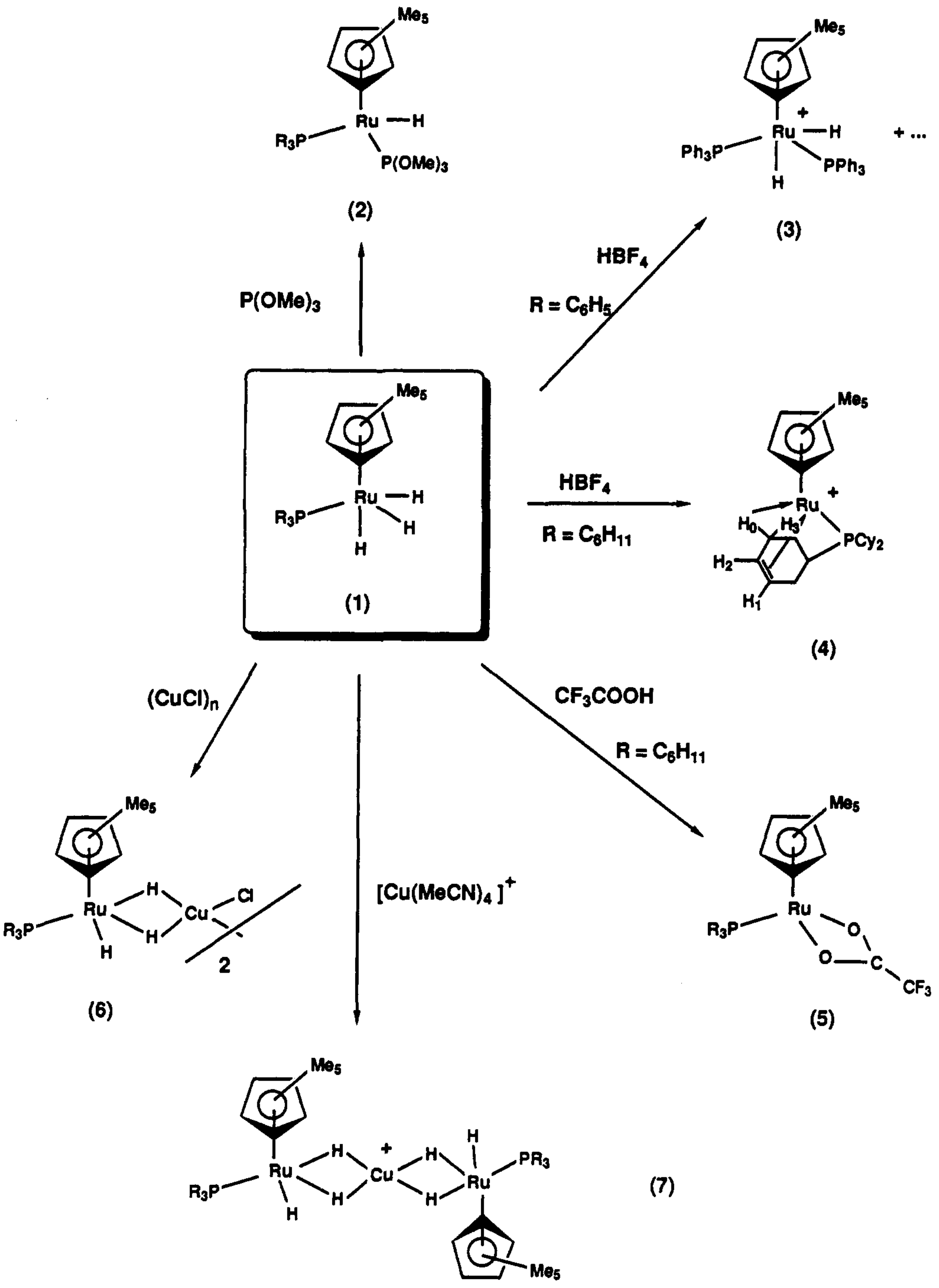
Scheme I. Reactivity of Cp*RuH$_3$PR$_3$ (1) toward Substitution, Protonation, and Lewis Acid Addition



would lead to a 16-electron hydridoalkylruthenium(IV) derivative. Stabilization of the compound thus occurs through a β-elimination reaction. Formation of an unstable olefin dihydrogen compound followed by elimination of H_2 and coordination of a C–H bond adjacent to the olefinic group complete the mechanism. The interesting part of this mechanism is the existence of a "spontaneous" β-elimination step probably driven by H_2 evolution.

The protonation of **1b** was carried out with an acid containing a coordinating anion in order to try to stabilize an intermediate. Thus, **1b** reacted with CF_3COOH in hexane, but not in acetone, yielding a red-purple solution from which purple crystals were obtained upon recrystallization from methanol. The compound was analyzed for Cp*Ru(OCOCF$_3$)(PCy$_3$) (**5**) and was characterized by spectroscopic means (^{1}H NMR C_5Me_5 δ 1.55 ppm (15 H), PCy$_3$ δ 1.32–1.91 ppm (33 H); infrared ν(CO) 1620 cm^{-1}). The low ν(CO) stretch is characteristic of a bidentate mode of coordination of the trifluoroacetato anion, whereas the dark (purple) color is usually associated with 16-electron ruthenium complexes. We assume that the compound is an 18-electron species (Scheme I), although some bidentate–monodentate exchange could exist. The CF_3COO^- anion has trapped the "Cp*RuPCy$_3^+$" fragment before the first C–H activation reaction proceeds. **5** is thus similar to the intermediate proposed in the dehydrogenation process.

Reactions of Cp*RuH$_3$PCy$_3$ with Copper Salts. Copper(I) salts are good Lewis acids and have been used to prepare Lewis acid–Lewis base adducts with various hydrido complexes of transition metals.[17,18] With the hope of aiding the characterization of the peculiar trihydrides

$Cp^*RuH_3PR_3$ and, in particular, of being able to discriminate a hydride from coordinated dihydrogen in a hypothetical hydrido dihydrogen derivative, we carried out the reaction of **1b** with $[CuCl]_n$ and $[Cu(MeCN)_4]BF_4$. **1b** reacts smoothly at room temperature with $1/n$ equiv of $[CuCl]_n$ in toluene. Prolonged reaction leads again to the π complex $[Cp^*Ru(\eta^6\text{-}PhMe)]^+$ through a mechanism that has not been investigated. However, when the reaction is stopped after 2 h, a high yield of the creamy white hydrocarbon-soluble complex $[Cp^*Ru(PCy_3)H_3(CuCl)]_2$ (**6**) is obtained. The solid-state infrared spectrum of this compound shows a sharp peak for terminal hydrides at 2010 cm^{-1} and a broad peak for bridging hydrides centered at 1740 cm^{-1}. Interestingly, the bridging hydrides in these transition-metal hydride copper adducts always show a strong distinct absorption.

Similarly, the reaction of **1b** with 1 or $^1/_2$ equiv of $[Cu(MeCN)_4]PF_6$ leads smoothly to $[(Cp^*RuH_3PCy_3)_2Cu]PF_6$ (**7**). Again the infrared spectrum reveals a ν(Ru–H) band at 2005 (m, sh) cm^{-1} and two distinct bridging hydrides at 1790 (m, br) and 1710 (m, br) cm^{-1}.

The room-temperature ^1H NMR spectrum of both compounds shows the Cp* ligand at 2.1 and 2.23 ppm, respectively, the phosphine protons between δ 1.2 and 2.2 ppm, and the hydrides as a doublet at δ −10.37 and −10.38 ppm, respectively, with a J_{HP} coupling constant significantly reduced by comparison with that observed for the starting trihydride **1b** (13 and 14.5 Hz, respectively, as compared to 22.5 Hz in **1b**).[10] However, as in **1b**, the three hydrides are not distinguishable at room temperature. Since we know from earlier studies on **1** and from low-temperature studies on **6** and **7** that the central hydrogen atom is not coupled to phosphorus but to the two extreme H atoms only, this result implies an increase in these Ru–H distances, which is expected upon Cu coordination, a change in the H–Ru–P angle, which is also expected, or more likely a combination of both.

The structure of **6** has been determined by an X-ray diffraction study (Figure 3). The structure lies on a center of symmetry and consists of a "$Cu_2(\mu\text{-}Cl)_2$" unit bridging two $Cp^*RuH_3PCy_3$ moieties. Each copper atom is bonded to two chlorine atoms and two hydrides, as predicted. The geometry around ruthenium is that of a classical piano stool. The hydride atoms were found in a difference Fourier map and refined as isotropic atoms. Although the high esd prevented a detailed discussion of distances involving these atoms, a few points deserve some comments. First, as we proposed, the Lewis acid is bonded to two hydrides, the third one remaining terminal. The P–Ru–H(2) angle is 97° and can explain the absence of coupling between the central hydride of $Cp^*RuH_3PR_3$ and the phosphine. The H(1)–H(2) distance is 1.65 (7) Å, an order of magnitude found for other trihydrides showing "anomalous behavior" or exchange coupling. The ruthenium–copper distance is very short (2.651 (2) Å) and comparable to known Cu–Ru distances[23] but may not be indicative of direct Ru–Cu bonding. Finally, the geometry around copper is almost square planar.

Table II. Selected Bond Distances (Å) and Angles (deg) for $\{[Cp^*RuH[P(C_6H_{11})_3]](\mu\text{-}H)_2(CuCl)\}_2$ (6)[a]

Ru–Cu	2.651 (2)	Ru–C(1)	2.261 (5)
Ru–P	2.304 (3)	Ru–C(2)	2.296 (5)
Ru–H(1)	1.60 (5)	Ru–C(3)	2.268 (5)
Ru–H(2)	1.50 (5)	Ru–C(4)	2.221 (6)
Ru–H(3)	1.60 (6)	Ru–C(5)	2.213 (5)
Cu···Cu′	3.086 (2)		
Cu–Cl	2.258 (3)	Cu–Cl′	2.360 (2)
Cu–H(2)	1.65 (5)	Cu–H(3)	1.76 (5)
Cu–Ru–P	97.8 (1)	P–Ru–G*	137.3 (2)
Cu–Ru–H(1)	96 (2)	H(1)–Ru–H(2)	64 (3)
Cu–Ru–H(2)	34 (2)	H(1)–Ru–H(3)	118 (3)
Cu–Ru–H(3)	40 (2)	H(1)–Ru–G*	119 (2)
Cu–Ru–G*	120.5 (2)	H(2)–Ru–H(3)	71 (3)
P–Ru–H(1)	70 (2)	H(2)–Ru–G*	125 (2)
P–Ru–H(2)	97 (2)	H(3)–Ru–G*	121 (2)
P–Ru–H(3)	76 (2)		
Ru–Cu–Cl	141.1 (1)	Cl–Cu–H(2)	162 (2)
Ru–Cu–Cl′	122.1 (1)	Cl–Cu–H(3)	105 (2)
Ru–Cu–H(2)	31 (2)	Cl′–Cu–H(2)	97 (2)
Ru–Cu–H(3)	36 (2)	Cl′–Cu–H(3)	157.1 (2)
Cl–Cu–Cl′	96.2 (1)	H(2)–Cu–H(3)	64 (3)
Ru–H(2)–Cu	114 (3)	Cu–Cl–Cu′	46.68 (5)
Ru–H(3)–Cu	104 (3)		

[a] G* represents the midpoint of the pentamethylcyclopentadienyl ligand. Primed atoms are symmetry-related ones (symmetry transformation $1-x$, $-y$, $1-z$).

Lowering the temperature of the NMR experiment leads in the case of **6** to the appearance of an AB_2 type spectrum for the hydrides with coupling constants varying as a function of temperature from ~70 Hz near 230 K to ~20 Hz at 188 K (Figure 4: 188 K, 21 Hz; 193 K, 26.2 Hz; 198 K, 34.1 Hz; 203 K, 42.0 Hz; 213 K, 52.5 Hz; 233 K, 70 Hz). The chemical shifts of the different hydrides are respectively, at low temperature, −11.5 (A) and −9.4 (B) ppm. This behavior is typical of compounds of type **1** and of a series of trihydride derivatives reported by us and others.[10,13] Only the temperature range and the amplitude of the coupling constants vary according to the compound. The phenomenon was first attributed to fluxionality at high temperature and observation of H–H bonding at lower temperature. The existence of a "nonclassical interaction" between a hydride and a coordinated H_2 moiety[10] or even of a trihydrogen ligand was postulated to account for the apparent nonrotation of H_2. Yet, soon after the discovery of coupling constants as high as 1400 Hz that could not be interpreted by simple chemical models, Heinekey, Zilm, et al.[14] as well as Weitekamp, Labinger, et al.[15] assumed the phenomenon to be due to an exchange coupling similar to what is observed for electrons in the EPR spectra of biradicals. The amplitude of the coupling would be related to large-amplitude motions of the hydrides, thus explaining the variation as a function of temperature. In the case of **6**, it is difficult to imagine how such a large-amplitude vibration can develop freely with two of the hydrides linked to copper. It might be assumed that a normal fluxional process would be coupled to the quantum phenomenon. The AB_2 spectra may then be observed only when the apparent fluxional motion of the copper from H(3) to H(1) is faster than the NMR time scale.

The case of **7** is even more complex. Thus, although the three hydrides appear equivalent at room temperature, when the temperature is lowered the signal separates first into two broad peaks and then into three distinct signals (Figure 5). For consistency with the X-ray numbering (structure of **6**), they are called H_1 (δ −9.22, $J_{H_1H_2}$ = 45 Hz, J_{H_1P} = 22 Hz), H_2 (δ −11.92, $J_{H_2H_3}$ = 6 Hz, $J_{H_2P} \approx 0$ Hz), and H_3 (δ −10.40, J_{H_3P} = 15 Hz). These attributions are derived mainly from the J_{HP} coupling constants. Thus,

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(23) For some recent examples of Ru–Cu distances, see: (a) McCarthy, P. J.; McPartlin, M.; Powell, H. R.; Salter, I. R. *J. Chem. Soc., Chem. Commun.* **1989**, 395. (b) Brown, S. D.; McCarthy, P. J.; Salter, I. D.; Bates, P. A.; Hursthouse, M. B.; Colquhoun, I. J.; McFarlane, W.; Murray, M. *J. Chem. Soc., Dalton Trans.* **1988**, 2787. (c) Brown, S. D.; Salter, I. D.; Toupet, L. *J. Chem. Soc., Dalton Trans.* **1988**, 757. (d) Adatia, T.; McCarthy, P. J.; McPartlin, M.; Rizza, M.; Salter, I. D. *J. Chem. Soc., Chem. Commun.* **1988**, 1106 and references therein.

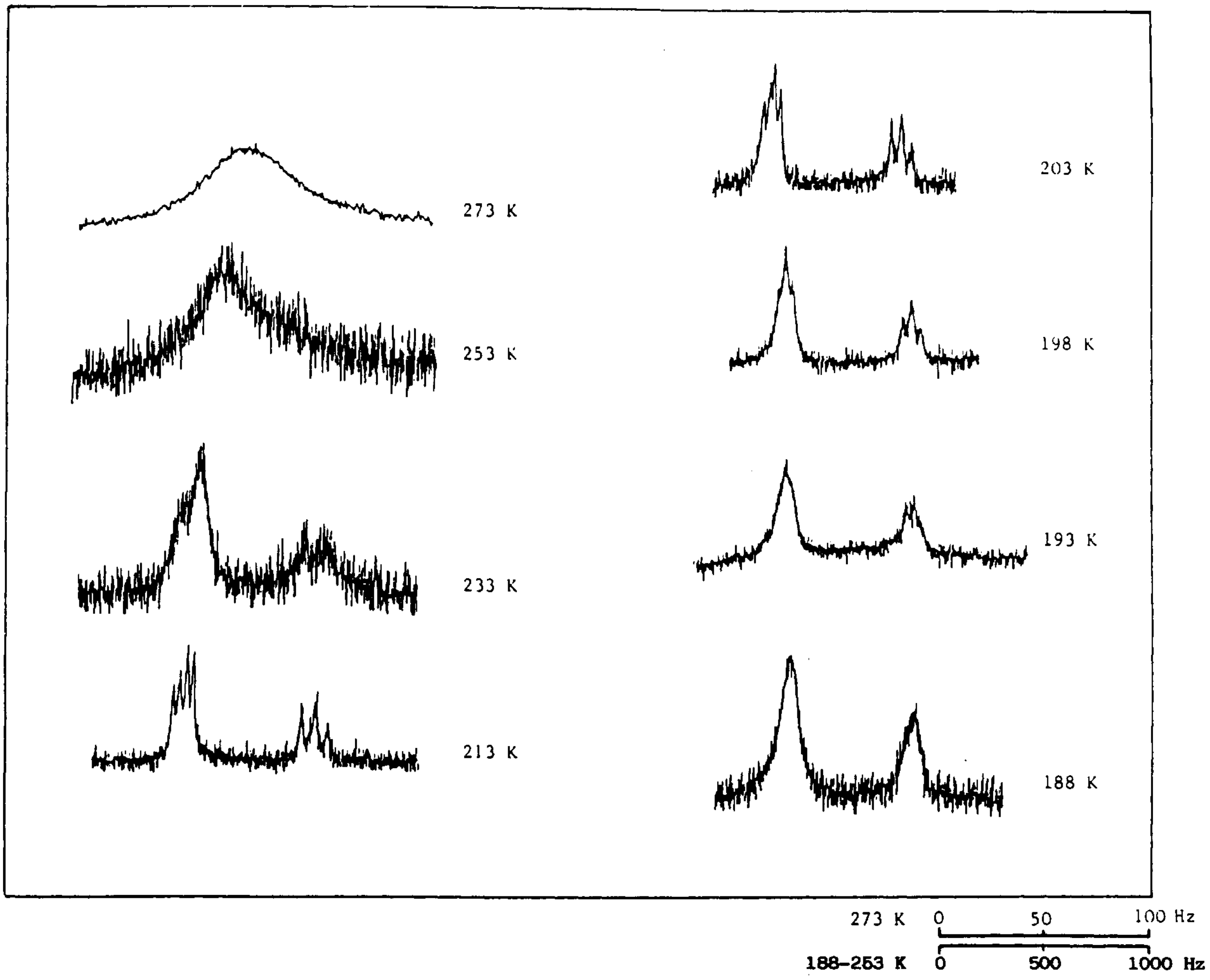

Figure 3. Variation of the high-field ^1H NMR spectrum (250 MHz) of $\{Cp^*RuH[P(C_6H_{11})_3](\mu\text{-}H_2)(CuCl)\}_2$ (6) as a function of temperature.

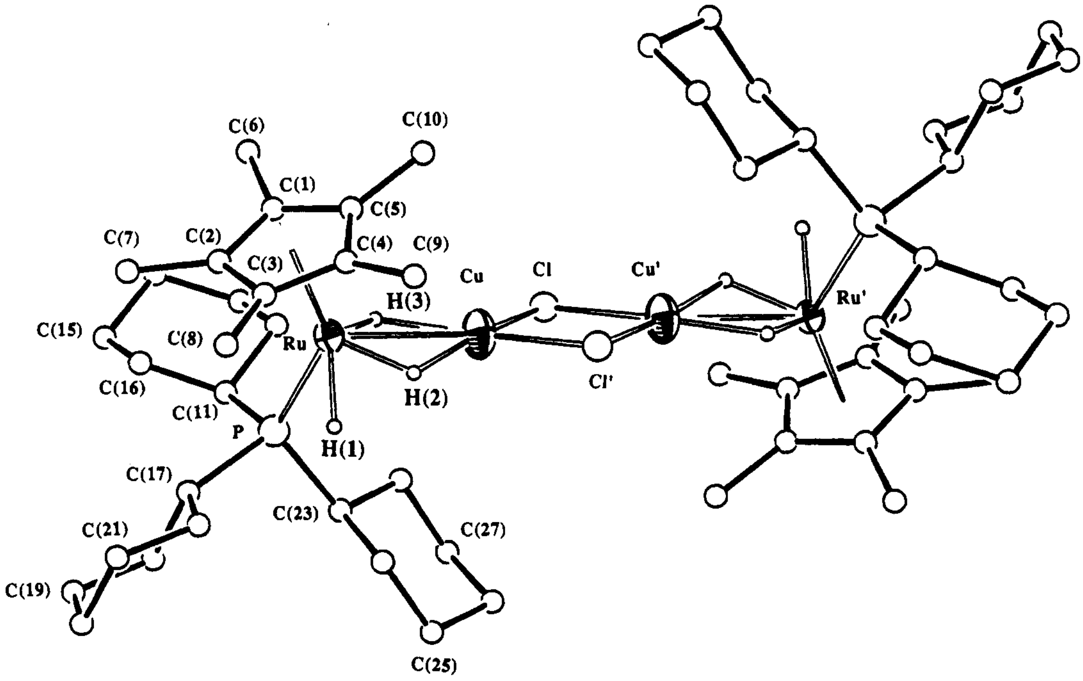

Figure 4. Ortep view of $\{\{Cp^*RuH[P(C_6H_{11})]_3\}(\mu\text{-}H_2)(CuCl)\}_2$ (6) (all hydrogen atoms except hydrides are omitted for the sake of clarity).

H_2, not coupled with phosphorus, is the central hydride, whereas H_3, showing a reduced J_{HP} coupling constant, is probably linked to copper. Such decreases in the magnitude of coupling constants upon coordination to copper has been observed previously.[18,24]

Our first proposal to explain this phenomenon was the formation of a H–H bond. This was plausible since $M(H_2)$

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(24) He, X. D.; Fernandez-Baeza, J.; Chaudret, B.; Folting, K. G.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 5000.

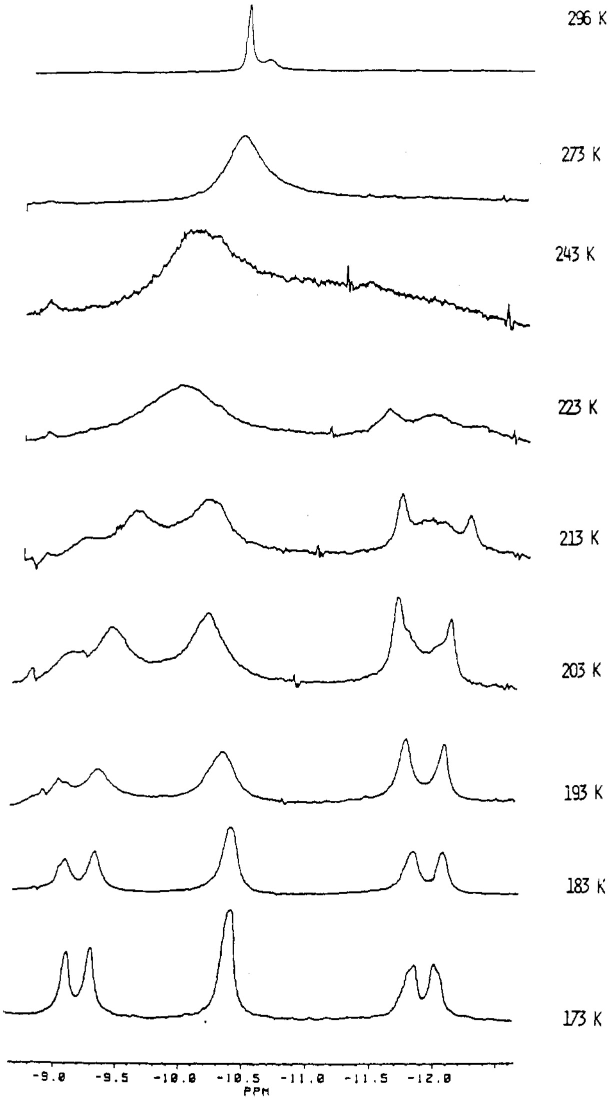

Figure 5. Variation of the high-field $^1H\{^{31}P\}$ NMR spectrum (250 MHz) of $\{[Cp^*RuH[P(C_6H_{11})_3]\}(\mu\text{-}H_2)Cu\}PF_6$ (7) as a function of temperature.

$\rightleftharpoons M(H)_2$ equilibria are now well documented, in particular with ruthenium compounds.[7] However, the recent findings on exchange coupling in these derivatives bring us a more satisfactory proposal. Thus, since "Cu^+" is a stronger Lewis acid than CuCl, the H(Ru)–Cu bonds are probably stronger and the barrier to fluxionality higher. However, H_1 can vibrate freely and H_1H_2 coupling can develop. The presence of three particles is not necessary for exchange coupling, although never observed before. If we keep in mind the large uncertainties in H–H distances, it is noteworthy that the H_1–H_2 distance seems similar to that found for $Cp^*RuH_3PPh_3$ and thus makes the H–H exchange coupling plausible. Significantly, $J_{H_2H_3}$ (6 Hz), for which H–H distances must be somewhat higher, is a classical scalar coupling.

Conclusion

The chemical properties of compounds of type 1 are those expected for ruthenium(IV) trihydrido complexes rather than for molecular hydrogen derivatives. Thus, we did not observe any D_2 incorporation upon leaving 1 under 2 atm of D_2 for several days. H_2 elimination is difficult, whether thermally or photochemically, while substitution of H_2 by the two-electron-donor ligand L is either difficult (L = $P(OMe)_3$) or impossible (L = pyridine). Protonation generally destablizes the complex, but in the case of **1b**, we observed an interesting dehydrogenation reaction. The formation of H–H bonds in the coordination sphere of ruthenium and subsequent elimination of H_2 is caused by initial hydride protonation followed by reduction of electron density favoring the formation of a second dihydrogen ligand. The "spontaneous" dehydrogenation of the hydrocarbon ligand implies the formation of a third mole of H_2 in the coordination sphere of ruthenium. This type of mechanism can be of great significance for hydrocarbon dehydrogenation, and intermolecular reactions of this type are presently being studied in detail.[25]

Table III. Experimental Data for the X-ray Diffraction Studies on 4 and 6

	4	6
mol formula	$C_{28}H_{46}BF_4OPRu{\cdot}C_2H_6O$	$C_{56}H_{102}Cl_2Cu_2P_2Ru_2$
color	yellow	brown
habit	prismatic blocks	
mol wt	647.59	1237.51
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$P2_1/c$
a, Å	9.305 (1)	12.2131 (8)
b, Å	16.101 (2)	10.7975 (8)
c, Å	10.621 (1)	22.7072 (18)
β, deg	97.92 (1)	104.16 (1)
V, Å^3	1576.1 (3)	2903.4 (4)
Z	2	2
D_{calcd}, g cm^{-3}	1.365	1.416
$F(000)$	680	1296
cryst dimens, mm	0.46 × 0.52 × 0.42	0.27 × 0.27 × 0.57
linear abs coeff, cm^{-1}	5.81	14.1
diffractometer	Siemens-Stoe AED-2	
temp, K	293	293
scan type	$\omega/2\theta$	
monochromator	oriented graphite cryst	
radiatn	Mo Kα (λ = 0.71069 Å)	
2θ range, deg	3–45	3–50
no. of rflns measd	$\pm h,\pm k,\pm l$	$\pm h,\pm k,+l$
std rflns	3 every 1 h	
no. of data measd	8842	11128
no. of unique total data	4111	4975
R_{merg} equiv rflns	0.0247	0.0248
no. of unique obsd data	4052 ($I > 3.0\sigma(I)$)	3916 ($I > 2.0\sigma(I)$)
abs cor	ψ-scan method	empirical (DIFABS)
min, max abs cor	0.708, 0.814	0.874, 1.124
final R, R_w	0.043, 0.046	0.040, 0.042

Finally, the use of copper salts as Lewis acids allowed us to prepare interesting new adducts that definitely show a classical structure in the solid state. However, they show an anomalous behavior characterized in their ^1H NMR spectra by an AB_2 (**6**) or ABC (**7**) type spectrum for the hydrides. In our opinion, this reflects the possibility for **6** to undergo chemical fluxionality whereas, due to stronger RuHCu bonds, this is more difficult in the case of **7**. However, vibration of the hydrides can lead in both cases to the appearance of exchange coupling as previously observed on some trihydride derivatives of Ru, Ir, and Nb. This is the first observation of such exchange coupling in the case of only two hydrogen atoms.

Experimental Section

General Procedure. All manipulations were conducted under an inert atmosphere of argon with use of standard Schlenk tube techniques. Microanalyses were performed by the "Centre de Microanalyse du CNRS" or in our laboratory. Infrared spectra were obtained as Nujol mulls or in KBr with a PE 683 grating

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[25] (a) Chaudret, B.; Dahan, F.; He, X. D. *J. Chem. Soc., Chem. Commun.* **1990**, 1111. (b) Rondon, D.; Chaudret, B.; He, X. D.; Labroue, D. *J. Am. Chem. Soc.*, in press.

Table IV. Fractional Atomic Coordinates (×10^4) for the Non-Hydrogen Atoms of $\{Cp^*Ru[(C_6H_9)P(C_6H_{11})_2]\}BF_4 \bullet CH_3CH_2OH$ 4[a]

atom	*x*	*y*	*z*
Ru	−222 (1)	5000 (1)	8712 (1)
P	1835 (1)	4837 (1)	7714 (1)
B	9878 (11)	3074 (4)	3148 (7)
C(1)	−2136 (6)	5209 (4)	7263 (6)
C(2)	−2426 (6)	5525 (4)	8479 (6)
C(3)	−2379 (6)	4848 (5)	9336 (6)
C(4)	−2071 (7)	4108 (4)	8663 (6)
C(5)	−1932 (6)	4242 (4)	7393 (6)
C(6)	−2300 (10)	5720 (6)	6056 (7)
C(7)	−2835 (9)	6397 (5)	8749 (10)
C(8)	−2773 (7)	4859 (6)	10671 (6)
C(9)	−2033 (8)	3228 (5)	9213 (9)
C(10)	−1812 (8)	3724 (5)	6357 (7)
C(11)	1976 (6)	5492 (3)	6308 (5)
C(12)	1167 (6)	5110 (6)	5105 (4)
C(13)	1058 (9)	5746 (5)	3991 (6)
C(14)	2536 (11)	6032 (6)	3767 (7)
C(15)	3387 (9)	6404 (6)	4987 (7)
C(16)	3501 (8)	5752 (5)	6073 (6)
C(21)	2404 (5)	3771 (3)	7323 (5)
C(22)	1821 (7)	3098 (4)	8095 (7)
C(23)	2126 (9)	2229 (4)	7553 (9)
C(24)	3738 (9)	2104 (4)	7590 (10)
C(25)	4388 (9)	2816 (5)	6862 (9)
C(26)	4067 (7)	3664 (4)	7367 (7)
C(31)	3142 (6)	5268 (3)	9012 (4)
C(32)	2994 (6)	4792 (4)	10199 (4)
C(33)	1462 (7)	4784 (4)	10499 (5)
C(34)	704 (7)	5599 (4)	10396 (5)
C(35)	1066 (6)	6148 (4)	9463 (5)
C(36)	2610 (7)	6167 (4)	9163 (6)
F(1)	10541 (13)	2943 (8)	2047 (12)
F(2)	8675 (15)	2607 (10)	2812 (14)
F(3)	9383 (11)	3851 (7)	3134 (10)
F(4)	10548 (12)	2922 (7)	4312 (11)
C(1S)*	4747 (25)	3209 (15)	2882 (22)
C(2S)*	5143 (20)	3944 (13)	3437 (18)
O(1S)*	5640 (22)	3005 (12)	1900 (21)

[a] Starred atoms correspond to the ethanol solvent molecule.

Table V. Fractional Atomic Coordinates[a] (×10^4) for the Non-Hydrogen Atoms of $\{\{Cp^*RuH[P(C_6H_{11})_3]\}(\mu\text{-}H)_2(CuCl)\}_2$ (6)

atom	*x*	*y*	*z*
Ru	6883 (1)	2451 (1)	6273 (1)
Cu	5820 (1)	899 (1)	5418 (1)
Cl	6163 (1)	−680 (2)	4836 (1)
P	8011 (1)	3394 (1)	5727 (1)
C(1)	7725 (4)	1457 (5)	7142 (2)
C(2)	7782 (4)	2745 (4)	7276 (2)
C(3)	6656 (4)	3210 (4)	7167 (2)
C(4)	5900 (4)	2211 (4)	6969 (2)
C(5)	6557 (4)	1126 (4)	6954 (2)
C(6)	8690 (5)	564 (5)	7292 (3)
C(7)	8821 (4)	3474 (6)	7576 (2)
C(8)	6345 (5)	4488 (5)	7331 (2)
C(9)	4629 (4)	2269 (5)	6839 (3)
C(10)	6106 (6)	−184 (5)	6838 (3)
C(11)	9450 (4)	2722 (4)	5772 (2)
C(12)	9422 (4)	1288 (5)	5735 (3)
C(13)	10584 (4)	776 (6)	5722 (3)
C(14)	11477 (5)	1183 (6)	6262 (3)
C(15)	11509 (5)	2578 (6)	6312 (4)
C(16)	10351 (5)	3103 (6)	6324 (3)
C(17)	8389 (5)	5029 (5)	5956 (2)
C(18)	9070 (5)	5749 (5)	5585 (3)
C(19)	9515 (6)	6960 (6)	5900 (3)
C(20)	8596 (7)	7758 (5)	6016 (4)
C(21)	7923 (8)	7043 (6)	6385 (5)
C(22)	7471 (6)	5838 (6)	6063 (4)
C(23)	7480 (6)	3542 (6)	4896 (3)
C(24)	6334 (6)	4225 (8)	4715 (3)
C(25)	5953 (8)	4446 (8)	4019 (4)
C(26)	5926 (8)	3216 (9)	3665 (5)
C(27)	7095 (8)	2567 (10)	3844 (4)
C(28)	7466 (8)	2320 (7)	4541 (3)
C(23)′	7235 (12)	3102 (19)	4867 (8)
C(24)′	6029 (12)	3683 (17)	4673 (7)
C(25)′	5532 (17)	3282 (20)	4000 (7)
C(26)′	6284 (12)	3723 (17)	3578 (7)
C(27)′	7489 (13)	3148 (17)	3794 (7)
C(28)′	8032 (15)	3550 (19)	4460 (7)

[a] Primed atoms represent disordered atoms for a cyclohexyl ring (C(23)–C(28)).

diffractometer. NMR spectra were recorded on Bruker WH90, WM250, or AC200 spectrometers.

$Cp^*RuH(PPh_3)P(OMe_3)_3$ (2). **2** was prepared from the reaction of **1a** (0.300 g, 0.60 mmol) with $P(OMe)_3$ (0.060 mL, 0.68 mmol) in a toluene solution (10 mL). The mixture was stirred for 4 h at 90 °C. The solvent was removed under reduced pressure from the resulting yellow solution. Crystallization from pentane afforded 0.318 g of an orange-yellow crystalline solid (**2**; 85%). Anal. Calcd for $C_{31}H_{40}P_2O_3Ru$: C, 59.61; H, 6.57. Found: C, 60.46: H, 6.04. IR (Nujol, cm^{-1}): 1940, ν(RuH) (w, br); 1080 (s); 1030 (vs); 740 (s, br); 690 (s); 520 (s, br). ^{1}H NMR (benzene-d_6; in ppm, referenced to TMS): 7.03–8.04 m (15 H, PPh_3); 3.22 d (9 H, $P(OMe)_3$, J_{PH} = 11 Hz); 1.90 t (15 H, Cp*, $J_{PH_{obs}}$ = 1.5 Hz); −12.0 dd (1 H, hydride, J_{PH} = 35 Hz; J_{PH} = 17.5 Hz). $^{31}P\{^1H\}$ NMR (benzene-d_6; in ppm, referenced to H_3PO_4): 72.6 d ($P(OMe)_3$, J_{PP} = 58 Hz); −0.3 d (PPh_3).

$[Cp^*RuH_2(PPh_3)_2]BF_4$ (3). **1a** (0.200 g, 0.40 mmol) was dissolved in 10 mL of acetone, and a solution of $HBF_4\cdot Et_2O$ (0.060 mL, 0.44 mmol) then was added at −78 °C. The mixture was stirred for 2 h. The solution was then concentrated in vacuo to yield **3** as an orange precipitate (yield ca. 42%). Anal. Calcd for $C_{46}H_{47}P_2BF_4Ru$: C, 65.04; H, 5.53. Found: C, 64.30; H, 5.80. IR (Nujol, cm^{-1}): 1980, ν(RuH) (m, br). ^{1}H NMR (acetone-d_6; in ppm, referenced to TMS): 7.30–7.87 (30 H, PPh_3); 1.56 (15 H, Cp*); −6.84 t (2 H, J_{PH} = 30 Hz).

$Cp^*Ru(OCOCF_3)(PCy_3)$ (5). The reaction of **1b** (0.260 g, 0.50 mmol) with 0.045 mL of CF_3COOH (0.58 mmol) in 15 mL of hexane at room temperature for 3 h yielded a purple solution. The volatiles were removed under vacuum to give a purple solid, which was recrystallized from methanol, yielding 0.236 g of **5** as a purple crystalline solid (75%). Anal. Calcd for $C_{30}H_{48}PF_3O_2Ru\cdot MeOH$: C, 56.28; H, 7.87. Found: C, 56.06; H, 7.49. ^{1}H NMR (acetone-d_6; in ppm, referenced to TMS): 1.32–1.91 (33 H, PCy_3); 1.55 (15 H, Cp*).

$\{Cp^*Ru[C_6H_9P(Cy)_2]\}BF_4$ (4). **1b** (0.500 g, 0.96 mmol) was dissolved in 10 mL of acetone; 0.138 mL (0.96 mmol) of $HBF_4\cdot Et_2O$ was added at −78 °C. The solution was evaporated in vacuo, and the residue was dissolved in 15 mL of ethanol. **4** crystallized from this solution as a yellow solid, yield 10%. Alternatively, the same reaction was conducted in hexane. The yellow precipitate separating out from the solution was found to be the spectroscopically pure complex, yield ~90%. Anal. Calcd for $C_{28}H_{48}PRuBF_4$: C, 55.7; H, 7.95. Found: C, 55.2; H, 8.22. ^{1}H NMR (acetone-d_6; in ppm, referenced TMS): 4.04 dt (1 H, J_{HH} = 6.5 6.5, 1.2 Hz); 3.85 t (^{1}H, J_{HH} = 6.5 Hz); 3.18 (1 H, J = 2 Hz), 2.04 (15 H, Cp*); 1–2 mc (27 H, PCy_3); −10.5 (1 H, agostic proton, J_{PH} − 21 Hz).

$[Cp^*Ru(PCy_3)H_3(CuCl)]_2$ (6). $(CuCl)_n$ (0.070 g, 0.71 mmol, based on "CuCl" units) was added to a solution of **1b** (0.350 g, 0.68 mmol) in 15 mL of toluene. The mixture was stirred for 2 h, after which the solution was filtered and evaporated under vacuum to 5 mL. **6** crystallized from this solution as an orange-brown crystalline, yield 80%. Anal. Calcd for $C_{28}H_{46}PRuCuCl$: C, 54.4; H, 8.25. Found: C, 54.2; H, 8.5. IR (Nujol, cm^{-1}): 2010 $\nu(Ru\text{–}H)_{terminal}$ (m, br); 1700–1780, RuHCu (m, br). ^{1}H NMR (toluene-d_8; in ppm, referenced to TMS): 2.10 (15 H, Cp*); 1.4–2.2 (33 H, PCy_3); −10.37 d (3 H, hydrides, J_{PH} = 13 Hz). $^{31}P\{^1H\}$ NMR (benzene-d_6, in ppm, referenced to H_3PO_4): 74.9 s.

$\{[Cp^*Ru(PCy_3)H_3]_2Cu\}PF_6$ (7). The procedure used for the preparation of **6** was followed with use of 0.400 g (0.78 mmol) of **1b** and 0.300 g (0.80 mmol) of $[Cu(CH_3CN)_4]_4PF_6$. Crystallization from toluene yielded 0.724 g of brown **7** (77%). Anal. Calcd for $C_{56}H_{42}P_3CuF_6$: C, 53.9; H, 8.2. Found: C, 53.95; H, 8.9. IR (Nujol, cm^{-1}): 2005 (m, br) ν(RuH); 1790 (m, br), 1710 (m, br) ν(RuHCu). ^{1}H NMR (acetone-d_6; in ppm, referenced to TMS): 2.23 (30 H, Cp*); 1.2–2.2 m (66 H, PCy_3); −10.38 d (6 H, hydrides, J_{PH} = 14.5 Hz).

X-ray Data Collection, Structure Determination, and Refinement for {$Cp^*Ru[(C_6H_9)P(C_6H_{11})_2]$}$BF_4 \cdot CH_3CH_2OH$ (4) and {$[Cp^*RuH[P(C_6H_{11})_3](\mu\text{-}H)_2(CuCl)$}$_2$ (6). Crystals of 4 were obtained by recrystallization from ethanol and those of 6 by recrystallization from toluene/hexane.

The crystallographic data are summarized in Table III. Unit cell parameters were obtained from least-squares refinements of 62 (4) and 50 (6) carefully centered reflections in the 2θ range 20–35°. Data were corrected for Lorentz and polarization effects. Absorption corrections were also applied to the data on the basis of a series of ψ scans for 4 and by using the method of Walker and Stewart[26] for (6).

Both structures were solved by Patterson and difference Fourier techniques and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters for non-hydrogen atoms not involved in disorder. In 4, the fluoride groups of the BF_4^- anion were found disordered around the B atom, but no simple way of modeling this disorder was obtained and, eventually, only the four more intense peaks around boron were used in the refinement. Additionally, a disordered ethanol molecule was also present in the crystal structure of 4 and only the three highest peaks were included to account for this crystallization molecule. For 6, one of the cyclohexyl rings bonded to the P atom was observed distributed in two positions, C(23)–C(28) and C(23)′–C(28)′, with refining occupancy factors of 0.708 (8) and 0.292 (8), respectively. Hydrogen atoms for 4 were placed at idealized positions and included in the last cycles of refinement riding on carbon atoms with a fixed thermal parameter. Carbon-bonded hydrogen atoms (except those of the disordered C_6H_{11} ring) were found in difference Fourier maps for 6 and refined riding on carbon atoms with a common thermal parameter. The three hydrides present in 6 were clearly found and were refined as normal isotropic atoms. The last cycles of refinement were carried out on the basis of 308 and 298 variables for 4 and 6, respectively. Unit weights were used in the first stages of the refinement, and then a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, was used, with K = 1.000 and g = 0.004 50 for 4 and K = 1.234 and g = 0.0005 for 6. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 27.

All calculations used the SHELX76 package[28] run on a VAX 11/780 computer. Tables IV and V collect the atomic coordinates for both complexes. Additional crystallographic data are available as supplementary material.

Acknowledgment. F.A.J. and A.O. are grateful to the Comision Interministeriel de Ciencia y Tecnologia (CICYT; Grant No. PPB 86-0101) and the Subdireccion General de Cooperacion Internacional for financial support. T.A., B.C., F.A.J., and A.O. thank "Action Intégrée France-Espagne".

Supplementary Material Available: For both structures, tables of anisotropic temperature factors, hydrogen coordinates, full experimental details for X-ray analysis, complete bond lengths and angles, and least-squares planes (28 pages); lists of structure factors (45 pages). Ordering information is given on any current masthead page.

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Organometallic Salts with Large Second-Harmonic-Generation Powder Efficiencies: (*E*)-1-Ferrocenyl-2-(1-methyl-4-pyridiniumyl)ethylene Salts

Seth R. Marder,* Joseph W. Perry, and Bruce G. Tiemann

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

William P. Schaefer

Division of Chemistry and Chemical Engineering,† California Institute of Technology,
Pasadena, California 91125

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A series of salts of the form (E)-(η-C_5H_5)Fe(η-C_5H_4)CH=CH(4-C_5H_4N-1-CH_3)$^+X^-$ has been synthesized. Variation of the counterion leads to materials with second-harmonic-generation powder efficiencies at 1907-nm fundamental as large as 220 times that of a urea reference standard. This is the largest value reported for an organometallic compound. The crystal structure of the nitrate salt, which had a powder SHG efficiency 110 times that of urea, was determined: $(FeC_{18}H_{18}N)^+NO_3^-$, monoclinic, *Cc* (No. 9), a = 17.618 (4) Å, b = 10.780 (3) Å, c = 12.528 (3) Å, β = 133.18 (2)°, Z = 4.

Introduction

There is currently considerable interest in the synthesis of new materials with large second-order optical nonlinearities.[1] The induced polarization of a molecule by an electric field is given by the power series

$$\rho(E) = \alpha \cdot \mathbf{E} + \beta \cdot\cdot \mathbf{EE} + \gamma \cdot\cdot\cdot \mathbf{EEE} + \ldots \qquad (1)$$

Second-order nonlinear optical effects including second-harmonic generation (SHG) and the linear electrooptical effect, both of which are technologically significant, arise from the first hyperpolarizability, β. It is

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