

Synthesis and Reactions of Cp-Linked Phosphine Complexes of Rhodium

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Received April 6, 1998

The linked Cp ligand $[\text{C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2]^-$ has been used to synthesize several rhodium derivatives. Reaction with $[\text{RhClL}_2]_2$, where $\text{L} = \text{C}_2\text{H}_4$, C_8H_{14} , or CO , gives $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{L})$ complexes, which have been characterized by single-crystal X-ray diffraction. Reaction of the ethylene complex with CO or PMe_3 gives the carbonyl- and phosphine-substituted derivatives, respectively. Irradiation of the ethylene complex in the presence of hydrogen gives a new binuclear polyhydride, also structurally characterized, in which the chelating ligand spans the two metal centers. Reaction of the ethylene complex with iodine leads to the formation of the diiodide $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{RhI}_2$, which in turn can be converted to the dihydride $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{RhH}_2$ by reaction with $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2\text{H}_2$. The reactivity of the dihydride toward C–H bond activation has been investigated. While benzene does not give a stable oxidative addition adduct, pentafluorobenzene yields $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{C}_6\text{F}_5)\text{H}$, which was structurally characterized as its chloro derivative. Reaction of the dihydride with C_6F_6 gives the η^2 complex $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\eta^2\text{-C}_6\text{F}_6)$, also structurally characterized.

Introduction

Since the discovery of ferrocene in 1951 by T. J. Kealy and P. L. Pauson,¹ a wide range of cyclopentadienyl analogues have become available as ligands for organometallic complexes.² Among them, phosphine-substituted cyclopentadienyl anions have been prepared by several methods³ and have been used mainly in the synthesis of both homo-⁴ and heterobimetallic⁵ complexes. Indeed, because of its two different functionalities, these ligands have proven to be particularly efficient at holding two metal centers of a very different nature (for example, early and late transition metals) in close proximity to each other, the goal here being to achieve new and useful reactions with the two metals

operating in concert.⁶ Nevertheless, true examples of reactions involving both metallic sites have remained rare.

If one or several atoms separate the cyclopentadienyl ring from the phosphine group, the ligand can act as a chelate, where the two binding sites are connected to the same metal center. In contrast to the bridging case, only a few examples of this coordination mode can be

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found in the literature.^{3d,h,7} Mathey was the first to observe such a chelate with a carbonyl manganese complex.^{3d} Irradiation was required in order to release CO, allowing the formation of a coordination site for the phosphine. Butenschon used a ligand of this type to isolate some alkyne adducts of cobalt involved in the cyclootrimerization reaction of alkynes.^{7c} Wang has shown that a chelating phosphino-cyclopentadienyl ligand can prevent the loss of phosphine, usually observed under thermal or photochemical conditions, in a carbonyl iron complex.⁷ⁱ Fryzuk^{7e} and Erker^{7j} used the chelating properties of similar ligands to synthesize some otherwise unstable Zr compounds. Quite recently, Bergman reported a chelating phosphino-cyclopentadienyl system in which a *tert*-butyl group on the Cp ring results in the formation of chiral complexes.⁸

Rhodium complexes bearing both a cyclopentadienyl ring and a phosphine have been extensively studied by Jones for the cleavage of C–H,⁹ C–S,¹⁰ C–F,¹¹ and C–C¹² bonds. Nevertheless, one limitation associated with the use of those complexes is their lack of long-term thermal stability. The mode of decomposition usually observed is a loss of phosphine by either the initial rhodium complex or a product, and the free phosphine produced then reacts with the initial Cp*Rh(PR₃) fragment leading to the formation of the unreactive bis-phosphine Cp*Rh(PR₃)₂.

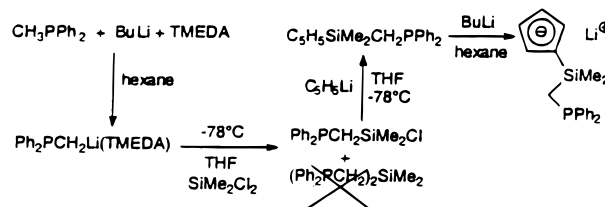
In this paper, we describe the preparation of a new class of thermally stable Rh complexes by working with a tethered phosphine derivative. The ligand employed has been reported in the literature by Schore,^{3e} and we have found that it reacts with [RhClL₂] (L = C₂H₄, CO, or C₈H₁₄) to give mononuclear chelate complexes of the formula (η⁵:η¹-C₅H₄SiMe₂CH₂PPh₂)Rh(L). Similar compounds have already been prepared^{7f} with a CH₂CH₂ link between the Cp and the phosphine ligands, but little was reported of their reactivity. The chiral ligand system investigated by Bergman with the fragment [(η⁵:η¹-3-Bu^tC₅H₃CH₂CH₂PMe₂)Ir] showed diastereotopic selectivity for cyclohexane C–H activation. Here, we report the behavior of these SiMe₂CH₂-linked complexes in several chemical reactions including ligand substitution, reaction with H₂, and C–H bond activation.

Results

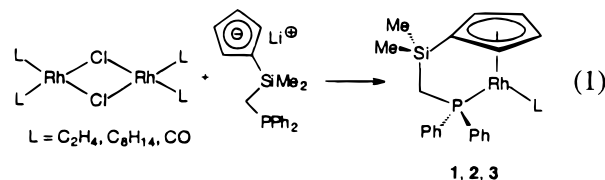
Ligand Synthesis. The ligand Li[C₅H₄SiMe₂CH₂-PPh₂] was prepared by a modification of the method reported by Schore et al. in 1979.⁵ Reaction of Li-(TMEDA)CH₂PPh₂ with neat dimethyldichlorosilane in THF at –78 °C leads to the formation of Ph₂PCH₂SiMe₂-Cl only. Further reaction with LiCp followed by deprotonation with BuLi gives the desired anionic ligand (Scheme 1).

Reaction of the Ligand with Rh Complexes. Reaction of this ligand with [RhCl(C₂H₄)₂]₂ in THF gives

Scheme 1



a new compound, formulated as the mononuclear species (η⁵:η¹-C₅H₄SiMe₂CH₂PPh₂)Rh(C₂H₄) (**1**) (eq 1). The



¹H NMR spectrum of this complex displays a high-field singlet at δ –0.03 for the two SiMe groups, a doublet at δ 2.17 for the PCH₂ group coupled to the phosphorus (*J*_{H–P} = 13.6 Hz), and two multiplets at δ 5.18 and 5.90 for the Cp hydrogens, as well as aromatic multiplets for the phenyl rings. The ethylene hydrogens appear as broad singlets at δ 1.26 and 2.84, indicating slow rotation of the ethylene ligand. The ³¹P NMR spectrum shows a doublet at δ 49.1 with *J*_{Rh–P} = 206 Hz, typical of a CpRh^I phosphine complex.¹³

Complex **1** was also characterized by single-crystal X-ray diffraction (Table 1). **1** crystallizes in triclinic space group *P* $\bar{1}$ with one molecule within the asymmetric unit. The structure (Figure 1) confirms coordination of the cyclopentadienyl ring and the phosphine to a single metal center. The bonding of the ethylene ligand is typical of those for other rhodium–ethylene complexes,^{7f,14} with *d*_{Rh–C} = 2.111(3) and 2.102(3) Å and *d*_{C–C} = 1.399(5) Å. Other distances and angles are listed in Table 2.

The ligand has also been reacted with the cyclooctene dimer, [RhCl(C₈H₁₄)₂]₂, under the same conditions used for preparation of **1** (eq 1). In this case, a mixture of two products was obtained in a ratio of 4:1. The major product exhibits ¹H and ³¹P NMR spectra almost identical to those of **1**, which allowed us to assign it as the cyclooctene analogue of **1**, (η⁵:η¹-C₅H₄SiMe₂CH₂PPh₂)-Rh(C₈H₁₄) (**2**). The ¹H spectrum of the minor product displays a Cp pattern with four different resonances, showing that the complex is not symmetrical. Other ¹H resonances were difficult to identify, obscured by the resonances of **2**. While it was not possible to isolate the minor product, slow evaporation of a solution of the mixture in hexane leads to the formation of crystals of **2**. The X-ray structure (Figure 2) shows again that **2** is mononuclear. The bond distances are almost the same as those for the ethylene adduct, with *d*_{Rh–C} = 2.119(4) and 2.101(4) Å and *d*_{C–C} = 1.421(5) Å. Other distances and angles are given in Table 2.

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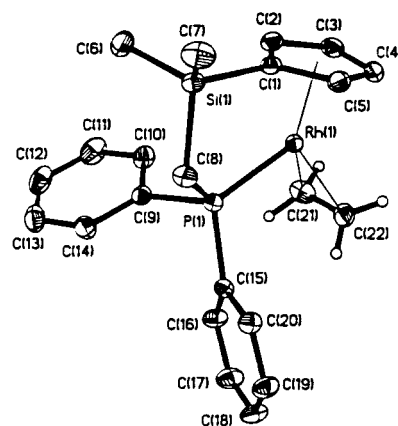
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Table 1. Summary of Crystallographic Data for 1, 2, 3, 7, 8, 9, 11, 14, and 15

	1	2	3	7	8	9	11	14	15
chemical formula	RhSiPC ₂₂ H ₂₆	RhSiPC ₂₃ H ₃₆	RhSiPOC ₂₁ H ₂₂	Rh ₂ Si ₂ P ₂ C ₄₀ H ₄₆	RhSiPI ₂ C ₃₀ H ₂₂	RhSiPIC ₂₆ H ₂₇	RhSiPIC ₂₁ H ₂₅	RhSiPF ₅ C ₂₆ H ₂₂ ·CHCl ₃	RhSiPF ₆ C ₂₆ H ₂₂ ·THF
formula weight	452.41	534.54	452.36	850.71	678.15	628.35	566.28	746.22	678.48
cryst syst	triclinic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic
space group, Z	P1, 2	P1, 4	Pna2 ₁ , 4	P2 ₁ /n, 2	P2 ₁ /n, 4	P2 ₁ /c, 4	P2 ₁ /c	P1, 2	Pbca, 8
a, Å	8.943(2)	9.6128(1)	10.8949(2)	12.0882(3)	9.2390(1)	11.3429(1)	7.5458(2)	8.2849(1)	12.0080(1)
b, Å	10.310(4)	16.0784(2)	11.9047(1)	11.2970(2)	14.6931(1)	13.7424(2)	17.0122(3)	11.7582(2)	18.5208(2)
c, Å	13.090(7)	17.2024(2)	15.6615(2)	13.7332(3)	16.4789(2)	15.7780(2)	16.8141(3)	16.2695(2)	26.1889(2)
α, deg	107.73(4)	98.314(1)	90	90	90	90	90	109.088(1)	90
β, deg	96.09(3)	93.302(1)	90	97.846(1)	98.366(1)	96.598(0)	94.927(1)	99.664(1)	90
γ, deg	111.60(3)	95.521(1)	203.130(5)	1857.85(7)	2213.20(4)	2443.16(5)	2150.46(8)	1472.36(4)	5824.35(9)
vol, Å ³	1035.8(10)	2611.72(5)	2031.30(5)	80	50	90	80	80	80
temp, °C	−40	−80	−80	−80	−50	−90	−80	−80	−80
ρ _{calc} , g cm ^{−3}	1.45	1.359	1.479	1.521	2.035	1.708	1.749	1.683	1.547
no. of data collected	3886	15 325	11 673	10 613	13 696	14 967	12 335	9111	12 279
no. of unique data	3628	10 845	4687	4272	5134	5757	4899	6416	3995
no. of obsd data (I > 2σ(I))	3418	8214	4132	3349	4708	5053	3670	5679	3037
no. of params varied	330	559	228	212	229	271	229	354	361
R ₁ (F _o), wR ₂ (F _o ²), (I > 2σ(I))	0.0249 ^a	0.0493, 0.0890	0.0312, 0.0548	0.0415, 0.0684	0.0237, 0.0523	0.0242, 0.0517	0.0507, 0.0947	0.0315, 0.0784	0.0564, 0.0880
R ₁ (F _o), wR ₂ (F _o ²), all data	0.0331 ^a	0.0750, 0.0980	0.0388, 0.0574	0.0650, 0.0754	0.0282, 0.0549	0.0317, 0.0543	0.0803, 0.1044	0.0376, 0.0816	0.0909, 0.0976
goodness of fit	2.02 ^a	1.02	1.067	1.053	1.086	1.037	1.073	1.025	1.122

^a R, R_w based on F_o as defined in ref 21.**Figure 1.** ORTEP drawing of ($\eta^5:\eta^1$ -C₅H₄SiMe₂CH₂PPh₂)-Rh(C₂H₄), **1**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms (except on ethylene) have been omitted for clarity.

Following an identical procedure, it was also possible to prepare the CO adduct ($\eta^5:\eta^1$ -C₅H₄SiMe₂CH₂PPh₂)-Rh(CO) (**3**) by reacting [RhCl(CO)₂]₂ with the bidentate ligand (eq 1). In this case, a single product was clearly obtained. **3** has been identified by its ¹H and ³¹P NMR spectra, displaying nearly identical features to those of **1** and **2**. The ¹H NMR spectrum of **3** displays a singlet at δ −0.08 for the two methyl groups on the silicon, a doublet at δ 2.12 for the PCH₂ group, two broad singlets at δ 5.62 and 5.72 for the Cp protons, and aromatic resonances between δ 7 and 8. A doublet is observed in the ³¹P spectrum at δ 45.31 with $J_{\text{Rh-P}} = 199$ Hz. The IR spectrum of **3** in THF solution exhibits a peak at 1937 cm^{−1}, as expected for a CO ligand attached to Rh^I.

Layering a solution of **3** in THF with hexane allowed growth of X-ray quality single crystals. The structure of **3** (Figure 3) shows again that the bidentate ligand chelates to a single metal center. The bond distance between the carbonyl group and the rhodium atom (1.811(4) Å) is identical to that found in the nonchelating rhodium carbonyl analogues.¹⁵

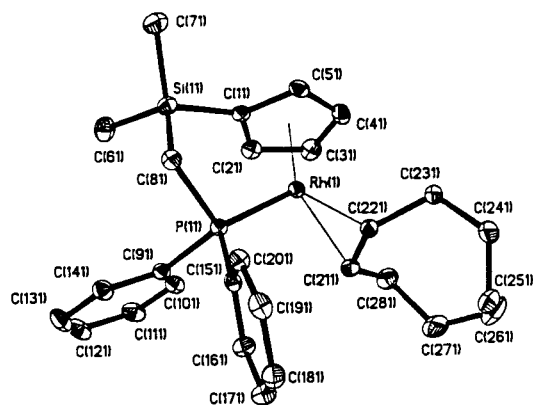
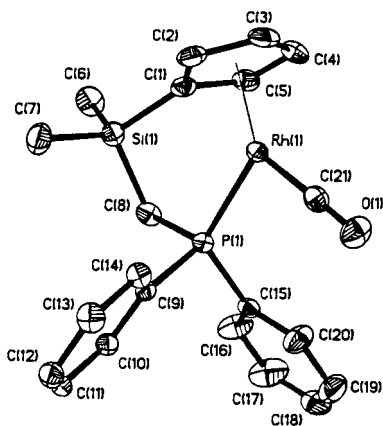
Crystal structures of nonchelating analogues of **1** and **3** have been previously reported.^{14,15} Consequently, an interesting comparison can be made of the structural changes induced by the chelating ligand. In general, the differences are small and the major effect (as already noticed by Poilblanc et al.^{7f}) involves a decrease of the angle Cp-Rh-P due to chelation. In the case of the CO adduct, this angle is 134.8° in CpRh(PPh₃)(CO),^{15a} compared to 124.4° in **3**. For the ethylene adduct, the values are 133.9° in CpRh(PPh₃)(C₂H₄)^{14b} and 126.6° in **1**. The ligand used by Poilblanc et al., where the phosphine is linked to the cyclopentadienyl ring through an ethylene moiety, causes a greater change since the angle Cp-Rh-P in the similar ethylene adduct is equal to 118.5°. This difference can be attributed to the fact that the Cp-C-C-P bond distance is smaller than the Cp-Si-C-P bond distance. In both cases, however, the chelate ligand leaves the opposite side of the Rh atom wide open for coordination. From this point of view, investigating the reactivity of the new complexes ap-

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Table 2. Selected Distances (Å) and Angles (deg) for [Rh]L₁L₂ ([Rh] = (η^5 : η^1 -C₅H₄SiMe₂CH₂PPh₂)Rh)

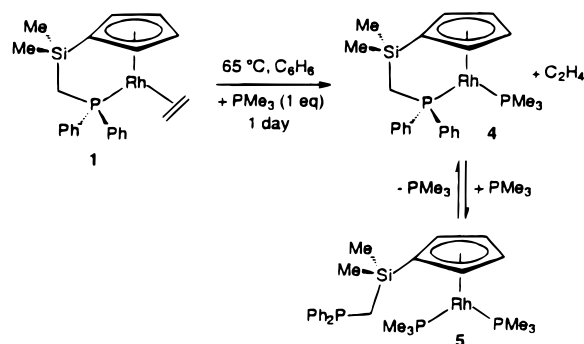
compound	L ₁	L ₂	d _{Rh-P}	d _{Rh-L1}	d _{Rh-L2}	Cp-Rh-L ₁	Cp-Rh-L ₂	Cp-Rh-P
[Rh](C ₂ H ₄) (1)	C ₂₁	C ₂₂	2.195	2.111	2.102	139.0 ^a		126.6
[Rh](COE) ^b (2)	C ₂₁	C ₂₂	2.201	2.119	2.101	141.1 ^a		124.3
			2.201	2.116	2.122	140.3 ^a		
[Rh](CO) (3)	C ₂₁		2.236	1.811		141.3		125.8
[Rh] ₂ (μ -H) ₂ (5)	H	H	2.215	1.649 ^c	2.836 ^d	127.0	129.1	124.4
[Rh]I ₂ (8)	I ₁	I ₂	2.289	2.664	2.677	126.5	122.1	130.1
[Rh](Ph)I (9)	C ₂₁	I ₁	2.255	2.070	2.668	120.8	125.1	121.8
[Rh](Me)I (11)	C ₂₁	I ₁	2.251	2.270	2.668	120.5	127.3	123.2
[Rh](C ₆ F ₅)Cl (14)	C ₂₁	I ₁	2.292	2.076	2.398	121.9	127.9	121.6
[Rh](C ₆ F ₆) (15)	C ₂₁	C ₂₆	2.264	2.057	2.051	140.8 ^a		122.2

^a Angle between Cp and olefin centroids. ^b Two molecules per asymmetric unit. ^c d_{Rh-H}. ^d d_{Rh-Rh}.

**Figure 2.** ORTEP drawing of (η^5 : η^1 -C₅H₄SiMe₂CH₂PPh₂)Rh(C₂H₄), **2**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.**Figure 3.** ORTEP drawing of (η^5 : η^1 -C₅H₄SiMe₂CH₂PPh₂)Rh(CO), **3**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

peared attractive, in addition to determining any increase in stability brought about by the chelating ligand.

Ligand Substitutions. Basic ligand substitution reactions were first examined to test the reactivity of the new complexes. **1** reacts with PMe₃ upon heating at 65 °C. If 1 equiv of PMe₃ is used, complete conversion of **1** into a new product (**4**) occurs after about 1 day. The ³¹P NMR spectrum of **4** displays two doublets of doublets, one for each phosphine ligand with both Rh-P and P-P couplings. The Rh-P coupling constants for the PPh₂ and PMe₃ ligands of 225 and 210 Hz, respectively, are consistent with a Rh^I complex.⁹ The P-P coupling is smaller, 56 Hz. In the ¹H NMR spectrum, formation of free ethylene (singlet at δ 5.24) can be monitored over the course of the reaction. The bound PMe₃ appears as a doublet of doublets due to couplings

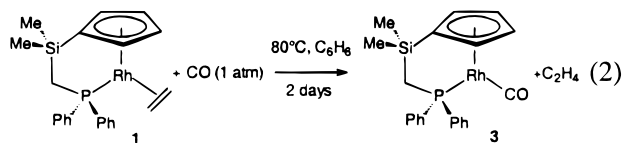
Scheme 2

with the P (J_{H-P} = 8.8 Hz) and the Rh (J_{H-Rh} = 1 Hz). The NMR data are consistent with **4** being the PMe₃ adduct (η^5 : η^1 -C₅H₄SiMe₂CH₂PPh₂)Rh(PMe₃) (Scheme 2). If 5 equiv of PMe₃ is used, the disappearance of **1** is about 7 times faster. This effect of the PMe₃ concentration on the rate of reaction suggests that the ligand substitution occurs by way of an associative mechanism, as already observed in the case of CpRh(CO)₂ by Basolo et al.¹⁶ Moreover, the use of an excess of PMe₃ (5 equiv) leads to the formation of a mixture of **4** and another product **5** in a ratio of 9:1. The ³¹P spectrum of **5** exhibits a doublet at δ -2.30 (J = 214 Hz) in a region corresponding to PMe₃ bound to the metal and a singlet at δ -20.6, consistent with noncoordinated diphenyl phosphine. In the ¹H NMR spectrum, the protons of the PMe₃ ligands appear as an AX₉A'X'₉ multiplet¹⁷ at δ 1.135 ($J_{H-P} + J_{H-P'} = 9.2$ Hz). These NMR data provide strong evidence that **5** is the bis(trimethylphosphine) complex (η^5 -C₅H₄SiMe₂CH₂PPh₂)Rh(PMe₃)₂, where the chelating phosphine has been displaced by PMe₃ and is now dangling away from the metal (Scheme 2). Addition of more PMe₃ to the mixture leads to the production of more **5**, and removal of the excess phosphine under vacuum allows the complete reversion of **5** into **4**. The facile reversibility of the reaction can be attributed to the chelating ability of the ligand. That is, if one side of the chelating ligand is easily displaced, the diphenylphosphine linked to the cyclopentadienyl ring stays in proximity to the metal center and can coordinate back to the metal, regenerating the initial rhodium complex.

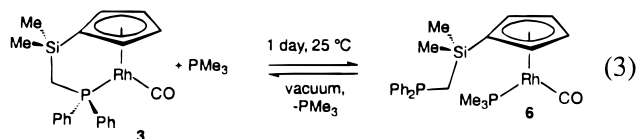
Under 1 atm of CO, **1** can be completely converted into **3** after 2 days at 80 °C in benzene (eq 2). No intermediate has been observed by NMR spectroscopy during the course of the reaction.

(16) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657-1663.

(17) Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics* **1983**, *2*, 535-538.



The reaction of the CO adduct **3** with PMe_3 has also been examined. In the presence of 2 equiv of PMe_3 in benzene at room temperature, 60% of **3** was converted, surprisingly not into **4** but into a new compound (**6**) displaying the following NMR spectral features. In the ^1H NMR spectrum, resonances are observed at δ 0.26 (s, 6 H), 1.04 (dd, $J_1 = 10$, 1.6 Hz, 9 H), 1.63 (s, 2 H), 5.05 (br s, 2 H), and 5.28 (br s, 2 H), as well as aromatic resonances that were difficult to assign due to overlap with the resonances of the starting material. In the ^{31}P NMR spectrum, a doublet was observed at δ 1.18 ($J = 187$ Hz) along with a singlet at δ -21.00. These NMR data provide strong evidence for the formulation of **6** as $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{PMe}_3)(\text{CO})$, where the phosphine of the chelating ligand has been again displaced by PMe_3 (eq 3). After a few days, small



amounts of **4** start to appear together with another unidentified compound of the following type $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{-SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{X})$ while **6** is still the major product. Neither running the reaction at higher temperature nor under irradiation allowed the clean formation of the expected product, **4**. Upon removal of PMe_3 under vacuum, **6** is almost completely converted into **3**, implicating an equilibrium in this transformation (eq 3), as already seen with **4** and **5**.

These first experiments demonstrate that the chelate effect can be easily overcome since reactions with only a slight excess of PMe_3 under mild conditions led to a loss of chelation. Nevertheless, if the excess of PMe_3 was removed, the chelate complex quantitatively reformed, a behavior that would not necessarily be observed in the case of a nonchelating ligand.

Reaction of 1 with H_2 . No reaction was observed between **1** and H_2 (1 atm) upon heating overnight at 100 °C in THF. When the same solution was irradiated under 1 atm of H_2 , the appearance of ethane and of a new hydride resonance can be monitored by NMR spectroscopy after 1 day. Independent experiments show that no reaction occurs between **1** and the solvent (THF or benzene) upon irradiation. The ^1H NMR spectrum of the hydride complex appears as a triplet of triplets at δ -12.91 with $J = 22.4$ and 15.0 Hz, a singlet at δ -0.07 (SiMe_2), a doublet at δ 2.17 with $J = 12.4$ Hz (CH_2), and two broad singlets at δ 3.61 and 5.46 (C_5H_4). Further irradiation leads to the decrease of this hydride complex and to the growth of a new one (**7**) exhibiting the same pattern of resonances, a triplet of triplets at δ -13.00 ($J = 22.6$, 15 Hz) (Figure 4), together with a singlet at δ -0.13, a doublet at δ 1.90 ($J = 14.4$ Hz), two broad singlets at δ 4.53 and 4.73, and two multiplets for the aromatic resonances at δ 7.29–7.37 and 7.67–7.74. Over the course of the

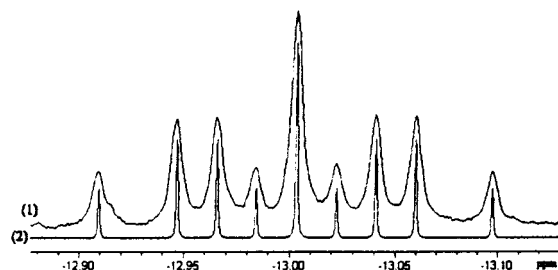


Figure 4. (1) ^1H NMR spectrum of **7** in the hydride region. (2) Simulated spectrum with the following values for the coupling constants $J_1 = 22.6$ Hz, $J_2 = 15$ Hz.

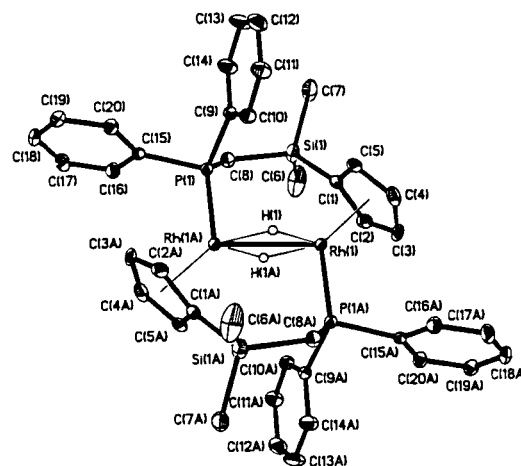
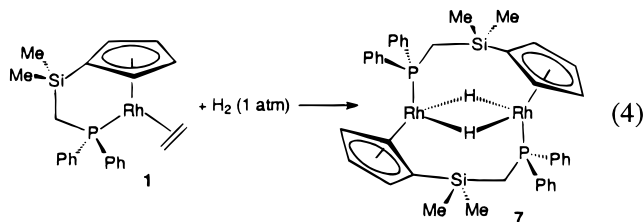


Figure 5. ORTEP drawing of $[(\eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\mu\text{-H})_2]$, **7**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms (except hydrides) have been omitted for clarity.

reaction, the brown solution gradually turns black, with the concomitant growth of small amounts of unidentified species. After 5 days of irradiation, the reaction nears completion as only 4% of the starting material is still present in the solution. The major product is the second hydride complex **7**, which accounts for 48% of the starting material, but small traces of the first hydride complex can still be observed (eq 4). In benzene solvent,



the photochemical reaction leads to the same major product but was more complicated by the fact that two other nonhydride-containing products could be observed. Nevertheless, crystals of the hydride complex **7** formed from the crude benzene solution upon standing for a few days.

7 crystallizes in monoclinic space group $P2_1/n$. The structure (Figure 5) shows that **7** is a dimer containing two bridging hydrides, $[(\eta\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\mu\text{-H})_2]$. The two metal centers are also connected by the initially chelating ligands. **7** lies on a crystallographic center of symmetry, rendering the two phosphines and the two rhodium centers magnetically equivalent, thereby giving rise to the triplet of triplets for the hydride

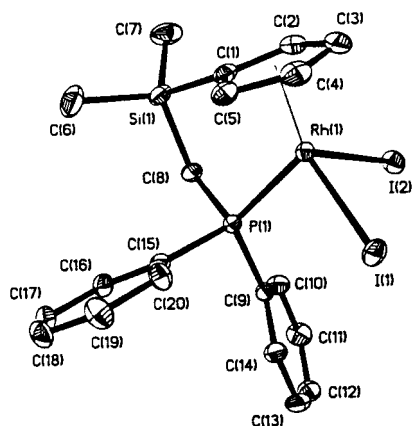
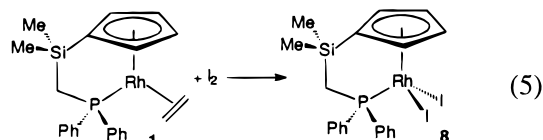


Figure 6. ORTEP drawing of $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{-RhI}_2$, **8**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

resonances observed in the ^1H NMR spectrum. Assignment of the coupling constants was accomplished through a $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of **7**, which shows a triplet due to residual coupling to two equivalent rhodiums with $J = 22.6$ Hz. In this complex, the formal oxidation state of the rhodium is $+2$,¹⁸ consistent with the intermediate value of the coupling constant in the ^{31}P spectrum, $J_{\text{P-Rh}} = 187$ Hz. No broadening of the NMR resonances of **7** is observed, however, due to the presence of a Rh–Rh bond, with $d(\text{Rh}–\text{Rh}) = 2.8357(5)$ Å. The long-term instability of **7** has precluded its isolation in sufficient quantities for elemental analysis. On the basis of the structure obtained for **7**, the first hydride product appearing in the photochemical reaction of **1** with H_2 could also be a Rh(II) bridging hydride dimer in which the ligands $\text{Li}[\text{C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2]$ are still chelating to a single metal center, rather than bridging two metal centers. Unfortunately, the extensive decomposition that accompanies the photochemical reaction does not allow us to conclude definitively whether this first hydride is an intermediate in the formation of **7**.

Because of the difficulties in isolating **7**, its reactivity has only been briefly explored. Under 1 atm of C_2H_4 , a small fraction of **7** ($\sim 40\%$) is converted back into the ethylene complex **1** after 7 days at 80°C . The reaction of **7** with CO is much cleaner since complete conversion of **7** into **3** is obtained after 3 days at 65°C . Several intermediates appeared during the course of the reaction, and among them, a new hydride complex was observed exhibiting a doublet of doublets at $\delta -13.08$ ($J_1 = 36.0$ Hz, $J_2 = 27.0$ Hz), which does not correspond to the resonances for the dihydride rhodium complex $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{RhH}_2$.

Synthesis of Rh(III) Complexes. The reaction of **1** with iodine leads to the formation of $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{RhI}_2$, **8** (eq 5). The ^{31}P NMR spectrum of **8**



shows a doublet at higher field ($\delta 23.1$, $J_{\text{P-Rh}} = 137$ Hz), consistent with the formation of a Rh^{III} compound.⁹ Compound **8** was characterized structurally (Figure 6),

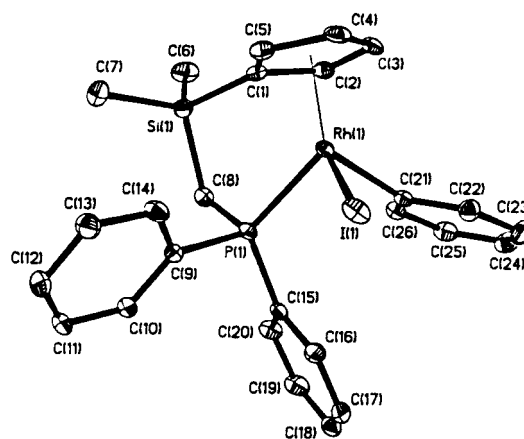
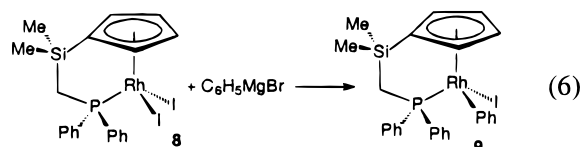


Figure 7. ORTEP drawing of $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{-Rh(Ph)I}$, **9**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

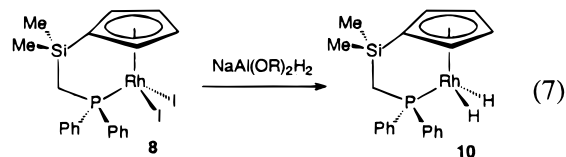
with the complex crystallizing in space group $P2_1/n$ with one molecule in the asymmetric unit. Selected distances and angles are given in Table 2.

Compound **8** appears to be synthetically useful since reaction with Grignard or lithium reagents allows for the formation of alkyl or aryl halide compounds of the general formula $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh(R)I}$ with R = an aryl or alkyl group. For example, the phenyl iodide complex $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh(C}_6\text{H}_5\text{)I}$ (**9**) has been synthesized by the reaction **8** with $\text{C}_6\text{H}_5\text{MgBr}$ (eq 6). Since the rhodium atom is bound to four



different substituents, loss of C_s symmetry occurs, and the ^1H NMR spectrum of **9** now exhibits two singlets at $\delta -0.04$ and 0.25 for the two $\text{Si}(\text{Me})_2$ groups and four multiplets at $\delta 5.26$, 5.60 , 5.63 , and 6.34 for the protons of the Cp ring. No change is observed for the resonances of the $\text{P}(\text{CH}_2)$ group, which still appears as a doublet. X-ray quality crystals of **9** have been obtained by layering a solution in CH_2Cl_2 with hexane. The X-ray structure confirms the formulation of **9** as the phenyl iodide product (Figure 7).

8 also reacts with hydride reagents. An unidentified paramagnetic compound is formed with Super-Hydride (LiEt_3H). Reaction of 4 equiv of Red-Al ($\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2\text{H}_2$) with **8** in THF leads to the formation of the dihydride compound $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{RhH}_2$ (**10**) (eq 7). The hydride resonance appears as a



doublet of doublets at $\delta -13.38$ ($J_{\text{H-P}} = 26.2$ Hz, $J_{\text{H-Rh}} = 30.8$ Hz) in the ^1H NMR spectrum. The ^{31}P spectrum shows a doublet at $\delta 55.3$ with $J_{\text{P-Rh}} = 172$ Hz. This

(18) For a review on Rh(II) complexes, see: Felthouse, T. M. *Prog. Inorg. Chem.* **1982**, 29, 73–166.

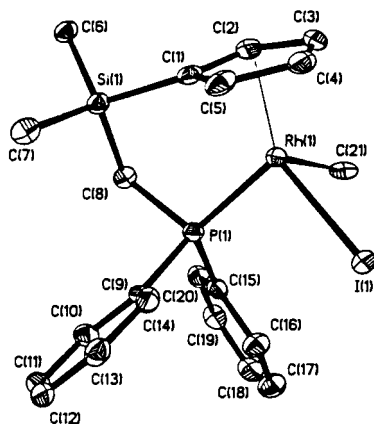
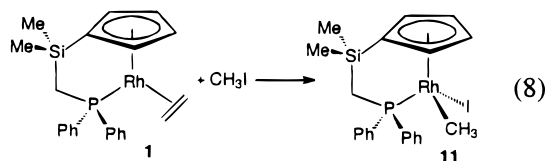


Figure 8. ORTEP drawing of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{-Rh}(\text{CH}_3)\text{I}$, **11**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

dihydride rhodium compound is very air sensitive but can be stored in THF solution under an inert atmosphere for several days without showing any sign of decomposition. Purification of **10** by column chromatography can be performed under inert conditions but was not efficient enough to give a sample suitable for elemental analysis. An attempted synthesis of **10** by reaction of the diiodide in THF with Na/Hg in the presence of H_2 was unsuccessful as it leads to an unidentified paramagnetic compound.

Werner¹⁹ has shown that nonchelated analogues of **1** react with CH_3I in THF to form the methyl iodide rhodium compound by oxidative addition in the C–X bond. By analogy, complete conversion of **1** into the methyl iodide compound, $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{-Rh}(\text{CH}_3)\text{I}$ (**11**), was obtained upon refluxing a solution of **1** in THF in the presence of 6 equiv of CH_3I for 7 h (eq 8). Crystals of **11** were obtained by layering a CH_2Cl_2



solution with hexane, and the structure of **11** was determined by X-ray crystallography (Figure 8). Similar reactions run with aryl halides did not lead to a clean oxidative addition of the C–X bond. Warming a solution of **1** at 120 °C in THF in the presence of 10 equiv of $\text{C}_6\text{H}_5\text{Cl}$ led only to decomposition. With $\text{C}_6\text{H}_5\text{Br}$ (10 equiv), at 75 °C in THF, **1** was converted into the dibromide complex after 2 days.

Aromatic C–H Bond Activation. Other cyclopentadienylrhodium ethylene complexes²⁰ have been used as precursors of reactive 16-electron Rh(I) fragments by photochemical dissociation of ethylene. These fragments can react with C–H bonds of alkanes or arenes to form an aryl- or alkyl hydride product. **1** absorbs light over the entire near-UV region to ~450 nm. As

mentioned above, the photolysis of **1** in benzene (380 nm band-pass filter) for 3 days did not result in the formation of the phenyl hydride complex $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{-SiMe}_2\text{CH}_2\text{PPh}_2)\text{-Rh}(\text{Ph})\text{H}$ and no change was observed in the starting material. Nor was there a thermal reaction of **1** with benzene at temperatures up to 80 °C. The independent synthesis of the phenyl hydride complex was, therefore, attempted in order to determine the stability of this complex.

The addition of AgPF_6 to a solution of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{-SiMe}_2\text{CH}_2\text{PPh}_2)\text{-Rh}(\text{Ph})\text{I}$ (**9**) in THF led to the formation of a new compound (**12**) exhibiting resonances in the ^1H NMR spectrum at δ 0.06 (s, 3 H) and 0.33 (s, 3 H) for the two SiMe groups, δ 2.75 (t, 1 H) and 3.19 (s, 1 H) for the PCH_2 group, and δ 4.88, 5.85, 6.26, and 6.49 (br s, 1 H each) for the Cp hydrogens, as well as aromatic multiplets for the phenyl rings. A doublet at δ 37.8 ($J_{\text{P-Rh}} = 162$ Hz) can be observed in the ^{31}P NMR spectrum. These NMR data are consistent with **12** being formulated as $[(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{-Rh}(\text{Ph})\text{-(THF)}](\text{PF}_6)$. Replacement of the THF solvent by benzene led to the decomposition of **12**, indicating that the THF ligand is labile. Since THF is only weakly bound to the metal, it was thought that **12** might react with hydride reagents at low temperature to form the aryl hydride complex.²¹ Addition of Red-Al to a solution of **12** in THF at –70 °C in an NMR tube led to an immediate change of color from orange to brown black. An NMR spectrum of the sample, maintained at –60 °C, did not show a resonance corresponding to a hydride but did show a singlet at δ 7.23 which can be attributed to benzene. This experiment indicates that the phenyl hydride rhodium compound, if it was formed as an intermediate, is unstable even at –60 °C. Consequently, the absence of a reaction between **1** and C_6H_6 upon photolysis should be expected, as the phenyl hydride product is likely to be unstable. Alternatively, oxidative addition might occur to form the unstable phenyl hydride compound, but this product immediately undergoes reductive elimination to regenerate **1**. Evidence to this effect was obtained by examination of arenes containing electron-withdrawing substituents.

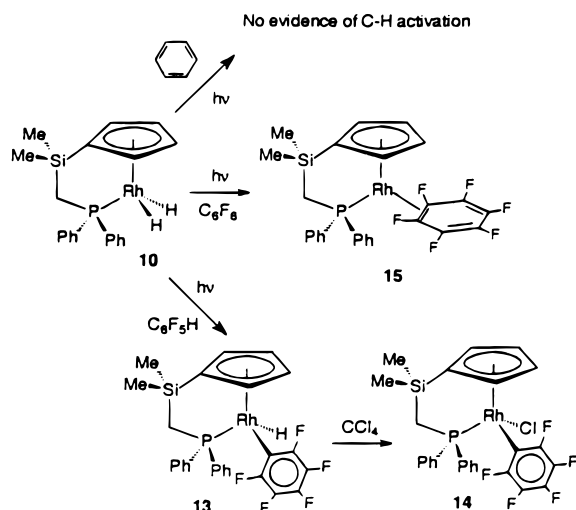
The formation of a Rh(III) hydride compound was observed by NMR spectroscopy upon irradiation of **1** in neat $\text{C}_6\text{F}_5\text{H}$. The reaction was very slow, and the total consumption of **1** required a week of photolysis and was accompanied by substantial decomposition. In contrast to the ethylene adduct, the dihydride compound (**10**) loses hydrogen more quickly upon photolysis. The same reaction performed with **10** instead of **1** went to completion after 7 h and led to the same hydride species (**13**). The ^1H NMR spectrum of **13** exhibits a doublet of doublets at δ –11.04 for the hydride, two singlets for the inequivalent SiMe₂ groups, two doublets of doublets at δ 2.75 and 3.08 for the CH_2 group, four multiplets for the Cp group, and three multiplets for the PPh_2 groups. Addition of CCl_4 to **13** led to its complete conversion to the air-stable chloride derivative $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{-Rh}(\text{Cl})(\text{C}_6\text{F}_5)$ (**14**) (Scheme 3). The ^1H NMR spectrum of **14** is similar to that observed for other alkyl or aryl halide complexes. The ^{31}P spectrum appears as a doublet of triplets. In contrast to **13**, the

(19) Werner, H.; Feser, R. *J. Organomet. Chem.* **1982**, 232, 351–370.

(20) (a) Belt, S. T.; Duckett, S. B.; Helliwell, M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1989**, 928–930. (b) Belt, S. T.; Helliwell, M.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, 115, 1429–1440. (c) Selmezy, A. D.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *Organometallics* **1994**, 13, 522–532.

(21) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, 106, 1650–1663.

Scheme 3



phosphorus of **14** is coupled to both fluorine atoms. Crystals of **14** have been obtained by layering a solution of **14** in CHCl_3 with hexane. A single-crystal X-ray structure is shown in Figure 9.

It has been shown that formation of an η^2 adduct is the first step in the oxidative addition of arenes to $\text{Cp}^*\text{Rh}(\text{PMe}_3)_3$.⁹ These labile complexes have been isolated by use of an aromatic compound containing no C–H bonds, such as perfluorobenzene. Irradiation of **1** in neat C_6F_6 led to the formation of a new Rh complex **15**, formulated as the $\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2\text{Rh}(\eta^2\text{-C}_6\text{F}_6)$. Here again, the reaction was very slow and required more than 1 week to go to completion. **15** was obtained more quickly starting from the dihydride complex (**10**) as only a few hours of irradiation is necessary for complete conversion of the starting material. The ^1H NMR spectrum of **15** displays a singlet at δ 0.05 for the equivalent SiMe_2 groups, a doublet at δ 2.57 for the methylene group, two broad singlets for the Cp ring, and aromatic multiplets for the diphenylphosphine. The ^{31}P spectrum of **15** appears as a doublet of triplets since the phosphorus is coupled to the rhodium and to two equivalent fluorines. Three multiplets can be observed in the ^{19}F NMR spectrum, each corresponding to the two fluorines in the ortho, meta, and para positions relative to the metal. A single-crystal X-ray structure of **15** is shown in Figure 10. The most noticeable feature of this structure is that the two fluorines in the proximity of the metal bend strongly away from the aromatic plane (38°). The angle between the $\text{Rh}\text{--}\text{C}_{21}\text{--}\text{C}_{26}$ plane and the aromatic plane is 109.6° . The ring and the remaining fluorines are planar. The reactions of arenes with the $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}$ fragment are summarized in Scheme 3.

Conclusion

This paper describes the synthesis and interconversions of a series of cyclopentadienyl complexes with attached phosphine ligands. The studies show that despite the intramolecular advantage of phosphine coordination, external ligands can displace the chelating PPh_2 group reversibly. In one case, a binuclear product is formed by way of the Cp–phosphine ligand bridging

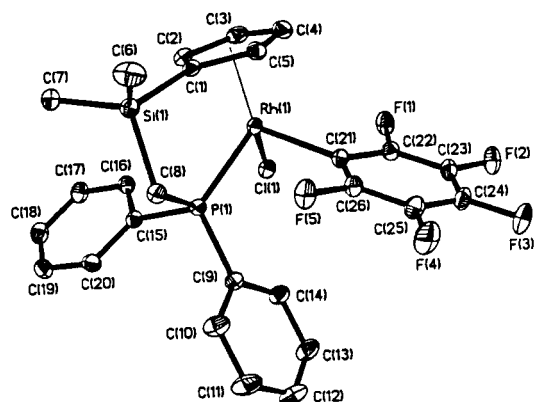


Figure 9. ORTEP drawing of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{C}_6\text{F}_5)\text{Cl}$, **14**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

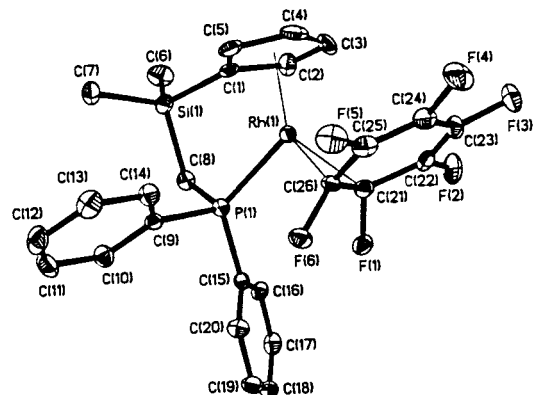


Figure 10. ORTEP drawing of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\eta^2\text{-C}_6\text{F}_6)$, **15**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

two metal centers. The unsaturated fragment $[(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}]$ does not form a stable oxidative addition adduct with benzene, but the electron-deficient arene $\text{C}_6\text{F}_5\text{H}$ does produce a stable product. An η^2 -arene complex is formed with hexafluorobenzene.

Experimental Section

General. All reactions, recrystallizations, chromatography, and routine manipulations, unless otherwise noted, were carried out at ambient temperature under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corp. Dri-Lab. All hydrocarbon solvents were distilled under nitrogen or vacuum from dark purple solutions of sodium benzophenone ketyl. Chlorinated solvents were distilled under vacuum from calcium hydride suspensions. Silica gel (200–400 mesh, 60 Å) for column chromatography was purchased from Aldrich Chemical Co. and dried under vacuum at 200°C . Silica gel plates (2 mm) used in preparative thin-layer chromatography contained a fluorescent indicator and were purchased from Analtech. $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$,²² $[\text{RhCl}(\text{COD})]_2$,²³ and $[\text{RhCl}(\text{CO})_2]_2$ ²² were prepared according to literature methods. Organic chemicals were purchased from Aldrich Chemical Co.

^1H (400 MHz) and ^{31}P (160 MHz) NMR spectra were recorded on a Bruker AMX-400 spectrometer. ^{19}F NMR spectra were recorded on a Varian 500 NMR spectrometer. All

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chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced to the chemical shifts of residual solvent resonances (C_6D_6 , δ 7.15; THF, δ 2.58). ^{19}F NMR spectra were referenced to external $\text{C}_6\text{H}_5\text{CF}_3$ (δ 0.00 with downfield chemical shifts taken to be positive). ^{31}P NMR spectra were referenced to external 30% H_3PO_4 (δ 0.0). Elemental analyses were performed by Desert Analytics. Infrared spectra were recorded by a Mattson Instruments 6020 Galaxy Series FTIR and processed with FirstAquire v1.52 software. Photolysis experiments were performed using a 200 W Hg(Xe) arc lamp (Oriol). A Siemens SMART CCD area detector diffractometer equipped with an LT-2 low-temperature unit or an Enraf-Nonius CAD4 was used for X-ray crystal structure determination.

Preparation of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{C}_2\text{H}_4)$, **1.** A 1.653 g amount of $\text{LiC}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2$ (5.05 mmol) was dissolved in 10 mL of dry THF. To this solution, a solution of 0.979 g of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (2.52 mmol) in 40 mL THF was added slowly. After the mixture was stirred for 1 h, the solvent was removed under vacuum. The residue was extracted with hexane (3×25 mL), and the solvent was removed from the combined extracts under vacuum, leaving 1.334 g (2.951 mmol) of a brown powder (**1**). Yield: 59%. For **1**: ^1H NMR (C_6D_6) δ -0.03 (s, 6 H), 1.26 (bs, 2 H), 2.17 (d, $J_{\text{H-P}} = 13.6$ Hz, 2 H), 2.84 (bs, 2 H), 5.18 (m, 2 H), 5.90 (m, 2 H), 6.99–7.08 (m, 6 H), 7.52–7.59 (m, 4 H); ^{31}P NMR (C_6D_6) δ 49.08 (d, $J_{\text{Rh-P}} = 206$ Hz). Anal. Calcd (found) for $\text{C}_{22}\text{H}_{26}\text{PRhSi}$: 58.41 (58.36) C, 5.79 (5.75) H.

Preparation of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{C}_6\text{H}_{14})$, **2.** A 0.154 g amount of $[\text{RhCl}(\text{C}_6\text{H}_{14})_2]_2$ (0.215 mmol) was reacted with 0.141 g of $\text{LiC}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2$ (0.431 mmol) using the same procedure as for **1**. A 0.204 g amount of a mixture was obtained containing 80% of **2** and 20% of an unidentified product. For **2**: ^1H NMR (THF- d_6) δ 0.01 (s, 6 H), 1.00–1.80 (m, 14 H), 2.38 (dd, $J_{\text{H-P}} = 13.6$ Hz, $J_{\text{H-Rh}} = 1.0$ Hz, 2 H), 4.99 (bs, 2 H), 5.64 (bs, 2 H), 7.29–7.34 (m, 6 H), 7.55–7.63 (m, 4 H); ^{31}P NMR (THF- d_6) δ 51.28 (d, $J_{\text{Rh-P}} = 210$ Hz). Anal. Calcd (found) for $\text{C}_{28}\text{H}_{36}\text{SiPRh}$: 62.92 (62.96) C, 6.74 (7.33) H. For the minor product, only some of the resonances could be observed: ^1H NMR (THF- d_6) δ -0.096 (s, 3 H), 0.197 (s, 3 H), 2.45 (d, $J_{\text{H-P}} = 12.8$ Hz, 1 H), 4.32 (bs, 1 H), 5.12 (bs, 1 H), 5.31 (bs, 1 H), 5.75 (bs, 1 H), 7.03–7.23 (m, 6 H), 7.38–7.50 (m, 4 H). ^{31}P NMR (THF- d_6) δ 51.28 (d, $J_{\text{Rh-P}} = 210$ Hz).

Preparation of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{CO})$, **3.** A 0.276 g amount of $[\text{RhCl}(\text{CO})_2]_2$ (0.708 mmol) was reacted with 0.494 g of $\text{LiC}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2$ (1.507 mmol) using the same procedure as for **1**. A 0.457 g amount of **3** (1.011 mmol) was obtained. Yield: 71%. ^1H NMR (C_6D_6): δ -0.08 (s, 6 H), 2.12 (d, $J_{\text{H-P}} = 13.6$ Hz, 2 H), 5.62 (bs, 2 H), 5.72 (m, 2 H), 6.97–7.07 (m, 6 H), 7.72–7.79 (m, 4 H). ^{31}P NMR (THF- d_6): δ 45.31 (d, $J_{\text{Rh-P}} = 199$ Hz). Anal. Calcd (found) for $\text{C}_{21}\text{H}_{22}\text{OPRhSi}$: 55.76 (55.38) C, 4.90 (4.32) H. IR (THF): 1937 cm^{-1} .

Preparation of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{PMe}_3)$, **4.** Under inert atmosphere, 34.7 mg of **1** (0.0768 mmol) was dissolved in 1 mL of C_6D_6 . The solution was placed in an NMR tube equipped with a Teflon seal, and 8 μL of PMe_3 (0.0773 mmol) was added. The NMR tube was heated at 65 $^\circ\text{C}$, and the reaction was monitored by ^1H and ^{31}P NMR spectroscopy. Clean and quantitative conversion to **4** was observed after about 1 day. The product was isolated by removal of the solvent under vacuum. For **4**: ^1H NMR (C_6D_6) δ -0.01 (s, 6 H), 0.87 (dd, $J_{\text{H-P}} = 8.8$ Hz, $J_{\text{H-Rh}} = 1$ Hz, 9 H), 2.38 (d, $J_{\text{H-P}} = 12.8$ Hz, 2 H), 5.47 (bs, 2 H), 6.10 (bs, 2 H), 7.00–7.19 (m, 6 H), 7.84–7.94 (m, 4 H); ^{31}P NMR (C_6D_6) δ 50.1 (dd, $J_{\text{P-Rh}} = 225$, $J_{\text{P-P}} = 57$ Hz), -2.84 (dd, $J_{\text{P-Rh}} = 211$ Hz, $J_{\text{P-P}} = 57$ Hz). Anal. Calcd (found) for $\text{C}_{23}\text{H}_{31}\text{P}_2\text{RhSi}$: 55.20 (54.89) C, 6.24 (6.00) H.

Preparation of $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{PMe}_3)_2$, **5.** Under inert atmosphere, 37 mg of **1** (0.0819 mmol) was dissolved in 1 mL of C_6D_6 and placed in a resealable NMR tube together with 42 μL of PMe_3 (0.406 mmol). The NMR

tube was heated in an oil bath at 65 $^\circ\text{C}$, and the reaction was monitored by NMR spectroscopy. After about 6 h, the reaction had gone to completion, giving a mixture composed of 90% of **4** and 10% of **5**. **5**, which is not stable in the absence of excess PMe_3 , has not been isolated. For **5**: ^1H NMR (C_6D_6) δ 0.29 (s, 6 H), 1.13 (m $\text{AX}_9\text{A}'\text{X}_9$, $J_{\text{H-P}} + J_{\text{H-P}'} = 9.2$ Hz, 18 H), 1.70 (s, 2 H), 4.72 (bs, 2 H), 5.54 (bs, 2 H), 7.52–7.58 (m, 4 H), other aromatic resonances obscured by those of **4**; ^{31}P NMR (C_6D_6) δ -2.30 (d, $J_{\text{Rh-P}} = 214$ Hz, 2 P), -20.6 (s, 1 P).

Reaction of **1 with CO.** A 10.5 mg (0.023 mmol) amount of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{C}_2\text{H}_4)$ (**1**) was dissolved in 1 mL of C_6D_6 in an NMR tube equipped with a Teflon seal. The solution was freeze–pump–thaw degassed 3 times, and 1 atm of CO was placed over the solution on a vacuum line. After 2 days of heating at 80 $^\circ\text{C}$, **1** had been quantitatively converted to $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{CO})$ (**3**), as determined by NMR spectroscopy. The product was isolated by removal of solvent under vacuum.

Reaction of **3 with PMe_3 .** A 3.3 μL (0.032 mmol) amount of PMe_3 was added to 6.8 mg (0.015 mmol) of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{CO})$ (**3**) dissolved in 1 mL of C_6D_6 . The reaction was monitored by ^1H and ^{31}P NMR spectroscopy over the next 6 days at room temperature. After 40 min, 60% of the starting material had been converted into $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{PMe}_3)(\text{CO})$ (**6**). For **6**: ^1H NMR (C_6D_6) δ 0.26 (s, 6 H), 1.04 (dd, $J_{\text{H-P}} = 10$ Hz, $J_{\text{H-Rh}} = 1.6$ Hz, 9 H), 1.63 (s, 2 H), 5.05 (m, 2 H), 5.28 (m, 2 H), 7.50–7.56 (m, 4 H), other aromatic resonances obscured by those of **3**; ^{31}P NMR (C_6D_6) δ 1.18 (d, $J_{\text{P-Rh}} = 187$ Hz, 1 P), -21.0 (s, 1 P). After 6 days, the composition of the obtained mixture was **3**, 25%; **6**, 55%; **4**, 5%; unidentified product, 15%.

Reaction of **1 with H_2 .** A 14.6 mg (0.032 mmol) amount of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{C}_2\text{H}_4)$ (**1**) was dissolved in 1 mL of THF- d_8 and placed in an NMR tube equipped with a Teflon seal. The solution was freeze–pump–thaw degassed 3 times, and the solution was placed under 1 atm of H_2 . The solution was then irradiated using a 200 W Xe–Hg lamp, and the changes were followed by NMR spectroscopy. After 5 days, 48% (determined by NMR) of **1** had been converted into the bridging hydride dimer $[(\mu\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\mu\text{-H})]_2$ (**7**). For **7**: ^1H NMR (THF- d_8) δ -13.00 (tt, $J_{\text{H-P}} = 15.0$ Hz, $J_{\text{H-Rh}} = 22.6$ Hz, 2 H), -0.13 (s, 12 H), 1.90 (d, $J_{\text{H-P}} = 14.4$ Hz, 4 H), 4.53 (bs, 4 H), 4.73 (bs, 4 H), 7.29–7.37 (m, 12 H), 7.67–7.74 (m, 8 H); ^{31}P NMR (THF- d_8) δ 44.9 (d, $J_{\text{P-Rh}} = 187$ Hz). The instability of **7** combined with its low yield prevented obtaining satisfactory elemental analysis.

Preparation of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{RhI}_2$, **8.** Under inert atmosphere, 76 mg of **1** (0.168 mmol) was dissolved in 25 mL of dry, olefin-free hexanes. A 43 mg amount of I_2 (0.169 mmol) in about 2 mL of dry diethyl ether was slowly added to the Rh solution at room temperature. A brown precipitate formed immediately, the solution was filtered in air, and the solid product was washed with ether and hexanes. Yield: 133 mg, 79%. For **8**: ^1H NMR (CDCl_3) δ 0.10 (s, 6 H), 2.98 (d, $J = 15.6$ Hz, 2 H), 5.67 (s, 2 H), 6.78 (m, 2 H), 7.33–7.40 (m, 6 H), 7.75–7.82 (m, 4 H); ^{31}P NMR (CDCl_3) δ 23.1 (d, $J = 137$ Hz). Anal. Calcd (found) for $\text{C}_{20}\text{H}_{22}\text{I}_2\text{PRhSi}$: 35.42 (35.14) C, 3.27 (3.29) H.

Preparation of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{C}_6\text{H}_5)\text{I}$, **9.** A 51 mg amount of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{RhI}_2$ (**8**) (0.075 mmol) was dissolved in 20 mL of dry THF and cooled to -40 $^\circ\text{C}$. A 0.04 mL amount of a solution of $\text{C}_6\text{H}_5\text{MgBr}$ (2 M in THF, 0.08 mmol) was added with stirring over 0.5 h, and the solution was allowed to warm to room temperature. The brown solution turned red as the solution warmed. The excess Grignard reagent was quenched with 0.1 mL of a saturated solution of NH_4Cl , the solution filtered in air, and the solvent removed. The remaining solid was passed through a short column of Al_2O_3 with CH_2Cl_2 as the eluent. A 39 mg amount of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{C}_6\text{H}_5)\text{I}$, **9**, was obtained after removal of solvent (62% yield). For **9**: ^1H NMR (CDCl_3) δ

−0.04 (s, 3 H), 0.25 (s, 3 H), 2.81 (d, $J = 14.8$ Hz, 2 H), 5.26 (bs, 1 H), 5.60 (bs, 1 H), 5.63 (bs, 1 H), 6.34 (bs, 1 H), 6.63–6.75 (m, 3 H), 7.07–7.22 (m, 3 H), 7.30–7.45 (m, 5 H), 7.55–7.60 (m, 2 H), 7.73–7.82 (m, 2 H); ^{31}P NMR (CDCl_3) δ 34.14 (d, $J = 154$ Hz). Anal. Calcd (found) for $\text{C}_{26}\text{H}_{27}\text{IPrRhSi}$: 49.70 (49.52) C, 4.33 (4.43) H.

Preparation of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{RhH}_2$, **10.** A 107 mg amount of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{RhI}_2$ (**8**) (0.158 mmol) was dissolved in dry THF under inert atmosphere. A 0.2 mL amount of a solution of Red-Al in toluene (65 wt %, 0.621 mmol) was added. The mixture was stirred for 10 min, and the solvent was removed under vacuum. The remaining solids were dissolved in 1 mL of a THF/hexane mixture (1:5) and passed through a SiO_2 column using the same solvent mixture as the eluent. Removal of the solvent under vacuum gave 51 mg (76% yield) of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{RhH}_2$ as a slightly impure oil. For **10**: ^1H NMR ($\text{THF}-d_6$) δ −13.38 (dd, $J_{\text{H-P}} = 26.2$ Hz, $J_{\text{H-Rh}} = 30.8$ Hz, 2 H), 0.09 (s, 6 H), 2.66 (d, $J_{\text{H-P}} = 14.4$ Hz, 2 H), 5.40 (m, 2 H), 5.53 (m, 2 H), 7.26–7.31 (m, 6 H), 7.71–7.78 (m, 4 H); ^{31}P NMR (THF) δ 55.3 (d, $J_{\text{P-Rh}} = 172$ Hz).

Preparation of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{CH}_3)\text{I}$, **11.** In a round-bottom flask, 62 mg of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{-Rh}(\text{C}_2\text{H}_4)$ (**1**) (0.137 mmol) was dissolved in 10 mL THF. A 50 μL sample of CH_3I (0.803 mmol) was added, and the mixture was stirred for 7 h under reflux. The solvent was removed, and the remaining solid was passed through an Al_2O_3 column using CH_2Cl_2 as the eluent. A 60 mg amount of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{CH}_3)\text{I}$ (**11**) was obtained following removal of the solvent (yield: 77%). For **11**: ^1H NMR ($\text{THF}-d_6$) δ −0.21 (s, 3 H), 0.34 (s, 3 H), 1.01 (dd, $J = 6.8$, 2.4 Hz, 3 H), 2.63 (t, $J = 13.6$ Hz, 1 H), 2.73 (ddd, $J = 20.4$, 14.8, 2 Hz, 1 H), 5.14 (bs, 1 H), 5.45 (bs, 1 H), 5.53 (bs, 1 H), 6.18 (bs, 1 H), 7.26–7.43 (m, 6 H), 7.57–7.63 (m, 2 H), 8.05–8.12 (m, 2 H); ^{31}P NMR ($\text{THF}-d_6$) δ 40.51 (d, $J_{\text{P-Rh}} = 160$ Hz). Anal. Calcd (found) for $\text{C}_{21}\text{H}_{25}\text{IPrRhSi}$: 44.52 (44.50) C, 4.42 (4.60) H.

Preparation of $[(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{C}_6\text{H}_5)](\text{THF})(\text{PF}_6)$, **12, and Reaction with Red-Al.** In a resealable NMR tube, 8.6 mg of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{C}_6\text{H}_5)$ (**7**) (0.0137 mmol) was dissolved in dry $\text{THF}-d_6$. A 3.5 mg amount of AgPF_6 (0.0138 mmol) was added, and the solution was filtered. For **12**: ^1H NMR ($\text{THF}-d_6$) δ 0.06 (s, 3 H), 0.33 (s, 3 H), 2.75 (t, $J = 16$ Hz, 1 H), 3.19 (t, $J = 14.8$ Hz, 1 H), 4.88 (bs, 1 H), 5.85 (bs, 1 H), 6.26 (bs, 1 H), 6.49 (bs, 1 H), 6.73–7.62 (m, 15 H); ^{31}P NMR ($\text{THF}-d_6$) δ 37.79 (d, $J_{\text{P-Rh}} = 162$ Hz). The solution was frozen in liquid N_2 , and 5 μL of Red-Al ($\text{NaH}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2$) was added. The mixture was warmed to -70 °C and rapidly shaken before being introduced into the NMR probe, which had previously been cooled to -60 °C. NMR spectra were recorded as the temperature of the probe was gradually increased to ambient temperature, showing the changes described in the text.

Preparation of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{H})(\text{C}_6\text{F}_5)$ (13**) and $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{Cl})(\text{C}_6\text{F}_5)$ (**14**).** In a resealable NMR tube, 75 mg of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{-Rh}(\text{H})_2$ (**10**) (0.176 mmol) was dissolved in neat $\text{C}_6\text{F}_5\text{H}$. The solution was irradiated with a 200 W Hg/Xe lamp for 7 h. The solvent was removed under vacuum, leaving a brown powder. The yield of the pentafluorophenyl hydride complex $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{H})(\text{C}_6\text{F}_5)$ (**13**) was determined by integration of the NMR resonances relative to an internal reference (hexamethylbenzene). Yield: 48%. For **13**: ^1H NMR (THF) δ −11.04 (dd, $J_{\text{H-P}} = 20$ Hz, $J_{\text{H-Rh}} = 30.8$ Hz, 1 H), −0.181 (s, 3 H), 0.468 (s, 3 H), 2.75 (dd, $J = 13.6$, 8.4 Hz, 1 H), 3.08 (dd, $J = 13.6$, 13.6 Hz, 1 H), 5.25 (m, 1 H), 5.64 (m, 1 H), 5.75 (m, 1 H), 5.88 (m, 1 H), 6.96–7.06 (m, 4 H), 7.35–7.48 (m, 4 H), 7.91–8.04 (m, 2 H); ^{31}P NMR (THF) δ 54.3 (d, $J_{\text{P-Rh}} = 154$ Hz). Addition of 50 μL of CCl_4 (0.517 mmol) to the solution of **13** in THF led quantitatively to the immediate formation of the chloro derivative $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{-Rh}(\text{Cl})(\text{C}_6\text{F}_5)$ (**14**). Purification of **14** was accomplished by

column chromatography on silica with CH_2Cl_2 as the eluent followed by recrystallization from CHCl_3 layered with hexanes. For **14**: ^1H NMR ($\text{THF}-d_6$) −0.047 (s, 3 H), 0.421 (s, 3 H), 2.86 (ddd, $J = 17.6$, 13.6, 2.4 Hz, 1 H), 3.06 (dd, $J = 13.6$, 13.6 Hz, 1 H), 4.94 (m, 1 H), 5.76 (m, 1 H), 5.97 (m, 1 H), 6.35 (m, 1 H), 7.10–7.38 (m, 6 H), 7.67–7.74 (m, 2 H), 8.03–8.10 (m, 2 H); ^{31}P NMR ($\text{THF}-d_6$) δ 34.3 (dt, $J_{\text{P-Rh}} = 154$ Hz, $J_{\text{P-F}} = 9.7$ Hz); ^{19}F NMR (C_6D_6) δ 93.5 (m, 2 F_{ortho}), 36.9 (m, 1 F_{para}), 33.6 (bs, 2 F_{meta}). Anal. Calcd (found) for $\text{C}_{26}\text{H}_{22}\text{ClF}_5\text{PrRhSi}$: 49.80 (49.59) C, 3.51 (3.21) H.

Preparation of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{C}_6\text{F}_6)$, (15**).** In a resealable NMR tube, 41 mg of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{-PPh}_2)\text{Rh}(\text{H})_2$ (**10**) (0.0962 mmol) was dissolved in neat C_6F_6 . The solution was irradiated for 7 h using a 200 W Hg/Xe lamp, and the solvent was removed under vacuum, leaving a brown powder. The product was recrystallized from a mixture of THF/hexane (1:99) at -40 °C. The yield of formation of the hexafluorobenzene complex $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\eta^2\text{-C}_6\text{F}_6)$ (**15**) was determined by NMR spectroscopy using hexamethylbenzene as an internal reference (93%). For **15**: ^1H NMR ($\text{THF}-d_6$) δ 0.05 (s, 6 H), 2.57 (d, $J = 13.6$ Hz, 2 H), 4.64 (bs, 2 H), 5.88 (bs, 2 H), 7.31–7.39 (m, 6 H), 7.70–7.78 (m, 4 H); ^{31}P NMR ($\text{THF}-d_6$) δ 45.4 (dt, $J_{\text{P-Rh}} = 200$ Hz, $J_{\text{P-F}} = 54.4$ Hz); ^{19}F NMR ($\text{THF}-d_6$) δ 53.3 (m, 2 F), 40.8 (m, 2 F), 26.1 (m, 2 F). Anal. Calcd (found) for $\text{C}_{26}\text{H}_{22}\text{F}_6\text{PrRhSi}$: 51.15 (51.16) C, 3.61 (3.61) H.

X-ray Structural Determination of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{-SiMe}_2\text{CH}_2\text{PPh}_2)\text{Rh}(\text{C}_2\text{H}_4)$, **1.** Crystals of $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{SiMe}_2\text{-CH}_2\text{PPh}_2)\text{Rh}(\text{C}_2\text{H}_4)$ were grown by slow evaporation from hexane. An orange prism of approximate dimensions $0.37 \times 0.52 \times 0.60$ mm was mounted on a glass fiber using epoxy and placed in a cold nitrogen stream at -40 °C on the diffractometer. Lattice constants were obtained from 25 centered reflections with values of χ between 5° and 70° on an Enraf-Nonius CAD4 diffractometer. Cell reduction revealed a triclinic crystal system. Data were collected at -40 °C in accord with the parameters found in Table 1. The intensities of three representative reflections, which were measured after every 60 min of X-ray exposure time, remained constant throughout the data collection, indicating crystal and electronic stability. The Molecular Structure Corp. TEXSAN analysis software package was used for data reduction, solution, and refinement. The space group was assigned as $P\bar{1}$ on the basis of intensity statistics. A Patterson map solution of the structure was used to locate the rhodium atom. The structure was expanded with the DIRDIF program to reveal all non-hydrogen atoms. An absorption correction was applied using the program DIFABS following isotropic refinement. Anisotropic refinement of all non-hydrogen atoms allowed for the use of a difference Fourier map for the location of the hydrogen atoms, whose coordinates and isotropic thermal parameters were subsequently refined. Full-matrix least-squares refinement of all atoms (on F) was executed until convergence was achieved, with $R_1 = 0.0249$ and $R_w = 0.0331$.²⁴ Fractional coordinates and thermal parameters are given in the Supporting Information.

X-ray Structural Determinations of **2, **3**, **7**, **8**, **9**, **11**, **14**, and **15**.** Single crystals of each compound were mounted under Paratone-8277 on glass fibers and immediately placed in a cold nitrogen stream at -50 to -90 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD area detector system equipped with a normal focus molybdenum-target X-ray tube operated at 1.5 kW (50 kV, 30 mA) for **8** and 2.0 kW (50 kV, 40 mA) for the remaining crystals. A total of 1321 frames of data (1.3

(24) Using the TEXSAN package, $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2} / \sum w|F_o|^2$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{-1/2}$ for a non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o , f' , and f'' : Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 30 s/frame using a detector-to-crystal distance of 5.09 cm (maximum 2θ angle of 56.54°) for all of the crystals except **3** (5 s/frame), **8** (10 s/frame), and **15** (60 s/frame). The total data collection time was approximately 6 h for 10 s/frame exposures and 13 h for 30 s/frame exposures. Frames were integrated with the Siemens SAINT program to 0.75 \AA for all of the data sets. The unit cell parameters for all of the crystals were based upon the least-squares refinement of three-dimensional centroids of >5000 reflections.²⁵ Data were corrected for absorption using the program SADABS.²⁶ Space group assignments were made on the basis of systematic absences and intensity statistics by using the XPREP program (Siemens, SHELXTL 5.04). The structures were solved by using direct methods and refined by full-matrix least-squares on F^2 .²⁷ For all of the structures (except as noted below), the non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogens were included in idealized positions, giving data:parameter ratios greater than 10:1. The Rh-bound hydride in **7** was

(25) It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10 times the listed value.

(26) The SADABS program is based on the method of Blessing, see: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.

(27) Using the SHELX95 package, $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$, $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [F_o^0(\text{Maximum of } 0 \text{ or } F_c^2) + (1 - f)F_c^2]$.

located from the difference Fourier map, and the positional and isotropic thermal parameters were refined. There was nothing unusual about the solution or refinement of any of the structures, with the exceptions of **2**, **7**, **14**, and **15**. Compound **2** crystallized with two independent molecules within the asymmetric unit. Compound **7** was found to lie on a center of symmetry, so that only one-half of the dimer was unique. Complex **14** crystallized along with one molecule of chloroform, and complex **15** crystallized along with one molecule of THF. Further experimental details of the X-ray diffraction studies are provided in Table 1. Positional parameters for all atoms, anisotropic thermal parameters, all bond lengths and angles, as well as fixed hydrogen positional parameters are given in the Supporting Information for all of the structures.

Acknowledgment is made to the U.S. Department of Energy, Grant No. FG02-86ER13569, for their support of this work.

Supporting Information Available: Tables of positional parameters for all atoms, anisotropic thermal parameters, all bond lengths and angles, and fixed hydrogen positional parameters for **1–3**, **7–9**, **11**, **14**, and **15** (58 pages). Ordering information is given on any masthead page.

OM980263Q