at −63 °C (chloroform slush) was added ^{n}BuLi (7.6 cm^3 of a 2.5 mol dm^{-3} solution). After being stirred for 3 h, the solution was allowed to warm to room temperature and Me_2Te_2 (5.4 g, 0.019 mol) added dropwise. After a further 2 h the mixture was worked up as in 1. The fraction boiling at ca. 144 °C (0.3 Torr) was further purified by flash column chromatography on silica (with rigorous exclusion of air), using 40–60 °C petroleum ether: yield 1.15 g, 15%; mass spectrum, *m/z* (relative intensity) 372 ($C_9H_{13}SbTe^+$, 25), 357 (100), 342 (48.5), 327 (51.5), 251 (38.5), 91 (36).

The stibonium salt prepared similar to the derivative of **6** had a melting point of 90–92 °C. Anal. Calcd for $C_{10}H_{16}ISbTe$: C, 23.4; H, 3.1. Found: C, 23.7; H, 3.2.

9. *o*-Chlorophenyl Methyl Telluride, *o*-$C_6H_4Cl(TeMe)$. The mono-Grignard reagent prepared from *o*-bromochlorobenzene[14] (19.1 g, 0.1 mol) was added via a cannula to a frozen suspension of tellurium powder (12.8 g, 0.1 mol) in thf (200 cm^3). The mixture was allowed to thaw and stirred at room temperature for 3 h giving an orange solution and leaving about 10% of the Te unreacted. The mixture was refrozen (−196 °C), iodomethane (12.9 g, 0.09 mol) added, and the mixture again allowed to attain room temperature. Following workup as in 1, fractionation in vacuo gave a pale yellow oil: bp 82 °C (0.4 Torr); yield 16.0 g, 64%; mass spectrum, *m/z* (relative intensity) 256 ($C_7H_7ClTe^+$, 96), 241 (100), 206 (33), 111 (23), 75 (40).

The telluronium salt prepared as in 1 had a melting point of 103–104 °C. Anal. Calcd for $C_8H_{10}ClITe$: C, 24.2; H, 2.5. Found: C, 24.2; H, 2.5.

10. 1,2-Bis(phenyltelluro)benzene, *o*-$C_6H_4(TePh)_2$. *o*-Bromoiodobenzene (7.08 g, 0.025 mol) was added to a frozen solution of (phenyltelluro)lithium[1] (0.05 mol). The mixture was allowed to thaw, stirred at room temperature for 3 h, and then worked up as in 1. Removal of the solvent gave a red oil, which was purified by flash column chromatography, leaving a pale yellow oil. Crystallization of this from petroleum ether (40–60 °C) gave yellow crystals: 7.8 g, 32%; mass spectrum, *m/z* (relative intensity) 490 ($C_{18}H_{14}Te_2^+$, 26), 408 (15), 282 (100), 207 (27), 152 (39), 77 (51). Anal. Calcd for $C_{18}H_{14}Te_2$: C, 44.5; H, 2.9. Found: C, 44.7; H, 3.0.

The tetrachloride was prepared by adding excess of a solution of chlorine in dichloromethane to a solution of **10** in the same solvent: mp 115–116 °C dec. Anal. Calcd for $C_{18}H_{14}Cl_4Te_2$: C, 34.4; H, 2.2. Found: C, 34.7; H, 2.3.

11. *o*-Chlorophenyl Methyl Sulfide, *o*-$C_6H_4Cl(SMe)$. A solution of sodium methyl sulfide, NaSMe, was prepared from MeSH (14.4 g, 0.3 mol) and sodium (6.9 g, 0.3 mol) in ethanol. The ethanol was distilled off under nitrogen and dry dmf (200 cm^3) added, followed by *o*-dichlorobenzene (14.7 g, 0.1 mol). The mixture was refluxed for 16 h and cooled and iodomethane (42.6 g, 0.3 mol) added slowly. The resulting solution was stirred for 0.5 h, hydrolyzed with water (200 cm^3), and extracted with diethyl ether (3 × 200 cm^3). The ether extracts were dried, the solvent was distilled off, and the residue was fractionated in vacuo: bp 60 °C (0.4 Torr); 14.3 g, 90%; ^{1}H NMR δ 2.21 (s, MeS), 6.8–7.3 (C_6H_4).

12. *o*-Chlorophenyl Methyl Selenide, *o*-$C_6H_4Cl(SeMe)$. A solution of lithium methyl selenide, LiSeMe (0.05 mol), was prepared,[4] the thf removed in vacuo, and dry dmf (150 cm^3) and *o*-dichlorobenzene (7.35 g, 0.05 mol) were added. The mixture was gently refluxed for 16 h and cooled and iodomethane (7.1 g, 0.05 mol) added dropwise. The product was isolated as described for **11**, fractionation in vacuo affording a pale yellow oil: bp 67 °C (0.5 Torr); yield 5.3 g, 52%; mass spectrum, *m/z* (relative intensity) 206 ($C_7H_7ClSe^+$, 100), 191 (74), 156 (29); ^{1}H NMR δ 2.2 (s, MeSe, $^2J(^{77}Se-^1H)$ = 12 Hz), 6.7–7.4 (C_6H_4); $^{77}Se\{^1H\}$ δ 201 (lit.[21] $^{77}Se\{^1H\}$ δ 201).

13. 1,2-Bis(methylthio)benzene, *o*-$C_6H_4(SMe)_2$. Lithiation of *o*-chlorophenyl methyl sulfide (12.2 g, 0.08 mol) with ^{n}BuLi (0.08 mol) in diethyl ether, followed by dropwise addition at 0 °C of Me_2S_2 (0.08 mol) and workup as in reaction 1, gave the product: bp 82 °C (0.4 Torr); 90%; ^{1}H NMR δ 2.20 (s, MeS), 7.0–7.4 (C_6H_4).

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Chloro- and Hydrido(pentamethylcyclopentadienyl)ruthenium Complexes: Anomalous NMR Behavior of $C_5Me_5RuH_3PR_3$ (R = $CHMe_2$, Cy)

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The reaction of $[Cp^*RuCl_2]_n$ (Cp^* = C_5Me_5) with 1 equiv of various phosphines (PR_3) leads to the ruthenium(III) derivatives $Cp^*RuCl_2(PR_3)$ (R = Me, Ph, Cy, or $CHMe_2$) (**1**–**4**). Reduction of these compounds by excess phosphine or zinc leads to the bis(phosphine) derivatives $Cp^*RuCl(PR_3)_2$ (R = Me) or the blue 16-electron complexes $Cp^*RuCl(PR_3)$ (R = Cy (**5**) or $CHMe_2$ (**6**)). A similar pink derivative, $Cp^*RuCl[P(CMe_3)_3]$ (**7**), is obtained in a single step from $[Cp^*RuCl_2]_n$, $P(CMe_3)_3$, and zinc. Carbonylation of **5** and **6** leads to the chloro carbonyl derivatives $Cp^*RuCl(CO)(PR_3)$ (R = Cy (**8**) or $CHMe_2$ (**9**)) which react further with $NaBH_4$ in ethanol to produce the hydrido carbonyl derivatives $Cp^*RuH(CO)(PR_3)$ (R = Cy (**10**) or $CHMe_2$ (**11**)). Direct reaction of $Cp^*RuCl_2(PR_3)$ with 2 equiv of $LiBHEt_3$ in THF or addition of 1 equiv of $LiBHEt_3$ to **5** or **6** leads to the formation of the trihydrido derivatives $Cp^*RuH_3(PR_3)$ (R = Me (**12**), Ph (**13**), Cy (**14**), $CHMe_2$ (**15**)); spectroscopic investigations at 293 K are all in favor of a fluxional ruthenium trihydrido formulation. However, in the case of the bulky phosphine derivatives at low temperature, "anomalous" ^{1}H NMR spectra are observed. An AB_2X spin system is observed for the hydrides, characterized by $J_{AX} \sim 0$ Hz, $J_{BX} \sim 30$ Hz, and a temperature-dependent J_{A-B} with values as high as 130 Hz. These observations are discussed, and an interpretation is proposed that involves an equilibrium between a classical trihydride (present at low temperature) and a species either showing a nonclassical interaction between a hydride and coordinated dihydrogen or containing a novel trihydrogen ligand.

Introduction

The chemistry of polyhydrido transition-metal complexes has received considerable attention in the last few years, principally because of their great reactivity toward hydrocarbons and as precursors for C–H activation reactions.[1,2]

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In our group, we have studied the chemistry of polyhydride phosphine ruthenium derivatives.[3-6] These complexes, particularly $RuH_6(PCy_3)_2$, reformulated as $RuH_2(H_2)_2(PCy_3)_2$[6] and $RuH_2(H_2)(PR_3)_3$ (R = $CHMe_2$ or Cy) have shown a great reactivity toward hydrocarbons and, in particular, are able to undergo H–D exchange between aromatic solvents and alkyl protons of the phosphine[3,5] or dehydrogenate saturated hydrocarbons.[5] However, like most of the hydride phosphine complexes of the transition metals, these products lose easily H_2 and dimerize to unreactive species.[1,3] During our investigations of the reactivity of $RuH_6(PCy_3)_2$, we have shown that addition of C_5Me_5H led to a species that was very active for H–D exchange reactions.[5] This led us to examine the chemistry of Cp* ruthenium complexes.

The C_5Me_5 ligand exhibits a very rich chemistry throughout the periodic table and has the remarkable ability to stabilize high-valent oxo complexes like Cp^*ReO_3[7] as well as low-valent derivatives like $Cp^*Ir(CO)_2$.[8] Furthermore, this ligand can stabilize reactive intermediates obtained upon UV irradiation of hydride precursors[9] which are able to undergo C–H activation reactions. It has also made possible the preparation of high-valent polyhydrido complexes with or without phosphines as coligands. We can quote, for example, Cp^*IrH_4,[10] $[Cp^*WH_4]_2$,[11] $Cp^*TaH_4L_2$[12] (L = PMe_3, PMe_2Ph, $P(OMe)_3$; L_2 = dmpe), and Cp^*ReH_6.[13] However, the ruthenium chemistry of this ligand has been limited to carbonyl derivatives starting from $[Cp^*Ru(CO)_2]_2$.[14]

Recently, a number of research groups have reported the preparation and chemistry of various non-carbonyl Cp*Ru derivatives including $RuCp^*_2$,[15] $[Cp^*Ru(CH_3CN)_3]^+$, and various $[Cp^*Ru(arene)]^+$,[16] the agostic $[Cp^*Ru(C_8H_{12})]^+$,[17] or the blue $[Cp^*_2Ru_2S_4]$,[18] but the easiest entry into this chemistry is the direct preparation of $(Cp^*RuCl_2)_n$ from $RuCl_3$ hydrate and Cp*H in ethanol.[19,20] This compound was used to prepare halo, organo, and hydrido, trimethylphosphine derivatives[19] and to develop a novel chemistry of ruthenium(IV) alkyl derivatives[21] which also led to interesting catalytic properties.[22]

We have looked for a general synthetic route for (pentamethylcyclopentadienyl)ruthenium polyhydrides and therefore have reacted $(Cp^*RuCl_2)_n$ with super hydrides in the presence of phosphines, since such a method had been found selective for the preparation of other ruthenium hydrido complexes.[23] When we started our work, a polyhydrido(cyclopentadienyl)ruthenium complex, namely, $RuCpH_3(PPh_3)$,[24] was already known, but after completion of part of this work[5] we became aware that two other groups prepared similar compounds by alternative methods. Paciello and Bercaw, as part of an extensive study of the reactivity of $Cp^*(PMe_3)M$ derivatives (M = Fe, Ru), obtained $Cp^*RuH_3(PMe_3)$ by hydrogenation of $Cp^*RuH(CH_2SiMe_3)_2(PMe_3)$,[25] while Suzuki et al. reported a very convenient synthesis of similar trihydrides ($Cp^*RuH_3(PR_3)$ with PR_3 = PMe_3, PEt_3, $P(CHMe_2)_3$, $P(Cy)_3$, $P(Ph_2Me)$, and PPh_3) through direct reaction of $Cp^*RuCl_2(PR_3)$ with $NaBH_4$ in ethanol.[26] We have de-

Table I. EPR and Magnetic Moment Data for Complexes 2–4

complex	*g*	μ_{eff}
$Cp^*RuCl_2(PPh_3)$ (2)	2.142	1.93477
$Cp^*RuCl_2(PCy_3)$ (3)	2.133	1.67281
$Cp^*RuCl_2[P(CHMe_2)_3]$ (4)	2.123	1.94652

Scheme I. Preparation of the Complexes: (i) L = PMe_3, PPh_3, PCy_3, $P(CHMe_2)_3$; (ii) Zn, L = PMe_3; (iii) Zn, EtOH (L = $P(CHMe_2)_3$, PCy_3); (iv) $2LiBHEt_3$; (v) $LiBHEt_3$; (vi) CO; (vii) $NaBH_4$, EtOH

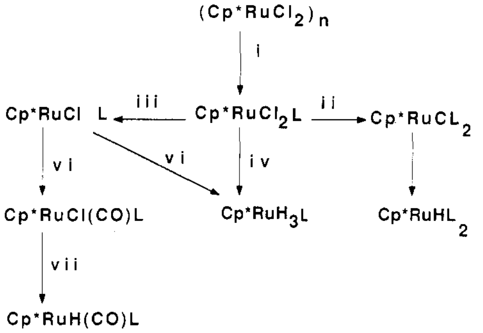

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Table II. ^{1}H NMR Data for Complexes 5–15 at Room Temperature[a]

compound	T, K	δ(Cp*)	J_{PH}, Hz	δ(H)	spectrum type	coupling const, Hz	T_1, ms	others
Cp*RuCl(PCy$_3$) (**5**)	293	1.59	1.5					1–4.7
Cp*RuCl(P-*i*-Pr$_3$) (**6**)	293	1.56						2.5, 1.1
Cp*RuCl(P-*t*-Bu$_3$) (**7**)	293	1.68						1.35
Cp*RuCl(CO)(PCy$_3$) (**8**)	293	1.74	1.5					1.4–1.1
Cp*RuCl(CO)(P-*i*-Pr$_3$) (**9**)	293	1.68	1.5					2.4, 1.25
Cp*RuH(CO)(PCy$_3$) (**10**)	293	2.09		−11.84	AX	J_{H-P} = 33.8		Cy 1.3–1.8
Cp*RuH(CO)(P-*i*-Pr$_3$) (**11**)	293	2.04		−11.86	AX	J_{H-P} = 34.6		2.4, 1.1
Cp*RuH$_3$(PMe$_3$) (**12**)	293	1.75		−10.35	A$_3$X	J_{H-P} = 22		1–1.5
Cp*RuH$_3$(PPh$_3$) (**13**)	293	1.94		−9.52	A$_3$X	J_{H-P} = 20		Ph 7–8
Cp*RuH$_3$(PCy$_3$) (**14**)	293	2.18		−10.94	A$_3$X	J_{H-P} = 22.5	190	large peaks 1.4–1.9
Cp*RuH$_3$(P-*i*-Pr$_3$) (**15**)	293	2.13		−10.95	A$_3$X	J_{H-P} = 22.5	622	1.14–1.7

[a] P-*i*-Pr$_3$ = P(CHMe$_2$)$_3$.

veloped a preparation of the complexes involving the direct reaction of the dichlorides Cp*RuCl$_2$(PR$_3$) with LiBHEt$_3$ or KBH(*sec*-Bu)$_3$.

We report in this paper the preparation of trihydridoruthenium derivatives as well as that of their precursors, including 16-electron chloro species Cp*RuClL (L = PCy$_3$, P(CHMe$_2$)$_3$), and that of chloro and hydrido carbonyl derivatives. Part of this work has been reported in a preliminary communication.[5]

During the course of our work we have found, especially for Cp*RuH$_3$L (L = P(CHMe$_2$)$_3$, PCy$_3$), that considering hydrogen atoms linked to a metal either as hydride or as coordinated molecular hydrogen did not entirely explain the spectroscopic properties observed at 193 K. This led us to propose a reformulation of the trihydride compound as containing a novel trihydrogen ligand.[27] Similar observations have been made by us on niobium complexes[28] and by Heinekey et al. on iridium derivatives.[29]

Results and Discussion

The addition of 1 equiv of a phosphine, PR$_3$ (R = Ph, CHMe$_2$, Cy), in ethanol to $1/n$[Cp*RuCl$_2$]$_n$ leads to precipitation in high yields of red microcrystals analyzing for Cp*RuCl$_2$(PR$_3$).[1-3] The complexes are air-stable paramagnetic ruthenium(III) species showing only one broad EPR band centered near 2.1. Their magnetic moment is consistent with the presence of one "single" unpaired electron in the molecule ($\mu_{eff} \approx 1.95$), and the complexes were thus formulated as monomeric 17-electron derivatives (Table I). In the case of PMe$_3$, the addition of $1/n$ equiv of ligands to [Cp*RuCl$_2$]$_n$ causes a color change but little precipitation. However, this solution can be further used for the preparation of the trihydrides (see Scheme I).

In the presence of an excess of a small phosphine in ethanol, the bis(phosphine) derivative Cp*RuCl(PR$_3$)$_2$ (R = Me) was obtained, as also described by other workers.[19] However, with large phosphines such as P(CHMe$_2$)$_3$ or PCy$_3$, a blue solution is obtained from which blue crystals analyzing for Cp*RuCl(PR$_3$) (R = CHMe$_2$, Cy) can be isolated after appropriate workup.[30] The same compounds are also obtained after reduction of Cp*RuCl$_2$(PR$_3$) with zinc in various solvents (ethanol, hexane, benzene, toluene). These complexes are diamagnetic and very air-sensitive and have been characterized by standard analytical methods. In particular, in ^{1}H NMR spectra, the Cp* ligand is observed as a singlet near δ 1.7 ppm and the phosphines show either a broad peak between δ 1 and 2 ppm (PCy$_3$) or doublets of doublets and heptets at δ 1.2 and 2.3 ppm (P(CHMe$_2$)$_3$), respectively (Table II).

Table III. ^{31}P NMR Data for Complexes 5–15[a]

compound	T, K	δ, ppm	solv
Cp*RuCl(PCy$_3$) (**5**)	293	44.85	(CD$_3$)$_2$CO
Cp*RuCl(PiPr$_3$) (**6**)	293	57.16	(CD$_3$)$_2$CO
Cp*RuCl(PtBu$_3$) (**7**)			
Cp*RuCl(CO)(PCy$_3$) (**8**)	293	51.15	C$_6$D$_6$
Cp*RuCl(CO)(P-*i*-Pr$_3$) (**9**)	293	58.62	C$_6$D$_6$
Cp*RuH(CO)(PCy$_3$) (**10**)	293	74.44	C$_6$D$_6$
Cp*RuH(CO)(PiPr$_3$) (**11**)	293	84.62	C$_6$D$_6$
Cp*RuH$_3$(PMe$_3$) (**12**)	293	79.14	C$_6$D$_6$
Cp*RuH$_3$(PPh$_3$) (**13**)	293	74.05	C$_6$D$_6$
Cp*RuH$_3$(PCy$_3$) (**14**)	293	83.93	C$_6$D$_6$
Cp*RuH$_3$(P-*i*-Pr$_3$) (**15**)	293	95.32	C$_6$D$_6$

[a] In C$_6$D$_6$ except **14** and **15** in C$_7$D$_8$.

The complexes show a single peak in ^{31}P NMR spectra (Table III), and the mass spectrum of the P(CHMe$_2$)$_3$ complex shows the parent ion at m/e 434 (Ru 102, Cl 37). Loss of P(CHMe$_2$)$_3$ is observed but apparently no fragmentation of the P–C bond.

A similar pink complex is obtained by reduction of a solution of (Cp*RuCl$_2$)$_n$ with zinc in the presence of 1 equiv of tri-*tert*-butylphosphine. The complex proposed as Cp*RuCl[P(CMe$_3$)$_3$] (**7**) is very air-sensitive, and crystals could not be isolated. However, in the ^{1}H NMR spectrum only the phosphine (δ 1.35 ppm) and the Cp* ligand resonances were observed in a 1:1 ratio.

Compounds **5** and **6** do not react with H$_2$, but with CO a rapid reaction occurs affording yellow complexes analyzing as Cp*RuCl(CO)(PR$_3$) (R = CHMe$_2$ (**8**), Cy (**9**)). In the presence of excess CO, a dicarbonyl complex, presumably Cp*Ru(CO)$_2$Cl, similar to the known CpRu(CO)$_2$Cl,[31] is obtained. The corresponding compounds Cp*Ru(CO)$_2$I and Cp*Ru(CO)$_2$H are known.[32]

Complexes **8** and **9** are yellow air-stable species showing a single ν_{CO} band near 1910 cm^{-1} in the IR spectrum as well as a doublet near δ 1.7 ppm in the ^{1}H NMR spectrum and a singlet in the ^{31}P NMR spectrum. They both react with NaBH$_4$ in ethanol at room temperature to give the cor-

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Table IV. Spectroscopic Data[a] for Compounds 14 and 15 at Different Temperatures

complex	T, K	J_{AB}, Hz	δ_A	δ_B	δ_M	J_{AX}, Hz	J_{BX}, Hz	J_M, Hz	T_1, ms
$Cp^*RuH_3(P\text{-}i\text{-}Pr_3)$	293				-10.95			21.9	620 ± 30
	203	131	-11.18	-10.67	-10.84				
	193	105	-11.15	-10.61	-10.79	0	31.3	20.9	100 ± 10
	183	82	-11.12	-10.58	-10.76	0	31.2	20.8	
	173	64	-11.09	-10.56	-10.73				
	168	57							
$Cp^*RuH_3(PCy_3)$	293				-10.90			22.03	190 ± 20
	193	93.5	-11.12	-10.45	-10.67	0	34.5	23	190 ± 20
	187	82.6	-11.15	-10.43	-10.91	0	33.1	22.07	
	178	61.7	-11.12	-10.41	-10.88	0			

[a] In C_7D_8.

responding hydrido carbonyl derivatives $Cp^*RuH(CO)(PR_3)$ [$PR_3 = P(CHMe_2)_3$, $P(Cy)_3$], similar to the one obtained by Nelson et al. by decomposition of formyl precursors.[32] In particular, they show a single IR ν_{CO} band near 1900 cm^{-1}. In ^{1}H NMR, they show a singlet or doublet for the Cp* ligand near 2 ppm and a high-field doublet near -11 ppm ($J_{P-H} \sim 35$ Hz; Table I). Interestingly, the blue complexes $Cp^*RuCl(PR_3)$ react slowly in ethanol (over 2 weeks at room temperature) to give the carbonyl complexes $Cp^*RuCl(CO)(PR_3)$. Although the decarbonylation of alcohols by ruthenium complexes is a well-known reaction,[33] it usually involves oxidative addition/reductive elimination on Ru(II)/Ru(0) derivatives whereas in our case the only plausible mechanism involves oxidative addition of alcohol to a ruthenium(II) complex to give transient Ru(IV). This shows that electron-rich Ru(II) species are able to perform typical reactions of Ru(0) derivatives and that the IV oxidation state is readily accessible in these species. Note that it has been shown recently that electron-rich osmium(II) species are good C–H activators through the Os(II)/Os(IV) couple.[34]

The $Cp^*RuCl(PR_3)$ derivatives are unusual examples of 16-electron complexes in this chemistry. Their chemical properties are being thoroughly investigated.

Preparation of the Trihydrides. Initially, the trihydrides were prepared by the reaction of the Ru(III) derivatives $Cp^*RuCl_2(PR_3)$ with 2 equiv of $LiBHEt_3$ in THF ($PR_3 = PPh_3$, PCy_3, $P(CHMe_2)_3$) at -80 °C. In the case of PMe_3, the intermediate Ru(III) species is not isolated but prepared in situ by addition of PMe_3 to $[Cp^*RuCl_2]_n$ (see Experimental Section). In each case, the solution turns red-brown, and after evaporation to dryness, redissolution in hexane, and filtration over an alumina column, white to beige solids analyzing for $Cp^*RuH_3(PR_3)$ can be obtained. However, the trihydrides can be obtained as conveniently by addition of 1 equiv of $LiBHEt_3$ to $Cp^*RuCl(PR_3)$ in THF.

The compounds were characterized by microanalysis ($PR_3 = PCy_3$, $P(CHMe_2)_3$), infrared, ^{1}H NMR, ^{31}P NMR ($PR_3 = PMe_3$, $P(CHMe_2)_3$, PPh_3, PCy_3), and mass spectroscopy ($PR_3 = PMe_3$, $P(CHMe_2)_3$). Their IR spectra all show one intense broad band near 2000 cm^{-1}.

The ^{1}H NMR spectrum of the compounds shows the phosphine protons together with the Cp* peak as a singlet near δ 2 ppm and the three hydrides as a sharp doublet near δ -10.5 ppm ($J_{PH} \sim 22.5$ Hz) as also recently described by Suzuki et al.[26] The integration ratio corresponds undoubtedly to one PR_3, one C_5Me_5, and three hydrides. Furthermore, the $\{^1H\}^{31}P$ NMR spectra of the compounds show a singlet which transforms into a quadruplet upon coupling with the hydrides, thus confirming the formulation. Finally, mass spectra were obtained for the trihydrides $Cp^*RuH_3(PMe_3)$ and $Cp^*RuH_3[P(CHMe_2)_3]$. The parent ion is observed at m/e 400 (Ru 102) for the triisopropylphosphine complex, but a much more intense peak is visible at m/e 398, corresponding to the loss of H_2. Also visible is the further loss of one and two isopropyl groups (m/e 356 and 312). The trimethylphosphine complex shows only an M–H_2 ion at m/e 314.

The mechanism of formation of the trihydrides seemed puzzling at first since the addition of 2 equiv of $LiBHEt_3$ or $KBH(sec\text{-}Bu)_3$ on Cp^*RuCl_2L produced a trihydride derivative in virtually quantitative yield.

However, we noticed that the addition of 1 equiv of $LiBHEt_3$ to $Cp^*RuCl_2(PR_3)$ ($PR_3 = PCy_3$, $P(CHMe_2)_3$) led to the blue complex $Cp^*RuCl(PR_3)$. Furthermore, as described earlier, the addition of 1 equiv of $LiBHEt_3$ to the blue complexes obtained by zinc reduction of $Cp^*RuCl_2(PR_3)$ in THF led to $Cp^*RuH_3(PR_3)$ ($PR_3 = PCy_3$, $P(CHMe_2)_3$). This suggested that in fact only one hydride came from the superhydride, the other two being given by the solvent. This is not indeed the case since no furan or dihydrofuran was found in the reaction solution by gas chromatography. In order to find out the origin of the extra hydrogen, we performed the reaction of $Cp^*RuCl(PR_3)$ with $LiBHEt_3$ in THF-d_8 and with $LiBDEt_3$ in THF-h_8. The first reaction yielded only the trihydride whereas a complicated mixture of hydride and deuteride compounds was obtained in the second case.

The origin of the extra hydrogen remains unclear; however, two reasonable proposals can be made. The first one concerns the presence of trace amounts of water; we checked that the reaction of $Cp^*RuCl(PR_3)$ with NaOH in wet acetone yielded a mixture of $Cp^*RuH_3(PR_3)$ and hydroxo compounds. The other hypothesis would be the involvement of a borohydride intermediate. Suzuki et al. have demontrated that the reaction of $Cp^*RuCl_2(PR_3)$ with excess of $NaBH_4$ in the absence of ethanol yielded $Cp^*Ru(BH_4)(PR_3)$ which reacts further with ethanol to give the trihydrides.[26] A similar intermediate could be possible in our case; then dehydrogenation of an ethyl group of the "super hydride" could occur. The possibility of such intermediates has already been invoked by Bergman et al. for explaining the formation of similar iridium derivatives.[10]

Spectroscopic Properties of the Trihydrides at Low Temperature. While the compounds show straightforward ^{1}H NMR spectra at 293 K, at low temperature, temperature-dependent AB_2X spectra were obtained. The data for $Cp^*RuH_3[P(CHMe_2)_3]$ and $Cp^*RuH_3PCy_3$ are given in Table IV and Figures 1–5. All the AB_2X spectra show common features: (i) a very large J_{A-B} (130–50 Hz), well outside the normal range of H–H coupling; (ii) $J_{A-X} \sim 0$ which is also very surprising in these "piano stool" derivatives; (iii) a normal J_{B-X} ($\sim$30 Hz); (iv) a J_{A-B} cou-

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[33] See Chaudret, B.; Cole Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546–1557 and references therein.

[34] Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 7964–7970.

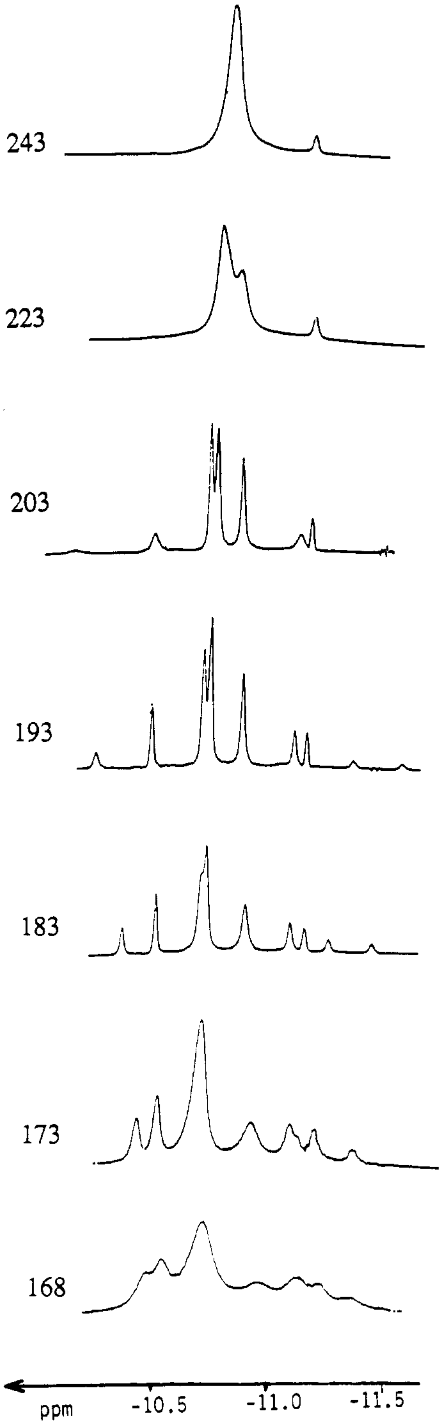


Figure 1. $\{^{31}P\}^1H$ NMR spectra of **15** at variable temperature.

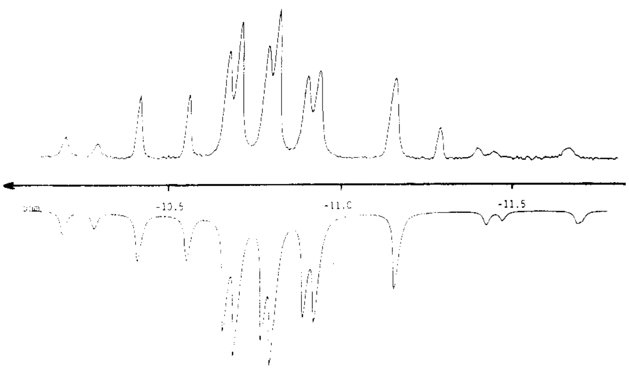


Figure 2. ^1H NMR observed and calculated spectra of $Cp^*RuH_3[P(CHMe_2)_3]$ at 193 K.

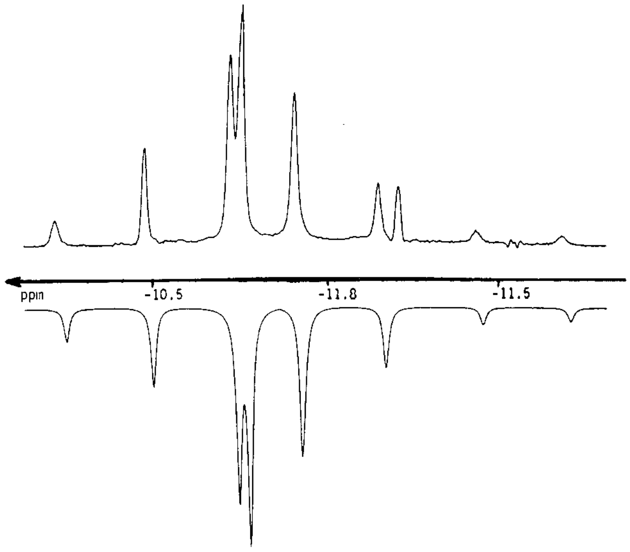


Figure 3. $\{^{31}P\}^1H$ NMR observed and calculated spectra of $Cp^*RuH_3[P(CHMe_2)_3]$ at 193 K.

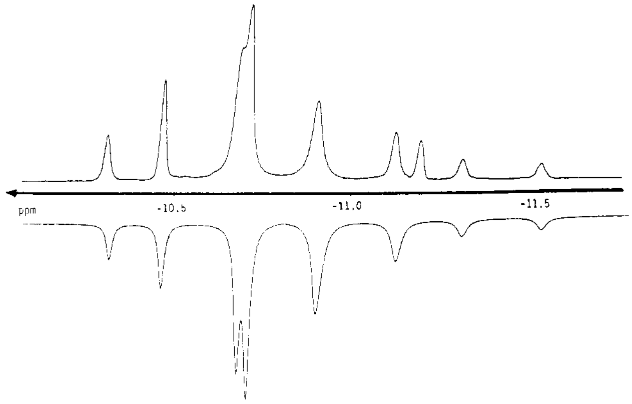


Figure 4. $\{^{31}P\}^1H$ NMR observed and calculated spectra of $Cp^*RuH_3[P(CHMe_2)_3]$ at 183 K.

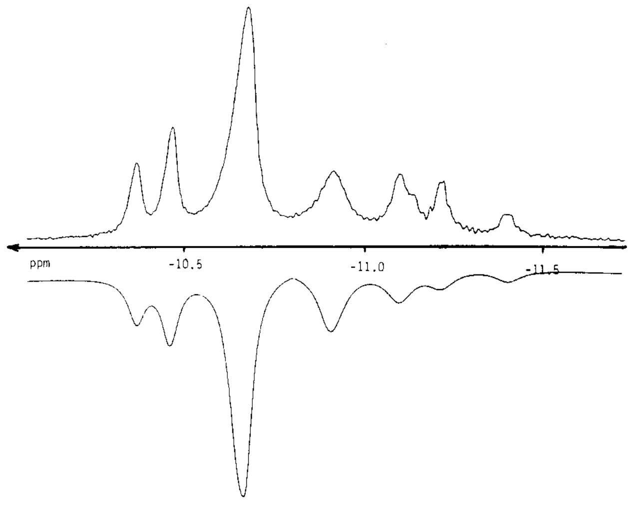
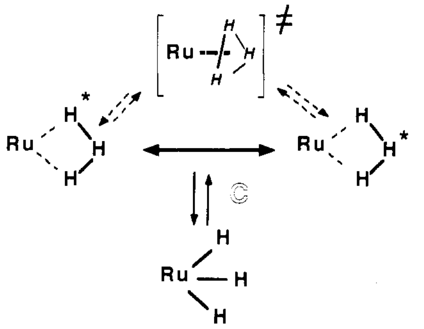


Figure 5. $\{^{31}P\}^1H$ NMR observed and calculated spectra of $Cp^*RuH_3[P(CHMe_2)_3]$ at 173 K.

pling constant varying according to the temperature (see Table IV and Figures 1–5).

The relaxation time T_1 of the "hydrides" was measured in the case of $Cp^*RuH_3[P(CHMe_2)_3]$ at room temperature (620 ms) and 193 K (100 ms) whereas for $Cp^*RuH_3[P(C_6H_{11})_3]$ a variable-temperature study gave a minimum of 80 ms at 230 K. These values are clearly in favor of H–H bonding[35] although they are somewhat high when com-

Scheme II. A Proposed Mechanism Explaining the Anomalous Spectroscopic Properties of 14 and 15



pared to those obtained for "normal" molecular hydrogen derivatives.[36]

For each compound we compared the δ and J_{HP} values observed at room temperature to the mean values $\delta_M = (\delta_A + 2\delta_B)/3$ and $J_M = (J_{AX} + 2J_{BX})/3$ observed at low temperature. We found little change as the temperature varied from 193 to 293 K. This is in favor of little structural change between the "low" and the "high" temperature forms.

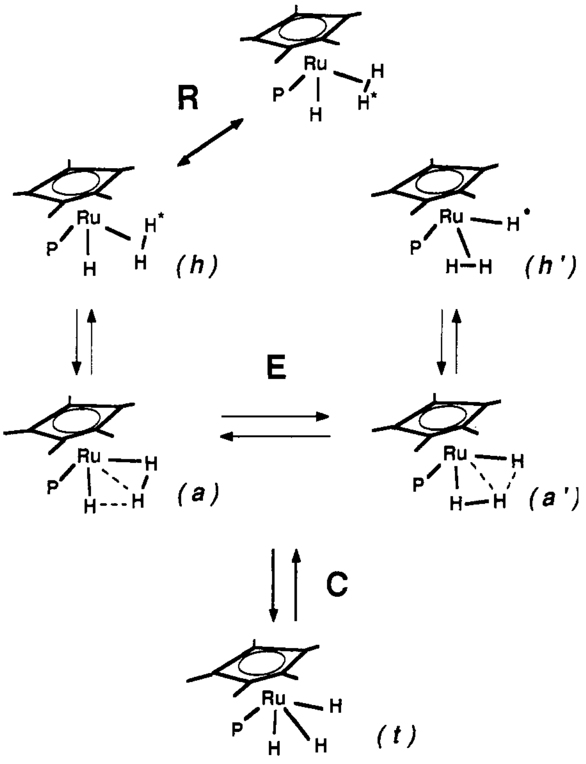
It is clear that the ground state of these compounds is a classical trihydride. This has been demonstrated by the crystal structure of $Cp^*RuH_3(PPh_3)$ recently obtained by Suzuki et al.[26] and is in agreement with the diminishing of the coupling constant observed at low temperature.

At higher temperature, the increase of the coupling constant could be explained either by an unexplained phenomenon in a classical trihydride—which seems unlikely but cannot be ruled out—or by an equilibrium between the trihydride and a new species showing a large J_{AB} coupling constant.

This new species could be a hydrido dihydrogen derivative; however, in such a case, if the hydride is the "A" part of the spectrum and the molecule of hydrogen the "B" part, then all the coupling constants are not understandable. The J_{AB} value should not exceed 140-Hz mean value between 278 Hz (J_{H-H} in molecular H_2) and little (no precedent)[35] for J_{H-H_2} coupling. We observe in the case of $Cp^*RuH_3[P(CHMe_2)_3]$ near the limit of fluxionality constants higher than 140 Hz even if the lines become broad and difficult to discern without ambiguity. However in the similar complex $Cp^*RuH_3(PMe_3)$, Paciello and Bercaw have observed coupling constants as high as 200 Hz at 168 K.[25]

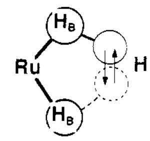
We thus need to invoke a link between the three hydrogen atoms. Burdett et al. have recently proposed that polyhydrogen structures (in particular an open trihydrogen ligand) could be stable.[37] Sweany has invoked this possibility as intermediate of hydride dihydrogen exchange.[38] Heinekey et al. have also observed large coupling constants (up to 500 Hz) in very similar iridium complexes, and they proposed a trihydrogen structure.[29]

Scheme III. An Alternative Mechanism Explaining the Anomalous Spectroscopic Properties of 14 and 15 (See Ref 27)



A trihydride–trihydrogen equilibrium could explain our observations at low temperature. Another problem is the fluxionality of these species at high temperature; a triangular transition state (formally H_3) could be invoked (Scheme II).

Another possibility is to see the phenomenon as an association of a hydride with dihydrogen with a rapid conversion of the central hydrogen atom H_A from bonding to H_B to bonding to $H_{B'}$ in a rapid motion (see also Scheme III, motion from a to a′).



In that case the central hydrogen would remain coupled to both H_B and $H_{B'}$. The fluxionality at high temperature could then be due to the rotation (R) of the dihydrogen (Scheme III). The later possibility was first proposed by us as a nonclassical interaction between a hydride and coordinated dihydrogen and could show similarity to the σ-bond metathesis mechanism.[39] We are not able so far to distinguish between these two proposals but both seem possible and able to explain the observed data (variation of H–H coupling, T_1). The driving force for the H–H association could be the formal reduction of a heptacoordinated ruthenium(IV) derivative into an octahedral ruthenium(II). We have already mentioned that all the polyhydride complexes of ruthenium, known so far, are octahedral ruthenium(II) derivatives,[6] and we have observed in an heptacoordinated ruthenium(IV) dihydride an equilibrium with a species containing a dihydrogen ligand in solution at room temperature.[40]

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(35) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032–4037.

(36) See, for example: (a) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (b) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780 and references therein.

(37) (a) Burdett, J. K.; Pourian, M. R. *Organometallics* **1987**, *6*, 1684. (b) Burdett, J. K.; Phillips, J. R.; Pourian, M. R.; Poliakoff, M.; Turner, J. J.; Upmacis, R. *Inorg. Chem.* **1987**, *26*, 3054.

(38) Sweany, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 6986 and references therein.

(39) Thomson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(40) Arliguie, T.; Chaudret, B. *J. Chem. Soc., Chem. Commun.* **1989**, 155.

Finally we must note that the phenomenon seems general for compounds of the type [$CpMH_3L$].

Heineky et al. studying complexes such as [$CpIrH_3(PR_3)$]$^+$[29] (vide supra) and Bergman studying [$Cp^*IrH_3(PMe_3)$]$^+$[41] have already mentioned large H–H coupling constants.

We have also described the same phenomenon in [Cp'_2NbH_3] (Cp′ = $C_5H_4SiMe_3$, $C_5H_3(SiMe_3)_2$)[28] whereas an early report by Labinger had mentioned a very large H–H coupling constant in [$Cp_2NbH_3(AlEt_3)$].[42] The phenomenon seems governed by steric and electronic factors in a way similar to normal dihydrogen complexes, but further experiments are necessary to define them precisely.

Conclusion

We report in this paper the preparation of ruthenium(II), ruthenium(III), and ruthenium(IV) pentamethylcyclopentadienyl derivatives. We have found an easy access to a new class of 16-electron ruthenium(II) derivatives that may become interesting new starting materials.

Finally we have observed for the first time[27] a new phenomenon that we propose to be an equilibrium between a trihydride and either a trihydrogen complex or a species that would show a link between a hydride and a coordinated dihydrogen moiety.

The only real difference between the two proposals is the mechanism we propose for explaining the fluxionality of these species at high temperature. Further work in this area is now in progress.

Experimental Section

All manipulations were conducted under an inert-atmosphere of argon. Microanalyses were performed by the Centre de Microanalyse du CNRS or in the laboratory. Infrared spectra were obtained as Nujol mulls or in solution in CH_2Cl_2 or in C_6H_{14} using a Perkin-Elmer PE 577 or PE 225 grating diffractometer. NMR spectra were obtained by using a Bruker WH 90 (90 MHz) or WM 250 (250 MHz) spectrometer operating in the Fourier transform mode with proton noise decoupling when recording ^{31}P NMR spectra.

[$(C_5Me_5)RuCl_2$]$_n$ (1) was prepared according to a published method.[19]

(η^5-C_5Me_5)$RuCl_2(PPh_3)$ (2). To (Cp^*RuCl_2)$_n$ (0.20 g, 0.65 mmol) was added triphenylphosphine (0.171 g, 0.65 mmol) in ethanol following the same method as for 4. The yield was ca. 85%. Anal. Calcd for $RuCl_2C_{28}H_{30}P$: C, 59.05; H, 5.31; Cl, 12.45; P, 5.44. Found: C, 58.9; H, 5.75; Cl, 12.54; P, 5.14. μ_{eff} = 1.3948.

(η^5-C_5Me_5)$RuCl_2(PCy_3)$ (3). To (Cp^*RuCl_2)$_n$ (0.200 g, 0.65 mmol) was added tricyclohexylphosphine (0.183 g, 0.65 mmol) in ethanol following the same method. The yield was ca. 90%. Anal. Calcd for $RuCl_2C_{28}H_{48}P$: C, 57.23; H, 8.23; Cl, 12.07. Found: C, 56.73; H, 8.32; Cl, 12.27. μ_{eff} = 1.6728.

(η^5-C_5Me_5)$RuCl_2$[$P(CHMe_2)_3$] (4). To (Cp^*RuCl_2)$_n$ (0.200 g, 0.65 mmol) was added triisopropylphosphine (130 μL, 0.65 mmol) in ethanol. The solution was stirred for 30 min and filtered. The orange solid obtained was dried under vacuum. The yield was ca. 80% based on (Cp^*RuCl_2)$_n$. Anal. Calcd for $RuCl_2C_{19}H_{36}P$: C, 48.8; H, 7.76; Cl, 15.17. Found: C, 48.7; H, 7.46; Cl, 14.96. μ_{eff} = 1.9465.

(η^5-C_5Me_5)$RuCl(PCy_3)$ (5). To (Cp^*RuCl_2)$_n$ (0.200 g, 0.65 mmol) in ethanol (20 mL) was added tricyclohexylphosphine (0.183 g, 0.65 mmol) and zinc (1.5 g). After being stirred for 2 h, the blue solution was filtered. $Cp^*RuCl(PCy_3)$ could be obtained with ethanol or hexane or THF; yield ca. quantitative. Recrystallization from hexane afforded blue crystals of the compound: yield ca. 20%; ^1H NMR (C_6D_6) δ (Cp*) 1.59 ppm; $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$) δ 44.85 ppm. Anal. Calcd for $RuClC_{28}H_{48}P$: C, 60.91; H, 8.76; Cl, 6.42; P, 5.61. Found: C, 60.77; H, 8.78; Cl, 6.26; P, 5.42.

(η^5-C_5Me_5)$RuCl$[$P(CHMe_2)_3$] (6). As for 5, using $P(CHMe_2)_3$ (130 μL, 0.65 mmol): yield ca. quantitative; ^1H NMR (C_6D_6) δ(Cp*) 1.56 ppm; $\{^1H\}^{31}P$ NMR δ 57.16 ppm; mass spectrum, parent ion *m/e* 434 (Ru 102, Cl 37), 360. Anal. Calcd for $RuClC_{19}H_{36}P$: C, 52.83; H, 8.40. Found: C, 52.14; H, 8.33.

(η^5-C_5Me_5)$RuCl$[$(CMe_3)_3$] (7). To ($RuCl_2Cp^*$)$_n$ (0.200 g, 0.65 mmol) in ethanol (20 mL) were added successively zinc (1.5 g) and tri-*tert*-butyl phosphine (130 mL, 0.65 mmol). After 2 h of stirring, the pink solution was filtered.

(η^5-C_5Me_5)$RuCl(CO)(PCy_3)$ (8). Carbon monoxide was bubbled in a solution of $Cp^*RuCl(PCy_3)$ in ethanol. The solution was stirred for 10 min. The solvent was removed under vacuum. $Cp^*RuCl(CO)(PCy_3)$ was obtained as a yellow powder and recrystallized from ethanol: yield 80%; IR (Nujol) ν_{CO} 1910 cm^{-1}. Anal. Calcd for $RuClC_{29}H_{48}PO$: C, 60.03; H, 8.34; P, 5.34. Found: C, 60.06; H, 8.34; P, 5.31.

(η^5-C_5Me_5)$RuCl(CO)$[$P(CHMe_2)_3$] (9). The preparation is analogous to that of $Cp^*RuCl(CO)(PCy_3)$: yield 75%; IR (Nujol) ν_{CO} 1910 cm^{-1}. Anal. Calcd for $RuClC_{20}H_{36}PO$: C, 52.22; H, 7.89; Cl, 7.71; P, 6.73. Found: C, 52.20; H, 7.91; Cl, 7.72; P, 6.22.

(η^5-C_5Me_5)$RuH(CO)(PCy_3)$ (10). To $Cp^*RuClCOPCy_3$ (0.100 g, 0.17 mmol) in ethanol (10 mL) was added an excess of $NaBH_4$ following the same method as for $Cp^*RuH(CO)$[$P(CHMe_2)_3$]: yield 76%; IR (hexane) ν_{CO} 1900 cm^{-1}. Anal. Calcd for $RuC_{29}H_{49}PO$: C, 63.82; H, 9.05. Found: C, 63.81; H, 9.34.

(η^5-C_5Me_5)$RuH(CO)$[$P(CHMe_2)_3$] (11). To $Cp^*RuCl(CO)$[$P(CHMe_2)_3$] (0.100 g, 0.22 mmol) in ethanol (10 mL) was added an excess of $NaBH_4$. After the solution was stirred for 4 h, the solvent was removed under vacuum and the yellow residue was extracted with hexane (10 mL) and recrystallized from diethyl ether: yield 62%; IR (hexane) ν_{CO} 1900 cm^{-1}. Anal. Calcd for $RuC_{20}H_{37}PO$: C, 56.45; H, 8.76. Found: C, 56.26; H, 8.97.

(η^5-C_5Me_5)$RuH_3(PMe_3)$ (12). To (Cp^*RuCl_2)$_n$ (0.200 g, 0.65 mmol) in ethanol (20 mL) was added trimethylphosphine (618 μL, 0.65 mmol). The solution was stirred for 30 min and then evaporated to dryness. The residue was dissolved in dry THF. To the solution cooled to −50 °C were added 2 equiv of a molar solution of $LiBHEt_3$ in THF. Then the same method used for Cp^*RuH_3[$P(CHMe_2)_3$] (15) was followed.

(η^5-C_5Me_5)$RuH_3(PPh_3)$ (13). To the dichloride $Cp^*RuCl_2(PPh_3)$ (0.100 g, 0.176 mmol) dissolved in cold (−50 °C) THF was added a molar solution of $LiBHEt_3$ in THF (352 μL, 2 × 0.176 mmol). The solution was allowed to warm to room temperature and was stirred for 4 h. The solvent was removed, and the residue was extracted with benzene (3 × 20 mL). Then, the solution was filtered on a column of Al_2O_3 under an inert-atmosphere of argon. Recrystallization from methanol/toluene (1:2) afforded white needles of the complex. Anal. Calcd for $RuC_{28}H_{33}P$: C, 67.04; H, 6.6. Found: C, 66.85; H, 6.63.

(η^5-C_5Me_5)$RuH_3(PCy_3)$ (14). As for 13 using 340 μL (2 × 0.170 mmol) of $LiBHEt_3$ in THF: IR ν_{RuH} 1995 (vst), 1902 cm^{-1} (w); yield ca. 80%. Anal. Calcd for $RuC_{28}H_{51}P$: C, 64.71; H, 9.9. Found: C, 64.59; H, 9.78.

(η^5-C_5Me_5)RuH_3[$P(CHMe_2)_3$] (15). As for 13 using 428 μL (2 × 0.214 mmol) of $LiBHEt_3$ in THF: yield 70%; IR ν_{RuH} 1993 (vst), 1902 cm^{-1} (w); mass spectrum, parent ion *m/e* 400 (Ru 102), 398, 356, 312. Anal. Calcd for $RuC_{19}H_{39}P$: C, 57.11; H, 9.84. Found: C, 56.9; H, 9.90.

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(41) Gilbert, T. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3502.

(42) Labinger, J. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A.; Eds.; Pergamon Press: Oxford, 1982; p 707.