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Synthesis and Reactivity of New Ruthenium Alkyls and Hydrides. Protonation of Cp*Ru($Me_2PCH_2PMe_2$)Me and X-ray Crystal Structure of Cp*$_2$Ru$_2$(μ-$Ph_2PCH_2PPh_2$)(AlH_5)

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Treatment of the pentamethylcyclopentadienylruthenium chloride tetramer [Cp*RuCl]$_4$ with bis(dimethylphosphino)methane (dmpm) in tetrahydrofuran affords three ruthenium(II) phosphine complexes, Cp*Ru(dmpm)Cl, [Cp*Ru(dmpm)(η^1-dmpm)]Cl, and Cp*$_2$Ru$_2$(μ-dmpm)$_2$Cl$_2$. Similar treatment of [Cp*RuCl]$_4$ with bis(diphenylphosphino)methane (dppm) in tetrahydrofuran or diethyl ether affords the dinuclear species Cp*$_2$Ru$_2$(μ-dppm)(μ-Cl)$_2$; in acetonitrile, this same reaction yields the mononuclear product Cp*Ru(dppm)Cl in high yield. The mononuclear complexes Cp*Ru(P-P)Cl (where P-P is dmpm or dppm) can be alkylated with dimethylmagnesium in diethyl ether to give the methyl complexes Cp*Ru(dmpm)Me and Cp*Ru(dppm)Me. Protonation of these Cp*Ru(P-P)Me complexes with trifluoroacetic acid results in the rapid reductive elimination of methane and formation of the trifluoroacetato complexes Cp*Ru(P-P)(η^1-O_2CCF_3); no ruthenium(IV) hydridomethyl intermediates could be detected. Treatment of Cp*$_2$Ru$_2$(dppm)$_2$Cl$_2$ with $LiAlH_4$ in diethyl ether yields the ruthenium aluminohydride complex Cp*$_2$Ru$_2$(μ-dppm)(μ-AlH_5), which can be converted to the ruthenium polyhydride complex Cp*$_2$Ru$_2$(μ-dppm)H_6 by treatment with methanol at low temperatures. The crystal structure of Cp*$_2$Ru$_2$(μ-dppm)(μ-AlH_5) shows that the aluminohydride unit is bound in a (μ-H)$_2$AlH(μ-H)$_2$ fashion.

Introduction

The activation of hydrocarbon C−H bonds and the functionalization of saturated hydrocarbons by soluble transition metal complexes have been intensively studied in the past decade,[1−5] and perhaps most notable is the finding that some organometallic complexes are able to activate methane.[6−15] The activation of alkanes can occur via two different pathways: oxidative addition to a coordinately unsaturated metal center via a so-called σ complex[7−12,16,17] and "heterolytic" addition across a reactive metal−ligand bond via a four-centered intermediate.[13−15,18−20] The intermediacy of a σ complex in the former mechanism has been suggested by the observation of proton exchange between the methyl and hydrido groups prior to the reductive elimination of methane and by the observation of an inverse kinetic isotope effect for the elimination of methane from a transition metal hydridomethyl complex.[16,17] Additional evidence has come from the direct observation of transition metal methane adducts M(CH_4)L$_n$ in low temperature matrix isolation studies[21−26] and the detection of cationic transition metal methane adducts M(CH_4)L$_n^+$ in the gas phase.[27,28] Little is known, however, about

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the *structures* of the intermediates generated during these C−H bond activation processes.

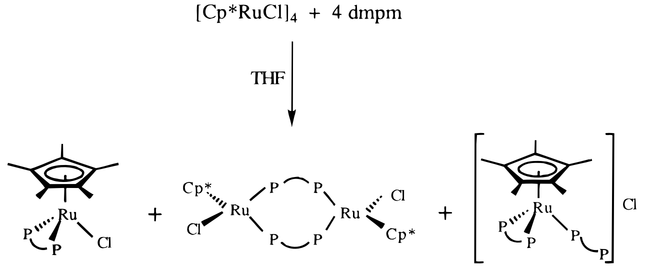
A potential alternative approach to the synthesis of σ complexes is the protonation of a transition metal alkyl compound. If reductive elimination can be slowed sufficiently and if the metal center is neither too electron-poor nor too electron-rich, then such protonation reactions may lead to alkyl/hydride products in which there is some interaction between the alkyl and hydride ligands. For example, protonation of $Cp^*Ru(PMe_3)_2Me$ with HBF_4 is known to afford a Ru^{IV} complex $[Cp^*Ru(PMe_3)_2Me(H)][BF_4]$,[29] but this species adopts a four-legged piano-stool structure in which the methyl and hydride ligands are mutually trans. Thus, in this complex, there are no interactions between the methyl and hydride groups like those present between the silyl and hydride ligands in electronically related manganese complexes of stoichiometry $CpMn(CO)L(SiR_3)H$.[30−32] Other $Cp^*Ru(PR_3)_2Me$ complexes are known,[29,33−35] but their reactions with acids have not been studied.

In order to promote interactions between the alkyl and hydride ligands attached to the same metal center, we have undertaken a study of electron-rich ruthenium complexes with chelating phosphines that have small bite angles. Phosphines such as bis(dimethylphosphine)methane (dmpm) and bis(diphenylphosphino)methane (dppm) cannot span trans positions in a four-legged piano-stool structure and will constrain the other two ligands to be mutually cis. This strategy has been successfully utilized to prepare the stable dihydrogen complex $[CpRu(dppm)(\eta^2\text{-}H_2)][PF_6]$; in contrast, the 1,2-bis(diphenylphosphino)propane complex $[CpRu(dppp)H_2][PF_6]$ is a classical hydride complex in which the two hydride ligands are mutually trans.[36,37] In this paper, we report preparations of electron-rich ruthenium(II) alkyls and hydrides and, in particular, our attempts to prepare *cis*-hydrido methyl complexes of stoichiometry $[Cp^*Ru(P\text{-}P)Me(H)]^+$ (where P-P is dmpm or dppm). We also report the crystal structure of a ruthenium aluminohydride complex $Cp^*_2Ru_2(\mu\text{-dppm})(\mu\text{-}AlH_5)$ and its conversion to the ruthenium polyhydride $Cp^*_2Ru_2(\mu\text{-dppm})H_6$.

Results and Discussion

In order to explore the reactivity of seven-coordinate Cp*Ru complexes that contain phosphines of stoichiometry $R_2PCH_2PR_2$, it is first necessary to synthesize suitable $Cp^*Ru(R_2PCH_2PR_2)Cl$ starting materials. Accordingly, the reactions of $[Cp^*RuCl]_4$[38−41] with bis(dimethylphosphino)methane (dmpm) and bis(diphenylphosphino)methane (dppm) have been investigated.

Reaction of $[Cp^*RuCl]_4$ with dmpm. Three different products have been obtained upon treatment of $[Cp^*RuCl]_4$ with 1 equiv of dmpm in tetrahydrofuran for 12 h. The reaction produces an orange solution (which contains two of the products) and an orange precipitate (which contains the third). The simple 1:1 coordination complex $Cp^*Ru(dmpm)Cl$, **1**, can be isolated from the reaction solution as pale orange crystals in moderate yield by removing the solvent and crystallizing the residue from diethyl ether. Compound **1** can be obtained in better yield by treatment of the cyclooctadiene complex $Cp^*Ru(COD)Cl$ with dmpm, and this is the preferred method of synthesis.[42] The piano-stool structure of **1** is clear from the ^1H and $^{31}P\{^1H\}$ NMR spectra (see Table 1). The most diagnostic features are the presence of two resonances for the inequivalent methylene protons in the backbone of the dmpm ligand and the two resonances for the PMe_2 protons. These PCH_2 and PMe_2 groups are diastereotopic since they can either be distal or proximal to the Cp* ring. These spectroscopic features are similar to those of the analogous cyclopentadienyl complex $CpRu(Cy_2PCH_2PCy_2)Cl$ (where Cy is cyclohexyl).[43]



(**1**) (**2**) (**3**)

As mentioned above, the reaction of $[Cp^*RuCl]_4$ with dmpm in tetrahydrofuran affords an orange precipitate. This precipitate consists of a single compound with the same empirical formula as **1**. ^1H and $^{31}P\{^1H\}$ NMR spectroscopy establishes that the orange product is the dmpm-bridged diruthenium complex $Cp^*_2Ru_2(\mu\text{-dmpm})_2Cl_2$, **2**. The ^1H NMR spectrum of **2** shows that the PCH_2 protons are equivalent and appear as a triplet of pseudotriplets at δ 2.00, while the PMe_2 protons appear as two virtually-coupled triplets at δ 1.63 and 1.43. The Cp* resonance is a singlet at δ 1.57. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows only a singlet at δ −20.8. The strong tendency of dmpm ligands to bridge between two metal centers has been observed in other ruthenium systems.[44]

The third product obtained from the reaction of $[Cp^*RuCl]_4$ with dmpm is ionic and was isolated directly from the reaction solution by recrystallization from tetrahydrofuran. The stoichiometry $[Cp^*Ru(dmpm)(\eta^1\text{-dmpm})]Cl$, **3**, is shown most clearly by its $^{31}P\{^1H\}$ NMR

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Table 1. ^{1}H and ^{31}P{^{1}H} NMR Data for the Ruthenium Complexes[a,b]

compd, solvent	^{1}H	assnmt	^{31}P
Cp*Ru(dmpm)Cl, CD_2Cl_2	1.72 (t, $^{4}J_{\mathrm{PH}} = 2.2$)	Cp*	−15.0 (s)
	1.51 (“t”, $^{2}J_{\mathrm{PH}} + {}^{4}J_{\mathrm{PH}} = 8.4$)	PMe_2	
	1.39 (“t”, $^{2}J_{\mathrm{PH}} + {}^{4}J_{\mathrm{PH}} = 9.0$)	PMe_2	
	3.36 (m)	PCH_2	
	3.13 (m)	PCH_2	
$Cp*_2Ru_2(\mu\text{-dmpm})_2Cl_2$, CD_2Cl_2	1.57 (br s)	Cp*	12.2 (s)
	1.63 (“t”, $^{2}J_{\mathrm{PH}} + {}^{4}J_{\mathrm{PH}} = 7.0$)	PMe_2	
	1.43 (“t”, $^{2}J_{\mathrm{PH}} + {}^{4}J_{\mathrm{PH}} = 5.1$)	PMe_2	
	2.00 (t“t”, $^{2}J_{\mathrm{PH}} = 14.1$,“$^{4}J_{\mathrm{PH}}$” = 7)	PCH_2	
Cp*Ru(dmpm)(η^1-dmpm)Cl, CD_2Cl_2	1.80 (d, $^{4}J_{\mathrm{PH}} = 1.8$)	Cp*	*d*
	1.71 (“t”, $^{2}J_{\mathrm{PH}} + {}^{4}J_{\mathrm{PH}} = 9.6$)	PMe_2 (η^2)[c]	
	1.50 (“t”, $^{2}J_{\mathrm{PH}} + {}^{4}J_{\mathrm{PH}} = 9.6$)	PMe_2 (η^2)	
	1.68 (d, $^{2}J_{\mathrm{PH}} = 7.5$)	PMe_2 (η^1)	
	1.16 (d, $^{2}J_{\mathrm{PH}} = 3.3$)	PMe_2 (η^0)	
	3.80 (m)	PCH_2 (η^2)	
	3.40 (m)	PCH_2 (η^2)	
	1.89 (d, $^{2}J_{\mathrm{PH}} = 6.9$)	PCH_2 (η^1)	
Cp*Ru(dmpm)Me, CD_2Cl_2	1.76 (s)	Cp*	−11.7 (s)
	1.46 (“t”, $^{2}J_{\mathrm{PH}} + {}^{4}J_{\mathrm{PH}} = 8.8$)	PMe_2	
	1.09 (“t”, $^{2}J_{\mathrm{PH}} + {}^{4}J_{\mathrm{PH}} = 8.8$)	PMe_2	
	3.36 (m)	PCH_2	
	3.00 (m)	PCH_2	
	−0.27 (br t, $^{3}J_{\mathrm{PH}} = 7.5$)	Ru-Me	
$Cp*_2Ru_2(\mu\text{-dmpm})_2(\eta^2\text{-}O_2CCF_3)_2$, CD_2Cl_2, −40 °C	1.68 (s)	Cp*	−20.8 (s)
	1.56 (“t”, $^{2}J_{\mathrm{PH}} + {}^{4}J_{\mathrm{PH}} = 9.6$)	PMe_2	
	1.47 (“t”, $^{2}J_{\mathrm{PH}} + {}^{4}J_{\mathrm{PH}} = 9.0$)	PMe_2	
	3.38 (t, $^{2}J_{\mathrm{PH}} = 11.0$)	PCH_2	
Cp*Ru(dmpm)(η^1-O_2CCF_3), CD_2Cl_2, −40 °C	1.64 (s)	Cp*	−15.8 (s)
	1.50 (“t”, $^{2}J_{\mathrm{PH}} + {}^{4}J_{\mathrm{PH}} = 7.4$)	PMe_2	
	1.31 (“t”, $^{2}J_{\mathrm{PH}} + {}^{4}J_{\mathrm{PH}} = 8.4$)	PMe_2	
	3.51 (m)	PCH_2	
	3.37 (m)	PCH_2	
Cp*Ru(dppm)Cl, CD_2Cl_2	1.65 (t, $^{4}J_{\mathrm{PH}} = 2.0$)	Cp*	12.7 (s)
	7.50 (m)	PPh_2	
	7.36 (m)	PPh_2	
	7.32 (m)	PPh_2	
	7.28 (m)	PPh_2	
	4.89 (m)	PCH_2	
	4.17 (m)	PCH_2	
Cp*Ru(dppm)Me, CD_2Cl_2	1.84 (t, $^{4}J_{\mathrm{PH}} = 2.4$)	Cp*	20.0 (s)
	7.46 (m)	o-PPh_2	
	7.37 (m)	o-PPh_2	
	7.04−7.20 (m)	p, m-PPh_2	
	4.54 (m)	PCH_2	
	4.11 (m)	PCH_2	
	0.00 (t, $^{3}J_{\mathrm{PH}} = 7.3$)	Ru-Me	
Cp*Ru(dppm)(η^1-O_2CCF_3), CD_2Cl_2, −50 °C	1.65 (t, $^{4}J_{\mathrm{PH}} = 2.0$)	Cp*	12.5 (s)
	7.40 (m)	PPh_2	
	7.39 (m)	PPh_2	
	7.31 (m)	PPh_2	
	7.29 (m)	PPh_2	
	5.62 (m)	PCH_2	
	5.32 (m)	PCH_2	
$Cp*_2Ru_2(\mu\text{-dppm})Cl_2$, $CDCl_3$	1.28 (s)	Cp*	35.0 (s)
	7.48 (m)	o-PPh_2	
	7.14 (s)	m-PPh_2	
	7.10 (s)	p-PPh_2	
	3.69 (t, $^{2}J_{\mathrm{PH}} = 10.2$)	PCH_2	
$Cp*_2Ru_2(\mu\text{-dppm})(AlH_5)$, CD_2Cl_2	1.48 (s)	Cp*	58.4 (s)
	7.32 (m)	o-PPh_2	
	7.11 (s)	m-PPh_2	
	7.09 (s)	p-PPh_2	
	3.20 (t, $^{2}J_{\mathrm{PH}} = 10.8$)	PCH_2	
	−13.96 (br d, $^{2}J_{\mathrm{PH}} = 22.8$)	Ru(μ-H)Al	
$Cp*_2Ru_2(\mu\text{-dppm})H_6$, C_6D_6	1.71 (s)	Cp*	64.7 (s)
	7.57 (m)	o-PPh_2	
	7.09 (br s)	m-PPh_2	
	7.01 (br s)	p-PPh_2	
	3.51 (t, $^{2}J_{\mathrm{PH}} = 9.6$)	PCH_2	
	−10.13 (br d, $^{2}J_{\mathrm{PH}} = 19.2$)	RuH	

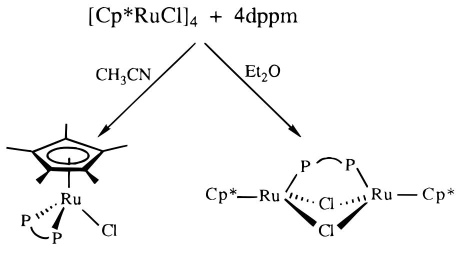
[a] All chemical shifts are reported in parts per million (ppm), while all coupling constants are in Hertz. [b] All spectra were taken at 25 °C except those specified. [c] η^2, η^1, and η^0 represent the bidentate dmpm ligand, the coordinated end of the unidentate dmpm ligand, and the dangling end of the unidentate dmpm ligand, respectively. [d] A_2BC spin system with $\delta_A = -18.6$, $\delta_B = 10.9$, $\delta_C = -56.3$, $J_{AB} = 39.4$, $J_{BC} = 27.2$.

spectrum, which consists of three resonances with relative intensities of 2:1:1. The two equivalent phosphorus nuclei of the bidentate dmpm ligand appear as a doublet at δ −18.6; the bound end of the η^1-dmpm ligand appears as a doublet of triplets at δ 10.9, while the dangling end of the η^1-dmpm ligand appears as a doublet at δ −56.3. The ^{1}H NMR spectrum is consistent with this structure: the backbone methylene protons of the bidentate dmpm ligand appear as two doublets of triplets at δ 3.80 and 3.40, each of intensity 1, while the corresponding protons of the unidentate dppm ligand appear as a doublet of doublets at δ 1.89 of intensity 2. The PMe_2 groups appear as two virtually-coupled triplets at δ 1.71 and 1.50 for the bidentate dmpm ligand and as two doublets at δ 1.68 and 1.16 for the η^1-dmpm ligand. The Cp* resonance is a doublet at δ 1.80. The hexachlorodizincate [$Zn_2Cl_6^{2-}$] salt of **3** can also been prepared in high yield by reduction of [Cp^*RuCl_2]$_2$ with zinc in the presence of excess dmpm in CH_2Cl_2.

An analogous cyclopentadienyl complex [CpRu(dppm)(η^1-dppm)]Cl was prepared by Bruce *et al.* via substitution of the triphenylphosphine group in [CpRu(dppm)(PPh_3)]Cl with dppm, but no spectroscopic characterization of this compound was described.[45]

The formation of the mononuclear monoadduct **1** is favored if the reactants are stirred for extended periods in tetrahydrofuran. In contrast, in solvents such as diethyl ether, the dinuclear complex **2** and the ionic diadduct **3** are insoluble and only these products can be isolated. The dimeric complex **2** cannot be converted into **1** even after being refluxed in tetrahydrofuran for 24 h. Attempts to convert the ionic diadduct **3** into **1** by heating to remove the second molecule of dmpm have been similarly unsuccessful.

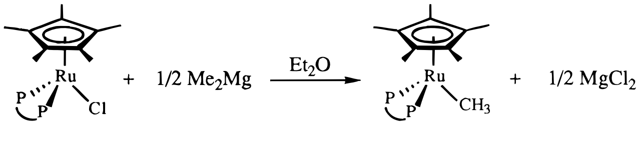
Reaction of [Cp*RuCl]$_4$ with dppm. Koelle and co-workers have reported the preparation of Cp*Ru(dppm)Cl, **4**, in modest yield (15%) by the addition of dppm to the mixed-valent complex $Cp^*_2Ru_2(\mu\text{-}Cl)_3$.[45,46] We have found that **4** can be prepared in higher yield (71%) by stirring a suspension of [Cp*RuCl]$_4$ and dppm in acetonitrile for 12 h, followed by removal of the solvent and recrystallization from diethyl ether. The ^{1}H NMR spectrum of **4** contains the diagnostic doublet of triplets at δ 4.89 and 4.17 due to the two inequivalent protons of the PCH_2 unit.



(**4**) (**5**)

Interestingly, when [Cp*RuCl]$_4$ is treated with dppm in diethyl ether or in tetrahydrofuran, dark red crystals of the dinuclear complex $Cp^*_2Ru_2(\mu\text{-dppm})Cl_2$, **5**,[46,47] are obtained in essentially quantitative yield. In these solvents, this product was obtained irrespective of the phosphine-to-metal ratio employed. The bridging nature of the dppm ligand is shown by the single environments for the PCH_2 protons. It is likely that the successful synthesis of the mononuclear compound Cp*Ru(dppm)Cl, **4**, in acetonitrile is due to the intermediacy of species[38,48,49] such as [Cp*Ru(MeCN)$_3$]$^+$ or [Cp*Ru(dppm)(MeCN)]$^+$ that prevent the formation of the diruthenium compound **5**.

Synthesis of the Alkylruthenium(II) Complexes Cp*Ru(dmpm)Me, 6, and Cp*Ru(dppm)Me, 7. Alkylruthenium(II) complexes can be obtained in high yield by treating Cp*Ru(dmpm)Cl with dimethylmagnesium in diethyl ether. The NMR spectrum of the product Cp*Ru(dmpm)Me, **6**, shows that the PCH_2 protons of the dmpm ligand are inequivalent (they appear as two doublets of triplets at δ 3.36 and 3.00); the ruthenium-bound methyl group appears as a triplet at δ −0.27 ($^3J_{PH}$ = 7.5 Hz). The related compound Cp*Ru(dppm)Me, **7**, can be prepared in high yield by treating Cp*Ru(dppm)Cl with dimethylmagnesium in diethyl ether.



6, P-P = dmpm

7, P-P = dppm

Protonation of Cp*Ru(dmpm)Me and Cp*Ru(dppm)Me. The protonation of the ruthenium methyl complexes was investigated in order to determine whether stable alkyl hydride species could be obtained. The reaction of Cp*Ru(dmpm)Me with trifluoroacetic acid in CD_2Cl_2 has been followed by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy (Figure 1). At −78 °C, the NMR signals due to **6** disappear immediately upon addition of HO_2CCF_3 to the solution. A ^{1}H NMR spectrum of the reaction mixture at −78 °C shows resonances due to a new complex **8**, along with a sharp peak at δ 0.20 due to methane (Figure 1b). Compound **8** is tentatively assigned the formula $Cp^*_2Ru_2(\mu\text{-dmpm})_2(\eta^1\text{-}O_2CCF_3)_2$, based on the similarity of its NMR spectrum to that of the chloro complex $Cp^*_2Ru_2(\mu\text{-dmpm})_2Cl_2$, **2**. The triplet at δ 3.39 is due to the equivalent protons of the PCH_2 units of the bridging dmpm ligands, while the two virtually-coupled triplets at δ 1.56 and 1.47 can be assigned to the PMe_2 groups. The Cp* resonance appears as a singlet at δ 1.57. The $^{31}P\{^1H\}$ NMR spectrum of **8** consists of a single peak at δ −20.8.

When solutions of **8** in CD_2Cl_2 are allowed to stand at −70 °C, the signals due to **8** slowly diminish and are replaced by a new set of signals, which can be assigned to the mononuclear complex Cp*Ru(dmpm)(η^1-O_2CCF_3), **9**. At −40 °C, this conversion goes rapidly to completion (Figure 1c). The ^{1}H NMR spectrum of **9** contains two multiplets at δ 3.51 and 3.37 due to the two inequivalent protons of the PCH_2 unit and two virtually-coupled triplets at δ 1.50 and 1.31 due to the two inequivalent sets of PMe_2 groups. The Cp* resonance appears as a singlet at δ 1.64. The $^{31}P\{^1H\}$ NMR spectrum of **9** consists of a singlet at δ −15.8.

When the analogous dppm compound Cp*Ru(dppm)Me, **7**, is treated with HO_2CCF_3 at −78 °C in toluene-d_8, the trifluoroacetate complex Cp*Ru(dppm)(η^1-O_2CCF_3), **10**, is produced instantaneously. No intermediate

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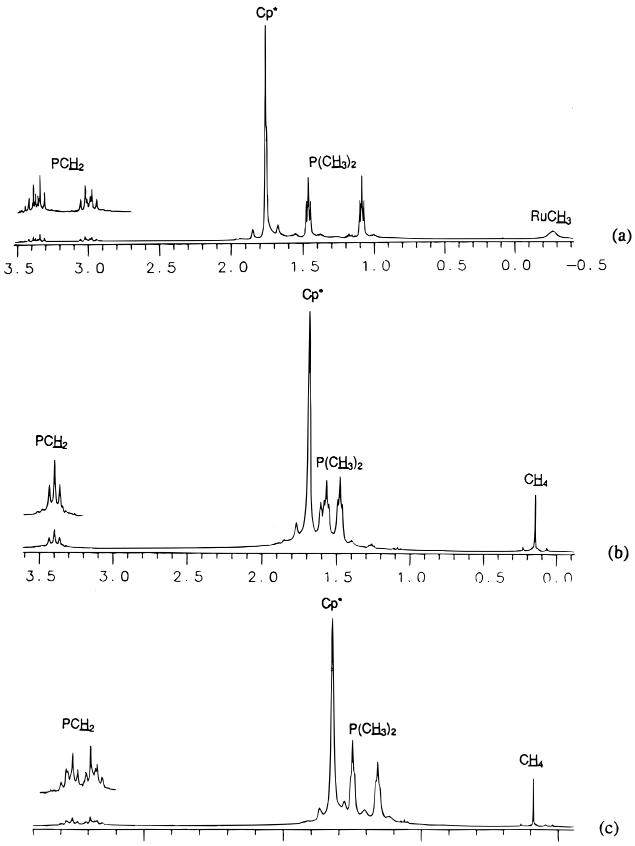


Figure 1. (a) ^{1}H NMR spectrum (300 MHz) of Cp*Ru(dmpm)Me in CD_2Cl_2 at −80 °C; (b) ^{1}H NMR spectrum (300 MHz) after treatment of Cp*Ru(dmpm)Me with HO_2CCF_3 in CD_2Cl_2 at −80 °C; (c) same reaction mixture at −40 °C.

analogous to **8** was observed at any temperature. The ^{1}H NMR spectrum of **10** shows two doublets of triplets at δ 5.62 and 5.32 for the PCH_2 unit of the dppm ligand, in addition to resonances for the phenyl groups and the Cp* ligand.

For both the dmpm and dppm complexes, protonation results in the immediate evolution of methane and no *cis*-methyl/hydride intermediates could be detected. When these protonations were carried out with HBF_4, similar results were obtained: methane elimination was rapid and no *cis*-methyl/hydride complex could be observed.

Synthesis, Structure, and Reactivity of the Aluminohydride Complex Cp*$_2$Ru$_2$(μ-dppm)(μ-AlH$_5$). There has been recent interest in the structures of transition metal aluminohydride complexes.[50−54] We find that treatment of Cp*$_2$Ru$_2$(μ-dppm)Cl$_2$, **5**, with $LiAlH_4$ in diethyl ether affords the aluminohydride complex Cp*$_2$Ru$_2$(μ-dppm)(μ-AlH$_5$), **11**. The IR spectrum of **11** shows two strong metal hydride stretches at 1779 and 1728 cm^{-1}. The ^{1}H NMR spectrum of **11** at 25 °C shows a doublet at δ −13.96 for the bridging AlH_5^{2-} group; the $^2J_{PH}$ coupling constant is 22.8 Hz

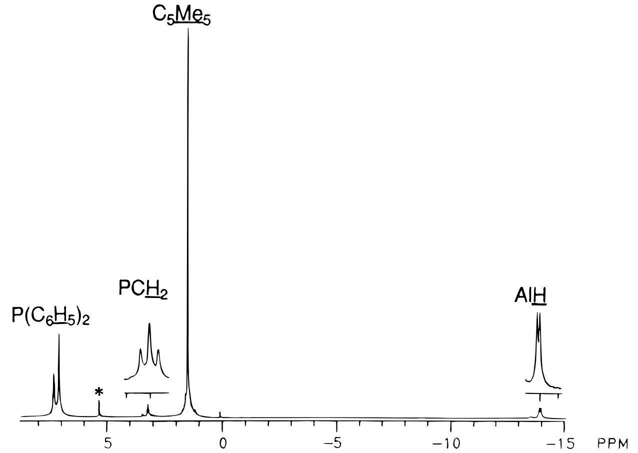
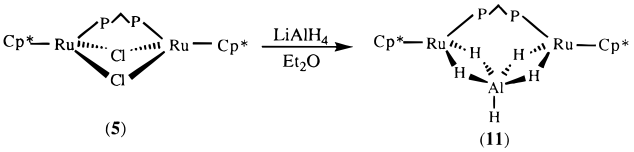


Figure 2. ^{1}H NMR spectrum (300 MHz) of Cp*$_2$Ru$_2$(μ-dppm)(μ-AlH$_5$), **11**, in CD_2Cl_2 at 25 °C. The asterisk indicates the solvent peak.



(Figure 2). Although the X-ray crystallographic results (see below) show that four of the hydrogen atoms in the AlH_5^{2-} group bridge to the ruthenium atoms and one is terminal on aluminum, we could not identify a separate resonance for the terminal hydride in the ^{1}H NMR spectrum. It is possible that the signals for the terminal hydrides on aluminum are lost in the base line, owing to broadening by the quadrupolar aluminum nucleus.[55] Variable-temperature ^{1}H NMR spectroscopy has shown no evidence of a fluxional process in **11**.

The aluminodeuteride isotopolog Cp*$_2$Ru$_2$(μ-dppm)(μ-AlD$_5$), **11**-d_5, has been prepared by the reaction of **5** with excess $LiAlD_4$. The metal deuteride stretches in **11**-d_5 appear at 1275 and 1255 cm^{-1}.

X-ray Single-Crystal Structure of 11. A single-crystal X-ray diffraction study of **11** has been performed in order to confirm its structure. Crystals of **11**, grown from diethyl ether at −20 °C, crystallize in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. There is no crystallographic symmetry imposed on the molecule, although the idealized symmetry of the molecules is C_{2v} (Figure 3). Crystal data are presented in Table 2, and selected bond distances and angles are collected in Table 3.

Molecules of **11** consist of two ruthenium centers bridged by a dppm ligand and an AlH_5^{2-} unit that is best written as (μ-H)$_2$AlH(μ-H)$_2^{2-}$. Each ruthenium atom is also η^5-bonded to a pentamethylcyclopentadienyl group. Interestingly, unlike all previously known AlH_5^{2-} units, which adopt distorted trigonal bipyramidal geometries,[53] the AlH_5^{2-} unit in **11** exhibits a slightly distorted square pyramidal geometry. The H−Al−H bond angles between the axial and four basal hydrogen atoms are almost identical: these bond angles average at 113(2)° with the largest deviation being 4°. The terminal hydrogen on aluminum occupies the axial site of the square pyramid. As expected, the terminal Al−H bond distance of 1.49(5) Å is much shorter than the bridging Al−H bond distances of 1.88(2) Å.

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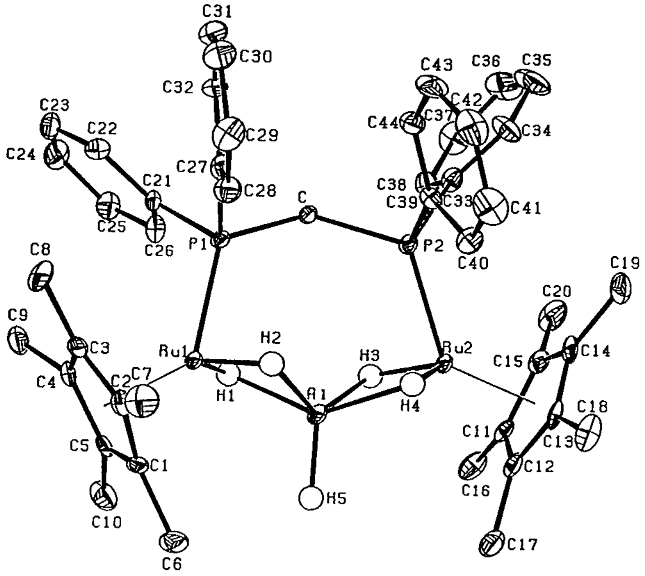


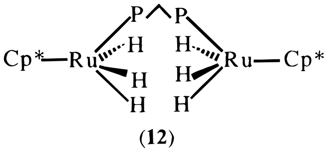
Figure 3. ORTEP drawing of $Cp^*_2Ru_2(\mu\text{-dppm})(\mu\text{-}AlH_5)$, **11**. The 35% probability density surfaces are shown, except for the hydrogen atoms which are represented as arbitrarily-sized spheres.

The Ru−H distances to the bridging hydride ligands refined to 1.55 Å. The Ru−Ru distance in **11** is greater than 4 Å, and thus, the ruthenium atoms are not bonded to each other. The Ru−P distances of 2.245(2) and 2.254(2) Å are well within the range found for other ruthenium bis(diphenylphosphino)methane complexes.[56]

Conversion of 11 to the Ruthenium Polyhydride $Cp^*_2Ru_2(\mu\text{-dppm})H_6$. Transition metal polyhydride complexes have been of interest especially since the recognition in 1983 that such species sometimes contain nonclassical dihydrogen ligands.[57] One of the most general methods for the synthesis of polyhydride complexes is the addition of $LiAlH_4$ to a metal chloride complex followed by protolysis.[58,59] In certain cases, such as in the present study, the transition metal aluminohydride complexes that are intermediates in such syntheses can be isolated if the protolysis step is omitted.

Protolysis of **11** with excess methanol in diethyl ether yields the diruthenium hexahydride complex $Cp^*_2Ru_2(\mu\text{-dppm})H_6$, **12**. The IR spectrum of **12** contains a broad

$$Cp^*_2Ru_2(\mu\text{-dppm})(AlH_5) \xrightarrow{MeOH}$$



(**12**)

peak at 1980 cm^{-1} that can be assigned to a Ru−H stretch. All six hydride ligands are evidently terminal hydrides; three are bound to each ruthenium atom. At 25 °C, the ^1H NMR signal for the hydride ligands in **12** is a doublet at δ −10.2 ($^2J_{HP}$ = 19.2 Hz).

Table 2. Crystal Data for $Cp^*_2Ru_2(\mu\text{-dppm})(AlH_5)$, 11

$C_{45}H_{57}P_2AlRu_2$	space group: $P2_1/c$
a = 17.025(4) Å	T = −75 °C
b = 10.063(2) Å	λ = 0.710 73 Å
c = 25.310(10) Å	ρ_{calcd} = 1.416 g cm^{-3}
β = 105.97(2)°	μ_{calcd} = 8.36 cm^{-1}
V = 4169(4) $Å^3$	transm coeff = 0.821−0.890
Z = 4	R_F = 0.042
mol wt = 889.02	R_{wF} = 0.049

Table 3. Selected Bond Distances and Angles for $Cp^*_2Ru_2(\mu\text{-dppm})(AlH_5)$, 11

Bond Distances (Å)

Ru(1)−P(1)	2.245(2)	Ru(2)−C(13)	2.234(7)
Ru(1)···Al	2.445(2)	Ru(2)−C(14)	2.245(7)
Ru(1)−H(1)	1.55(3)	Ru(2)−C(15)	2.244(7)
Ru(1)−H(2)	1.55(2)	Ru(2)−H(3)	1.55(3)
Ru(1)−C(1)	2.223(7)	Ru(2)−H(4)	1.55(3)
Ru(1)−C(2)	2.251(8)	Al−H(1)	1.88(2)
Ru(1)−C(3)	2.252(7)	Al−H(2)	1.88(2)
Ru(1)−C(4)	2.230(7)	Al−H(3)	1.88(2)
Ru(1)−C(5)	2.215(7)	Al−H(4)	1.88(3)
Ru(2)−P(2)	2.254(2)	Al−H(5)	1.49(5)
Ru(2)−Al	2.464(2)	P(1)−C	1.851(6)
Ru(2)−C(11)	2.224(7)	P(2)−C	1.872(6)
Ru(2)−C(12)	2.217(7)		

Bond Angles (deg)

P(1)−Ru(1)−Al	98.89(7)	Ru(1)−Al−Ru(2)	134.68(9)
P(2)−Ru(2)−Al	93.78(7)	H(1)−Al−H(2)	77(1)
Ru(1)−P(1)−C	120.9(2)	H(2)−Al−H(4)	84.2(10)
Ru(2)−P(2)−C	121.2(2)	H(3)−Al−H(4)	78(1)
P(1)−C−P(2)	125.3(4)	H(1)−Al−H(3)	88(1)
P(1)−Ru(1)−H(1)	84(1)	H(1)−Al−H(5)	109(2)
P(1)−Ru(1)−H(2)	88(1)	H(2)−Al−H(5)	117(2)
H(1)−Ru(1)−H(2)	97(1)	H(3)−Al−H(5)	113(2)
P(2)−Ru(2)−H(3)	89(1)	H(4)−Al−H(5)	111(2)
P(2)−Ru(2)−H(4)	90(1)	H(1)−Al−H(4)	140(1)
H(3)−Ru(2)−H(4)	99(1)	H(2)−Al−H(3)	130(2)

Mononuclear ruthenium trihydride complexes of the general type $Cp'Ru(PR_3)H_3$ (where Cp′ is cyclopentadienyl or pentamethylcyclopentadienyl) have been known for some time and were initially thought to be classical ruthenium trihydride complexes with trigonal bipyramidal structures of C_{3v} symmetry according to NMR and IR data.[58,59] A single-crystal X-ray diffraction study, however, has shown that $Cp^*Ru(PPh_3)H_3$ is a classical ruthenium trihydride that adopts a four-legged piano-stool structure of C_s symmetry in the solid state.[60] Later, Chaudret and co-workers observed unusually large coupling constants between the hydrides and proposed that there is an equilibrium between a classical trihydride and either a hydride/dihydrogen complex or trihydrogen complex.[61] Tritium labeling and theoretical studies by Zilm, Heinekey, and co-workers have shown that the large coupling constants between the hydrides are not due to the presence of nonclassical dihydrogen or trihydrogen ligands but instead are due to rapid pairwise quantum mechanical hydrogen exchange.[62] Most likely, **12** adopts a classical structure with two ruthenium trihydride centers bridged by a dppm ligand.

Experimental Section

All operations were carried out in a vacuum or under argon. Solvents were distilled under nitrogen from sodium/benzophe-

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none (pentane, diethyl ether, tetrahydrofuran), sodium (toluene-d_8, benzene-d_6), magnesium (methanol), or calcium hydride (dichloromethane-d_2) immediately before use. Bis(dimethylphosphino)methane (Strem), bis(diphenylphosphino)methane (Strem), pentamethylcyclopentadiene (Quantum Design), methanol-d_4 (Cambridge Isotopes), $LiAlH_4$ (Cerac), $LiAlD_4$ (Cambridge Isotopes), $RuCl_3{\cdot}3H_2O$ (Cerac), and zinc dust (Mallinckrodt) were used as received. Trifluoroacetic acid (Aldrich) was purified by addition of 1% v/v trifluoroacetic anhydride (Aldrich) followed by distillation under N_2. The compounds $[Cp^*RuCl_2]_2$[31,63] and $[Cp^*RuCl]_4$[38−40] were prepared via literature methods.

IR spectra were recorded on a Perkin-Elmer 599B infrared spectrometer as Nujol mulls between KBr plates. The ^1H NMR data were obtained on a General Electric QE-300 spectrometer at 300 MHz or on a General Electric NB-300 spectrometer at 300 MHz. The ^{13}C NMR data were obtained on a General Electric NB-300 spectrometer at 75 MHz or on a General Electric QE-300 spectrometer at 75 MHz. The $^{31}P\{^1H\}$ NMR data were recorded on a General Electric NB-300 spectrometer at 121 MHz. The ^2H NMR data were obtained on a General Electric NB-300 spectrometer at 46 MHz. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to TMS (^1H, ^2H, ^{13}C) or 85% H_3PO_4 (^{31}P). Microanalyses were performed by the University of Illinois Microanalytical Laboratory.

(Pentamethylcyclopentadienyl)chloro[bis(dimethylphosphino)methane]ruthenium(II), Cp*Ru(dmpm)Cl, 1. To a slurry of $[Cp^*RuCl]_4$ (0.593 g, 0.54 mmol) in tetrahydrofuran (40 mL) was slowly added a solution of dmpm (0.34 mL, 2.17 mmol) in tetrahydrofuran (40 mL). The solution turned orange immediately, and an orange precipitate formed after a few minutes. After the mixture had been stirred at room temperature for 12 h, the solvent was removed under vacuum and the residue was extracted with diethyl ether (2 × 80 mL). The extracts were filtered, and the filtrates were combined, concentrated to ca. 100 mL, and cooled to −20 °C to afford pale orange crystals. Yield: 0.37 g (63%). Mp: 247.1−248.6 °C. Anal. Calcd (found) for $C_{15}H_{29}ClP_2Ru$: C, 44.2 (44.2); H, 7.11 (7.31); Cl, 8.70 (8.12); P, 15.2 (14.9); Ru, 24.8 (24.6). IR (cm^{-1}): 1411 (m), 1290 (w), 1274 (w), 1151 (vw), 1075 (s), 1023 (m), 948 (s), 928 (vs), 868 (s), 840 (s), 731 (s), 701 (s), 652 (m), 613 (w), 448 (vw).

Bis(pentamethylcyclopentadienyl)dichlorobis[bis(dimethylphosphino)methane)]diruthenium(II), $Cp^*_2Ru_2(\mu\text{-dmpm})_2Cl_2$, 2. To a slurry of $[Cp^*RuCl]_4$ (2.10 g, 7.75 mmol) in tetrahydrofuran (120 mL) was added a solution of dmpm (1.20 mL, 7.66 mmol) in tetrahydrofuran (60 mL). The solution turned orange immediately, and an orange precipitate began to form. After the mixture had been stirred for 1 h, the precipitate was collected by filtration. Yield: 1.25 g (40%). Mp: 242−244 °C. Anal. Calcd (found) for $C_{30}H_{58}Cl_2P_4Ru_2$: C, 44.2 (44.3); H, 7.11 (7.02); Cl, 8.70 (8.82); P, 15.2 (14.2); Ru, 24.8 (25.2). IR (cm^{-1}): 1300 (w), 1293 (w), 1285 (w), 1137 (vw), 1062 (w), 951 (m), 937 (s), 928 (m), 900 (s), 849 (vw), 797 (m), 723 (s), 677 (w), 618 (m).

(Pentamethylcyclopentadienyl)bis[bis(dimethylphosphino)methane]ruthenium(II) Chloride, $[Cp^*Ru(dmpm)(\eta^1\text{-dmpm})]Cl$, 3. This product was isolated as yellow crystals in low yield by cooling the tetrahydrofuran filtrate obtained in the above reaction to −20 °C.

(Pentamethylcyclopentadienyl)bis[bis(dimethylphosphino)methane]diruthenium(II) Hexachlorodizincate, $[Cp^*Ru(dmpm)(\eta^1\text{-dmpm})]_2[Zn_2Cl_6]$, 3′. To a mixture of $[Cp^*RuCl_2]_2$ (0.61 g, 1.0 mmol) and zinc (0.065 g, 1.0 mmol) in CH_2Cl_2 (25 mL) was added dmpm (0.80 mL, 5.1 mmol). The reaction mixture was stirred at room temperature for 24 h, and then it was filtered to give a light orange solution. The solvent was removed under vacuum to give the product as yellow powder. The crude product can be recrystallized from dichloromethane. Yield: 0.81 g (60%). Anal. Calcd (found) for $C_{30}H_{58}Cl_6P_4Ru_2Zn_2$: C, 35.3 (36.2); H, 6.37 (6.74); Cl, 15.6 (16.6); P, 18.2 (16.5); Ru, 14.9 (13.9); Zn, 9.61 (8.00). The NMR data of **3′** are essentially the same as those of **3**.

(Pentamethylcyclopentadienyl)chloro[bis(diphenylphosphino)methane]ruthenium(II), Cp*Ru(dppm)Cl, 4. To a mixture of $[Cp^*RuCl]_4$ (0.49 g, 0.45 mmol) and bis(diphenylphosphino)methane (0.69 g, 1.80 mmol) was added acetonitrile (60 mL), and the resulting slurry was stirred for 12 h. An orange solution was obtained, and the solvent was removed under vacuum. The residue was extracted with diethyl ether (2 × 80 mL), and the extract was filtered. The filtrate was concentrated to ca. 130 mL and cooled to −20 °C to afford orange crystals. Yield: 0.91 g (71%). Anal. Calcd (found) for $C_{35}H_{37}ClP_2Ru$: C, 64.1 (64.4); H, 5.68 (5.71); Cl, 5.40 (6.13); P, 9.44 (9.11); Ru, 15.4 (13.9). IR (cm^{-1}): 1435 (s), 1302 (vw), 1182 (vw), 1157 (vw), 1094 (m), 1070 (vw), 1025 (m), 1000 (vw), 772 (w), 750 (m), 739 (m), 723 (s), 701 (s), 670 (vw), 652 (vw), 618 (vw), 534 (m), 514 (s), 486 (m), 450 (w).

Bis(pentamethylcyclopentadienyl)di(μ-chloro)(μ-bis(diphenylphosphino)methane)diruthenium(II), $Cp^*_2Ru_2(\mu\text{-dppm})(\mu\text{-Cl})_2$, 5. To a mixture of $[Cp^*RuCl]_4$ (1.70 g, 1.57 mmol) and dppm (1.20 g, 3.13 mmol) was added diethyl ether (140 mL). The resulting dark red solution was stirred at room temperature for 2 h and then filtered. The filtrate was concentrated to ca. 100 mL and cooled to −20 °C to afford dark red crystals. Yield: 2.37 g (82%). Anal. Calcd (found) for $C_{45}H_{52}P_2Cl_2Ru_2$: C, 58.3 (58.5); H, 5.61 (5.72); Cl, 7.65 (7.51); P, 6.69 (6.50); Ru, 21.8 (21.5). IR (cm^{-1}): 2243 (vw), 2211 (vw), 1586 (w), 1572 (w), 1482 (m), 1438 (s), 1308 (vw), 1276 (vw), 1178 (w), 1153 (w), 1091 (s), 1024 (m), 768 (m), 757 (s), 738 (s), 728 (s), 701 (s), 690 (s), 643 (m), 608 (vw), 518 (m), 493 (s), 443 (vw), 430 (vw), 398 (vw).

(Pentamethylcyclopentadienyl)methyl[bis(dimethylphosphino)methane]ruthenium(II), Cp*Ru(dmpm)Me, 6. To a solution of Cp*Ru(dmpm)Cl (0.369 g, 0.91 mmol) in diethyl ether (60 mL) was added dimethylmagnesium (3.4 mL of a 0.27 M solution in diethyl ether, 0.91 mmol). The resulting mixture was stirred at ambient temperature for 24 h to give a pale yellow solution. The solvent was removed under vacuum, and the residue was extracted into pentane (80 mL). The extract was filtered, and the filtrate was concentrated to ca. 10 mL and cooled to −20 °C to afford pale yellow crystals. Yield: 0.28 g (80%). Anal. Calcd (found) for $C_{16}H_{32}P_2Ru$: C, 49.6 (49.6); H, 8.34 (8.32); P, 16.0 (15.8); Ru, 26.1 (25.8). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 88.5 (s, C_5Me_5), 51.9 (t, $^1J_{PC} = 19.1$ Hz, PCH_2), 20.4 ("t", $^1J_{PC} + {}^3J_{PC} = 10.2$ Hz, PMe_2), 14.1 (t, $^1J_{PC} + {}^3J_{PC} = 11.1$ Hz, PMe_2), 11.0 (s, C_5Me_5), −14.6 (br s, RuMe).

(Pentamethylcyclopentadienyl)methyl[bis(diphenylphosphino)methane]ruthenium(II), Cp*Ru(dppm)Me, 7. To a solution of Cp*Ru(dppm)Cl (0.41 g, 0.63 mmol) in diethyl ether (90 mL) was added dimethylmagnesium (0.78 mL of a 0.81 M solution in diethyl ether, 0.63 mmol). The resulting mixture was stirred at ambient temperature overnight to give a yellow slurry. The solvent was removed under vacuum, and the residue was extracted into toluene (2 × 30 mL). The extract was filtered and concentrated to ca. 25 mL. Pentane (30 mL) was added to the filtrate, and the resulting mixture was cooled to −20 °C to afford yellow crystals. Yield: 0.34 g (85%). Anal. Calcd (found) for $C_{36}H_{40}P_2Ru$: C, 68.0 (68.4); H, 6.34 (6.46); P, 9.74 (9.30); Ru, 15.9 (14.0). IR (cm^{-1}): 1585 (vw), 1569 (vw), 1479 (m), 1432 (s), 1377(s), 1303 (vw), 1271 (vw), 1178 (vw), 1155 (vw), 1088 (s), 1024 (m), 998 (vw), 758 (w), 746 (m), 733 (m), 720 (s), 695 (s), 663 (vw), 648 (vw), 613 (vw), 537 (m), 514 (vw).

Bis(pentamethylcyclopentadienyl)bis(η^1-trifluoroacetato)bis[μ-bis(dimethylphosphino)methane]diruthenium(II), $Cp^*_2Ru_2(\mu\text{-dmpm})_2(\eta^1\text{-}O_2CCF_3)_2$, 8. A solution of Cp*Ru(dmpm)Me (0.029 g, 0.075 mmol) in CD_2Cl_2 (0.75 mL) was transferred to a NMR tube and cooled to −78 °C. To the NMR tube was added HO_2CCF_3 (0.007 mL, 0.091 mmol), and the mixture was vigorously shaken to assure

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(63) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161−1164.

thorough mixing of the reagents. The NMR tube was kept at −78 °C for several minutes before it was inserted into the precooled (−80 °C) NMR probe. ^1H and $^{31}P\{^1H\}$ NMR spectra show that Cp*Ru(dmpm)Me reacts with HO_2CCF_3 completely to give $Cp^*_2Ru_2(\mu\text{-dmpm})_2(\eta^1\text{-}O_2CCF_3)_2$, which is only stable below −70 °C.

(Pentamethylcyclopentadienyl)(η^1-trifluoroacetato)[bis(dimethylphosphino)methane]ruthenium(II), Cp*Ru(dmpm)(η^1-O_2CCF_3), 9. When the above solution of $Cp^*_2Ru_2(\mu\text{-dmpm})_2(\eta^1\text{-}O_2CCF_3)_2$ in CD_2Cl_2 was kept at −70 °C, it slowly isomerized to Cp*Ru(dmpm)(η^1-O_2CCF_3). At −40 °C, this transformation was instantaneous.

(Pentamethylcyclopentadienyl)(η^1-trifluoroacetato)[bis(diphenylphosphino)methane]ruthenium(II), Cp*Ru(dppm)(η^1-O_2CCF_3), 10. A solution of Cp*Ru(dppm)Me (0.03 g, 0.048 mmol) in CD_2Cl_2 (0.75 mL) was transferred to a NMR tube and cooled to −78 °C. To the NMR tube was added HO_2CCF_3 (0.01 mL, 0.13 mmol), and the mixture was vigorously shaken to assure thorough mixing of the reagents. The NMR tube was kept at −78 °C for several minutes before it was inserted into the precooled (−80 °C) NMR probe. ^1H and $^{31}P\{^1H\}$ NMR spectra showed that Cp*Ru(dppm)Me reacts with HO_2CCF_3 completely to give Cp*Ru(dppm)(η^1-O_2CCF_3) at −78 °C.

Bis(pentamethylcyclopentadienyl)(μ-η^2,η^2-pentahydridoaluminato)[μ-bis(diphenylphosphino)methane]diruthenium(II), $Cp^*_2Ru_2(\mu\text{-dppm})(AlH_5)$, 11. To a mixture of $Cp^*_2Ru_2(\mu\text{-dppm})Cl_2$ (1.06 g, 1.14 mmol) and $LiAlH_4$ (0.31 g, 8.17 mmol) was added diethyl ether (140 mL). The mixture was stirred at ambient temperature for 4 h and then allowed to settle for 30 min. The mixture was filtered, and the pale yellow filtrate was concentrated to ca. 35 mL and cooled to −20 °C to afford yellow crystals. Yield: 0.89 g (88%). Anal. Calcd (found) for $C_{45}H_{57}AlP_2Ru_2$: C, 60.8 (60.6); H, 6.46 (6.55); Al, 3.03 (2.77). IR (cm^{-1}): 1779 (s), 1728 (s), 1586 (vw), 1439 (w), 1355 (vw), 1307 (vw), 1262 (vw), 1185 (vw), 1156 (vw), 1092 (s), 1069 (w), 1028 (m), 798 (vw), 782 (m), 739 (s), 703 (s), 695 (s), 661 (m), 641 (m).

Bis(pentamethylcyclopentadienyl)(μ-η^2,η^2-pentadeuterioaluminato)[μ-bis(diphenylphosphino)methane]diruthenium(II), $Cp^*_2Ru_2(\mu\text{-dppm})(AlD_5)$, 11-$d_5$. This compound was prepared as for compound **11** except that $LiAlD_4$ was used and the reaction mixture was stirred at room temperature for 48 h to ensure completion of the reaction. IR (cm^{-1}): 1275 (s), 1255 (s), 1185 (vw), 1156 (vw), 1092 (m), 1068 (vw), 1029 (w), 782 (m), 763 (s), 739 (s), 698 (s), 646 (m), 515 (m), 496 (s).

Bis(pentamethylcyclopentadienyl)hexahydrido[μ-bis(diphenylphosphino)ethane]ruthenium(II), $Cp^*_2Ru_2(\mu\text{-dppm})H_6$, 12. To a solution of $Cp^*_2Ru_2(\mu\text{-dppm})(AlH_5)$ (0.147 g, 0.166 mmol) in diethyl ether (30 mL) at −78 °C was added methanol (1.5 mL). The solution turned purplish-red after it had been warmed to ambient temperature and stirred for 1.5 h. The solvent was removed under vacuum, and the residue was extracted into pentane (60 mL). The extract was filtered, and the filtrate was concentrated to ca. 10 mL and cooled to −20 °C to afford light maroon crystals. Yield: 0.06 g (42%). IR (cm^{-1}): 3089 (w), 3078 (w), 1980 (br, s), 1481 (s), 1436 (s), 1358 (w), 1184 (vw), 1155 (vw), 1095 (s), 1088 (m), 1067 (w), 1027 (w), 790 (s), 761 (s), 748 (m), 724 (vs), 705 (m), 692 (s), 650 (w), 520 (m), 510 (m), 500 (m), 450 (br, m).

Crystallographic Studies.[64] Single crystals of $Cp^*_2Ru_2(\mu\text{-dppm})(\mu\text{-}AlH_5)$ **11**, grown from pentane, were mounted on glass fibers using Paratone-N oil (Exxon) and were immediately cooled to −75 °C in a nitrogen stream on the diffractometer. Standard peak search and indexing procedures gave rough cell dimensions, and the diffraction symmetry was verified by examination of the axial photographs. Least-squares refinement using 25 reflections yielded the cell dimensions given in Table 2.

Data were collected in one quadrant of reciprocal space ($-h,+k,\pm l$). Systematic absences for $0k0$ ($k \neq 2n$) and $h0l$ ($l \neq 2n$) were consistent only with the space group $P2_1/c$. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. While corrections for crystal decay were unnecessary, absorption corrections were applied; the maximum and minimum transmission factors were 0.890 and 0.821, respectively. Systematically absent reflections were deleted, and symmetry equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\ \sigma(I)$ were used in the least-squares refinement.

The structure was solved by direct methods (SHELXS-86) and difference Fourier syntheses. The positions of the ruthenium and phosphorus atoms were deduced from an E-map. Subsequent least-squares refinement and difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms H(1)−H(5) surfaced in late difference Fourier maps; owing to high correlations between hydride positional parameters and metal atom variables, however, chemically similar metal−hydrogen bond lengths were constrained to be equal in length. The remaining hydrogen atoms were included in the refinement as fixed contributors in "idealized" positions with C−H = 0.96 Å. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.23/(\sigma(F_o)^2 + (pF_o)^2)$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. In the final cycle of the least-squares refinement, all non-hydrogen atoms were independently refined with anisotropic thermal coefficients and common isotropic thermal parameters were refined for four hydrogen atom groups representing aliphatic and aromatic hydrogens and bridging and terminal metal hydrides. Successful convergence was indicated by the maximum shift/error of 0.051 in the last cycle. Final refinement parameters are given in Table 2. The largest peaks in the final difference Fourier map were in the vicinity of the ruthenium atoms. A final analysis of the variance between observed and calculated structure factors showed a slight dependence on sin θ.

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Supporting Information Available: Tables of full crystallographic details, atomic coordinates including calculated hydrogen atom coordinates, and full bond distances and angles for **11** (11 pages). Ordering information is given on any current masthead page.

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(64) For a description of the crystallographic methods and programs employed, see: Jensen, J. A.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4977−4982.