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Novel Dirhodium Complexes Derived from Phosphaalkynes

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Phosphaalkynes, P≡CR (R = Bu^t, 1-adamantyl), react rapidly with the dirhodium compound $[Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C{\equiv}CCF_3)]$, affording the η^4: η^1 mono(phosphacyclobutadienyl) complexes $[Rh(\eta^5\text{-}C_5H_5)\{\mu\text{-}\eta^4{:}\eta^1\text{-}PC_3R(CF_3)_2\}\{Rh(CO)(\eta^5\text{-}C_5H_5)\}]$ (R = Bu^t, Ad). Reaction of one of these complexes (R = Bu^t) with $[W(CO)_5(THF)]$ leads to the novel, crystallographically characterized "flyover" compound $[Rh_2(\eta^5\text{-}C_5H_5)_2\{\mu\text{-}(1,2,4\text{-}\eta){:}\ (1,3,4\text{-}\eta)\text{-}PC_3Bu^t(CF_3)_2\}\{W(CO)_5\}]$. Both react with $[Fe_2(CO)_9]$, affording the dirhodium phosphacyclobutenyl complexes $[Rh_2(\eta^5\text{-}C_5H_5)_2(CO)\{\mu\text{-}\eta^1{:}\eta^3\text{-}PC_3R(CF_3)_2\}\{Fe(CO)_4\}]$ (R = Bu^t, Ad). Spectroscopic analysis suggests the last two complexes exist in two isomeric forms in solution. One complex (R = Ad) has been characterized by an X-ray diffraction study.

Introduction

The coordination chemistry of phosphaalkynes (P≡CR) is of considerable interest and has been reviewed extensively.[1] A particular feature of these compounds is their ability to undergo facile cyclization reactions within the coordination sphere of transition metals, and in this respect their behavior is similar to that of alkynes.[2] Via this route, many metal-coordinated phosphorus-containing heterocycles have been prepared, e.g. 1,2- and 1,3-diphosphacyclobutadienes[3,4] and 1,3,5-triphospha-2,4,6-tri-*tert*-butylbenzene.[5,6] In contrast, however, cyclooligomerization reactions between phosphaalkynes and other unsaturated systems (alkynes for example) are comparatively rare. Indeed, there are only a limited number of mono(phosphacyclobutadiene) complexes known, e.g. $[Co(\eta^5\text{-}C_5H_5)\{\eta^4\text{-}PC(Bu^t)C_2(SiMe_3)_2\}]$[7] and $[Rh(\eta^5\text{-}C_5H_5)\{\eta^4\text{-}PC(R)C_2Ph_2\}]$ (R = Bu^t, $NPr^i\text{-}SiMe_3$).[8] More recently, Johnson, Nixon, and co-workers have reported the coupling between phosphaalkynes and acetylenes in the coordination sphere of transition-metal carbonyl clusters.[9,10] To expand on this area, we have studied the reactivity of phosphaalkynes with the dimeric rhodium complex $[Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C{\equiv}CCF_3)]$ (**1**). This system was chosen because of its well-documented reactivity toward alkynes in which the products critically depend on the nature of the alkyne (Scheme 1).[11] Pentanedione complexes are favored with alkyl-substituted alkynes, whereas metallacyclopentadiene complexes are preferred for more polar alkynes. In this paper we report on the reactivity of phosphaalkynes with **1** and discuss the unusual reactivity of the products with some metal carbonyls.

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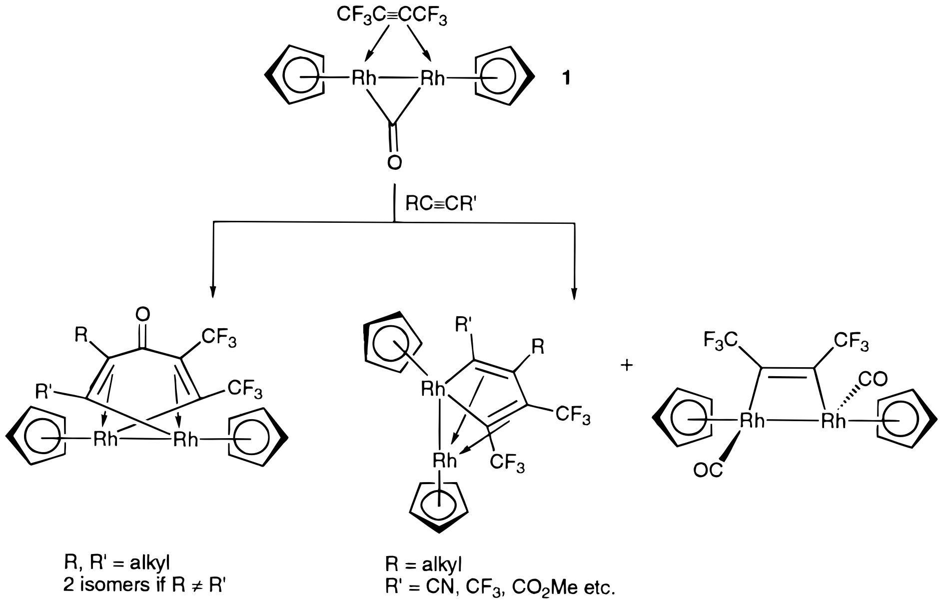
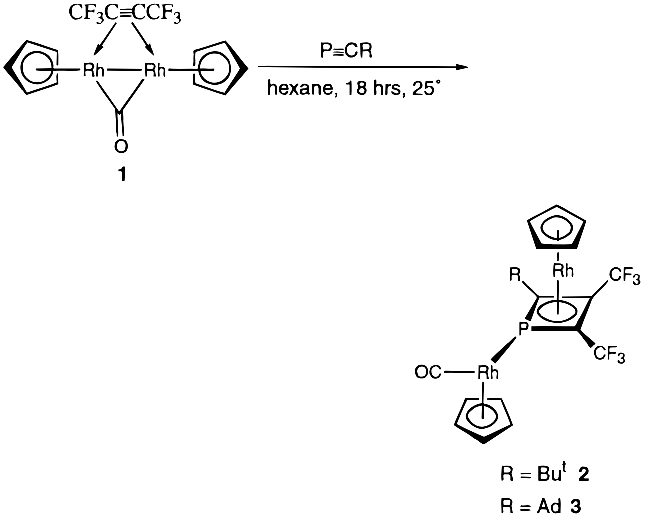
10.1021/om990516v CCC: $18.00

Scheme 1



Scheme 2



Results and Discussion

Treatment of the dimeric rhodium complex [$Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C{\equiv}CCF_3)$] (**1**) with the phosphaalkynes P≡CR (R = Bu^t, 1-adamantyl (Ad)) in hexane at −20 °C followed by warming to room temperature afforded the red air- and moisture-stable complexes **2** and **3**, respectively (Scheme 2), which were purified by recrystallization and isolated in ca. 50% yield. Both **2** and **3** were characterized by multinuclear NMR spectroscopy, mass spectrometry, and infrared spectroscopy. Additionally, the solid-state structure of **2** was determined by a single-crystal X-ray diffraction study. The spectroscopic data for **2** and **3** indicate that they are isostructural. Moreover, the NMR spectroscopic data for **2** are consistent with it retaining its solid-state structure in solution.

The ^{31}P NMR spectrum of complex **2** consists of a doublet of doublets of quartets centered at 23.5 ppm. The two large couplings of 251 Hz and 42.9 Hz can be assigned respectively to the σ and π one-bond interactions with the rhodium centers. The former coupling is in the same range as those seen for other one-bond interactions between an sp^2-hybridized phosphorus and a rhodium center, e.g. 218.5 Hz in the phosphaalkene complex [$Rh(\eta^1\text{-}MesP{=}CPh_2)Cl(PPh_3)_2$].[12] Similarly, the latter coupling is comparable with the $^1J_{P-Rh}$ couplings seen in other systems containing a phosphacyclobutadiene unit η^4 bound to a $Rh(\eta^5\text{-}C_5H_5)$ moiety, e.g. 37.3 Hz in [$Rh(\eta^5\text{-}C_5H_5)\{\eta^4\text{-}PC(Bu^t)C_2Ph_2\}$].[8] The resolution of the doublet of doublets into individual quartets is due to the coupling between the phosphorus and the proximate CF$_3$ group ($^3J_{PF}$ = 7.6 Hz). There is also evidence for a further coupling, but this is not clearly resolved, and it presumably arises from the $^4J_{PF}$ interaction of the phosphorus center with the more distant of the two CF$_3$ groups. These observations are reflected in the ^{19}F NMR spectrum, which shows two poorly resolved multiplets, namely a quartet at −52.6 ppm ($^5J_{FF}$ = 5.6 Hz) and a pseudo quintet at −54.0 ppm ($J \approx 6$ Hz). A further spectroscopic feature of interest is the resonance for the carbon of the terminal CO group at 195 ppm in the ^{13}C NMR spectrum. Both $^2J_{PC}$ and $^1J_{RhC}$ couplings of 32 and 83 Hz, respectively, are clearly visible. The latter coupling is in the range normally seen for one-bond interactions between a rhodium center and a terminal CO group (ca. 55−85 Hz).[13]

The solid-state structure of complex **2** is shown in Figure 1 with salient bond distances and angles collected in Table 1. The η^4-phosphacyclobutadiene ring is essentially planar and contains delocalized carbon−phosphorus and carbon−carbon bonds. The phosphorus−carbon bond lengths of the ring (P(1)−C(1) = 1.806(6) Å, P(1)−C(3) = 1.789(7) Å) are longer than expected for carbon−phosphorus double bonds (ca. 1.67 Å)[14] but shorter than typical phosphorus−carbon single bonds (ca. 1.85 Å).[14] Similarly, the carbon−carbon bond lengths (C(1)−C(2) = 1.459(9) Å, C(2)−C(3) = 1.456(8) Å) are shorter than expected for carbon−carbon single bonds (cf. C(1)−C(5) = 1.522(9) Å) but longer than expected

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[14] See ref 1d, p 96.

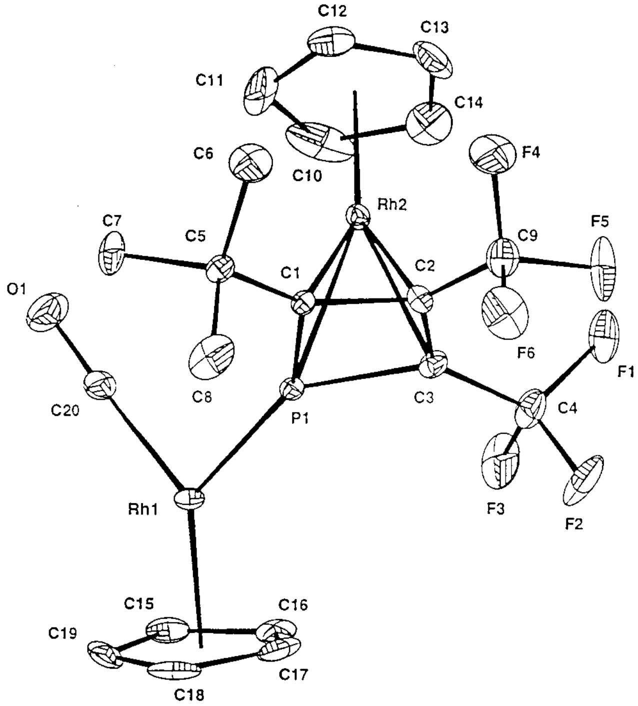


Figure 1. Molecular structure of complex **2**.

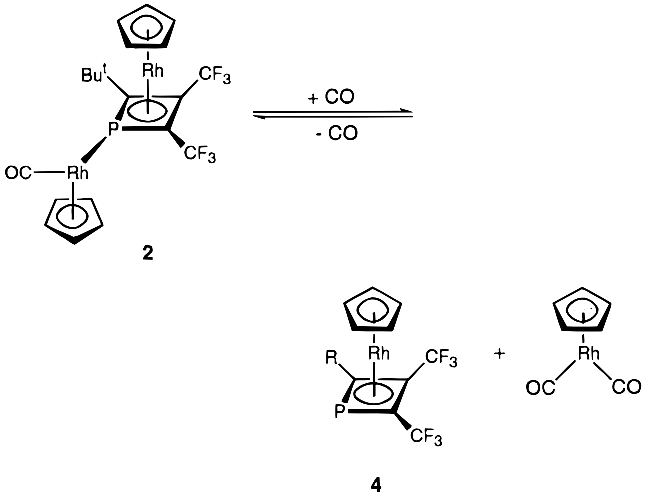
Table 1. Selected Bond Distances (Å) and Angles (deg) in Complex 2

Distances			
C(1)−P(1)	1.806(6)	Rh(2)−C(10)	2.195(8)
P(1)−C(3)	1.789(7)	Rh(2)−C(11)	2.167(8)
C(3)−C(2)	1.456(8)	Rh(2)−C(12)	2.194(8)
C(2)−C(1)	1.459(9)	Rh(2)−C(13)	2.228(8)
Rh(2)−C(1)	2.165(6)	Rh(2)−C(14)	2.203(8)
Rh(2)−C(2)	2.090(6)	Rh(1)−C(15)	2.246(6)
Rh(2)−C(3)	2.105(6)	Rh(1)−C(16)	2.282(6)
Rh(2)−P(1)	2.316(2)	Rh(1)−C(17)	2.218(7)
Rh(1)−P(1)	2.174(2)	Rh(1)−C(18)	2.297(7)
Rh(1)−C(20)	1.831(7)	Rh(1)−C(19)	2.256(7)
Angles			
P(1)−C(1)-C(2)	92.5(4)	Rh(2)−C(1)−C(2)	67.2(3)
C(1)−C(2)−C(3)	8.4(5)	Rh(2)−C(1)−P(1)	70.7(2)
C(2)−C(3)−P(1)	93.3(4)	Rh(2)−C(2)−C(1)	72.8(4)
C(3)−P(1)−C(1)	75.7(3)	Rh(2)−C(2)−C(9)	125.5(5)
Rh(1)−P(1)−C(3)	137.0(2)	Rh(2)−CF(2)−C(3)	70.2(4)
Rh(1)−P(1)−C(1)	145.6(2)	Rh(2)−C(3)−C(2)	69.1(4)
P(1)−Rh(1)−C(20)	89.8(2)	Rh(2)−C(3)−C(4)	125.8(5)
Rh(2)−P(1)−Rh(1)	136.06(8)	Rh(2)−C(3)−P(1)	72.5(2)
Rh(2)−C(1)−C(5)	128.7(4)		

for localized carbon−carbon double bonds (ca. 1.30−1.34 Å). The observation that the bond lengths are closer to the single-bond rather than the double-bond distances is a consequence of the increase in single-bond character arising from the donation of π electron density from the phosphacyclobutadiene ring to the rhodium center. A similar lengthening of the phosphorus−carbon double bonds of phosphaalkenes is observed upon η^2 coordination to metal centers.[15] The rhodium−phosphorus σ bond distance of 2.174(2) Å is comparable with that of 2.178(8) Å in the related hexarhodium complex $[Rh_2Cl_2\{Rh(\eta^5\text{-}C_5H_5)(\eta^4\text{-}P_2C_2Bu^t{}_2)\}_4]$.[16]

The formations of **2** and **3** can perhaps be explained by a mechanism which involves the initial coordination of the phosphaalkyne unit to a rhodium center in **1** which simultaneously causes the bridging carbonyl ligand to become terminal at the adjacent rhodium site. A [2 + 2] cycloaddition reaction between the phosphaalkyne and perfluorobutyne ligand forms the phosphacyclobutadiene ring, which inserts between the two rhodium centers to form the final product.

Scheme 3



When CO is bubbled through a solution of complex **2**, $^{31}P\{^1H\}$ NMR spectroscopic monitoring indicates the emergence of a doublet at −42.6 ppm (J_{PRh} = 34 Hz) with an accompanying decrease in the intensity of the resonance for complex **2**. The doublet presumably arises from complex **4**, in which the $(\eta^5\text{-}C_5H_5)RhCO$ fragment is lost as $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ (Scheme 3). The ^{31}P NMR data for complex **4** are consistent with those of similar known species, e.g. $[Rh(\eta^5\text{-}C_5H_5)\{PC(Bu^t)C_2Ph_2\}]$ (δ −48.75 ppm, $^1J_{PRh}$ = 37.3 Hz).[8] The process appears to be reversible, since removal of volatiles from the solution leads to a residue shown by $^{31}P\{^1H\}$ NMR spectroscopy to be entirely complex **2**.

The apparent lability of the $(\eta^5\text{-}C_5H_5)RhCO$ moiety opened up the possibility of displacing it with other metal fragments. To this end, the reactivity of complexes **2** and **3** with either $[W(CO)_5(THF)]$ or $[Fe_2(CO)_9]$ was examined with some interesting results. Stirring a solution of **2** with $[W(CO)_5(THF)]$ led to an orange solution from which the "flyover" complex **5** was isolated by chromatographic workup and purified by recrystallization in 25% yield from hexane (Scheme 4).

The $^{31}P\{^1H\}$ NMR spectrum of **5** consists of a doublet of doublets at 189.5 ppm with $^1J_{PRh}$ couplings of 63.7 and 44.4 Hz. The presence of two rhodium−phosphorus couplings suggests that as well as the rhodium−phosphorus σ bond there is also a π interaction between the P=C functionality of the flyover backbone and the adjacent rhodium center. Coordination of a phosphorus−carbon double bond in a π fashion usually causes reduction in the $^{31}P\{^1H\}$ chemical shift of the phosphorus, relative to the uncoordinated system. This leads to the conclusion that if the 1-phosphabutadiendiyl backbone of **5** were devoid of this π interaction, then its ^{31}P chemical shift would be higher, perhaps somewhere in excess of 300 ppm. This is indeed the region expected

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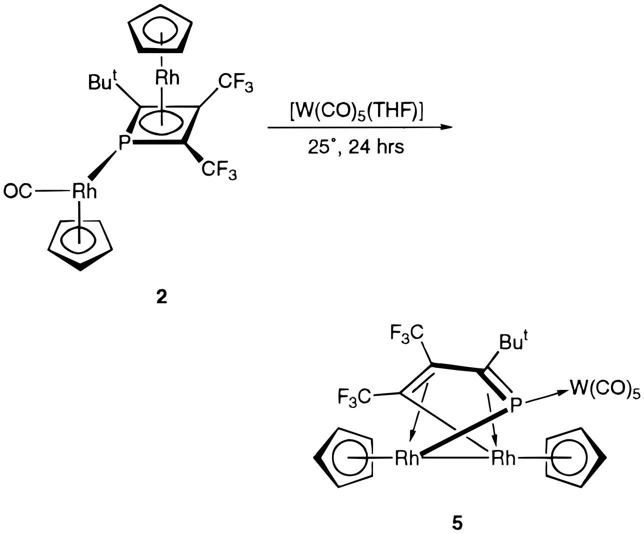
Scheme 4



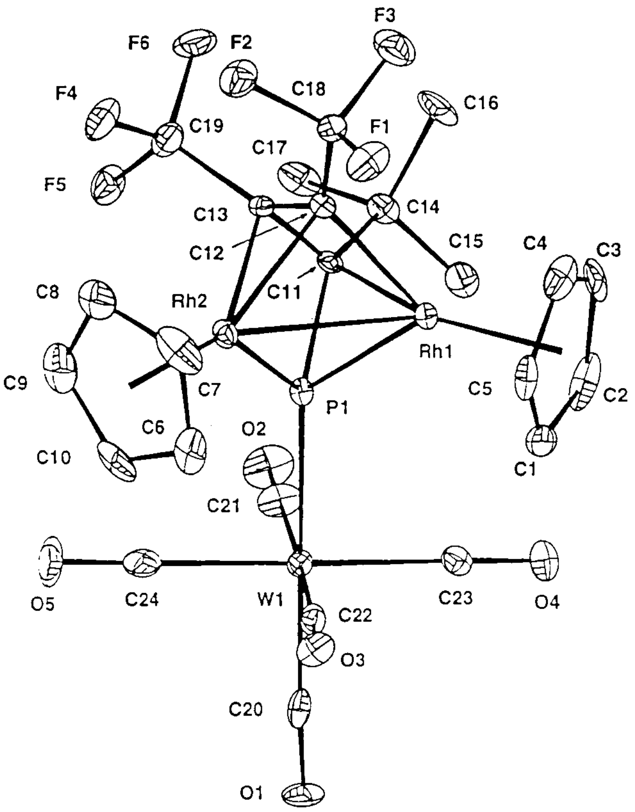


Figure 2. Molecular structure of complex **5**.

for metallophosphaalkenyl systems (ca. 300−600 ppm)[17] to which **5** is notionally related. The $^{31}P\{^1H\}$ NMR spectrum of **5** shows no evidence of fluorine−phosphorus coupling. This is reflected in the ^{19}F NMR spectrum, which shows two barely resolved multiplets ($J < 6$ Hz) due only to fluorine−fluorine coupling.

The structure of **5** in the solid state (Figure 2) was elucidated from a single-crystal X-ray diffraction study with pertinent bond distances and angles collected in Table 2. The structure displays a $(\eta^5\text{-}C_5H_5)_2Rh_2$ unit bridged by a phosphabutadienediyl group which spans in a "flyover" manner. The phosphorus center is additionally coordinated to a $W(CO)_5$ moiety. Similar dirhodium "flyover" complexes have been observed by Dickson and co-workers, although the bridging unit usually contains one more bridging atom than is observed in complex **5**, e.g. $[Rh_2(\eta^5\text{-}C_5H_5)_2\{\mu\text{-}(1,2,5\text{-}\eta)\text{:}(1,4,5\text{-}\eta)\text{-}C_4Me_2(CF_3)_2CO\}]$.[18,19] Related iron complexes have also been reported.[20] The bridging backbone of complex **5** consists of an alkenyl (C(12)−C(13)) and a phosphaalkenyl (P(1)−C(11)) unit connected by a short carbon−carbon single bond (C(11)−C(13)). The phosphorus−carbon distance (P(1)−C(11) = 1.739(8) Å) is intermediate between the expected values for phosphorus−carbon single bonds and phosphorus−carbon double bonds. Likewise, the alkenyl distance (C(12)−C(13) = 1.404(10) Å) is intermediate of the values seen for carbon−carbon single and double bonds, whereas C(11)−C(13) (1.512(11) Å) is in the region expected for a carbon−carbon single bond. These features suggest that the flyover backbone of **5** is comprised of localized double bonds which are slightly elongated as a consequence of their π interactions with the rhodium centers. The rhodium−rhodium distance of 2.6542(10) Å is unremarkable and is typical of that seen between two singly bonded rhodium sites.[21]

Table 2. Selected Bond Distances (Å) and Angles (deg) in Complex 5

Distances			
P(1)−C(11)	1.739(8)	Rh(2)−C(8)	2.220(10)
C(11)−C(13)	1.512(11)	Rh(2)−C(9)	2.193(11)
C(13)−C(12)	1.404(10)	Rh(2)−C(10)	2.204(10)
C(12)−Rh(1)	2.001(9)	Rh(1)−C(1)	2.230(10)
P(1)−Rh(2)	2.290(2)	Rh(1)−C(2)	2.220(10)
Rh(1)−Rh(2)	2.6542(10)	Rh(1)−C(3)	2.185(10)
Rh(2)−C(6)	2.211(9)	Rh(1)−C(4)	2.223(9)
Rh(2)−C(7)	2.258(9)	Rh(1)−C(5)	2.248(9)

Angles			
W(1)−P(1)−Rh(2)	132.41(10)	C(11)−C(13)−C(19)	124.5(7)
Rh(2)−P(1)−C(11)	87.6(3)	C(11)−C(13)−C(12)	104.3(7)
Rh(1)−P(1)−C(11)	65.0(3)	C(19)−C(13)−C(12)	128.6(8)
P(1)−C(11)−C(14)	133.2(7)	C(8)−C(12)−C(13)	131.1(8)
P(1)−C(11)−C(13)	101.1(5)	C(13)−C(12)−Rh(1)	99.9(6)
C(13)−C(11)−C(14)	124.1(7)	C(18)−C(12)−Rh(1)	126.5(6)
C(11)−P(1)−W(1)	138.6(3)		

The reaction between **2** or **3** with $[Fe_2(CO)_9]$ in hexane led to the air-stable red complexes **6** and **7**, respectively, the latter of which was purified by recrystallization from diethyl ether (Scheme 5). The $^{31}P\{^1H\}$ NMR spectrum of **6** consists of a doublet of doublets at 54 ppm, the $^1J_{PRh}$ and $^2J_{PRh}$ couplings being 171.8 and 81.2 Hz, respectively. These data suggest the presence of one compound, as shown in Scheme 5. An examination of the ^{19}F, ^1H, and ^{13}C NMR spectra, however, indicate a more complex picture. Complex **6** would be expected to give rise to one *tert*-butyl resonance and two cyclopentadienyl resonances in its ^1H NMR spectrum. Instead, there are *two tert*-butyl and *four* cyclopentadienyl resonances that are nearly overlapping, a situation which is also evident in the ^{13}C NMR spectrum of **6**. Moreover, the ^{19}F NMR

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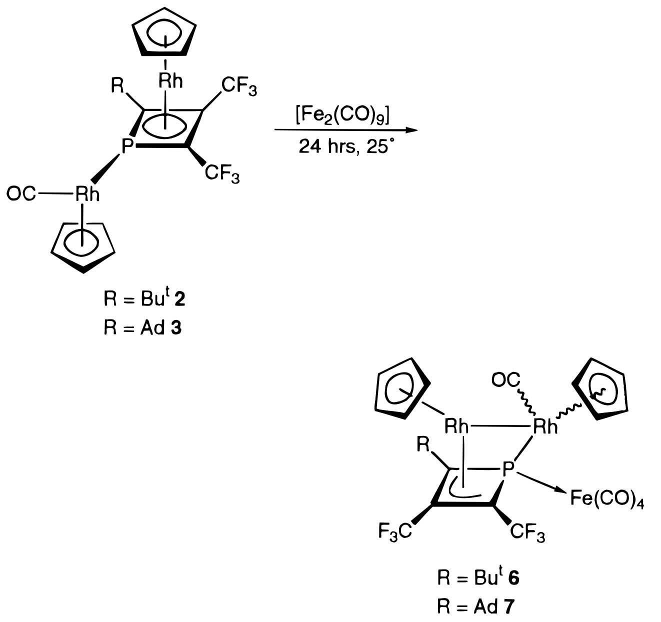
Scheme 5



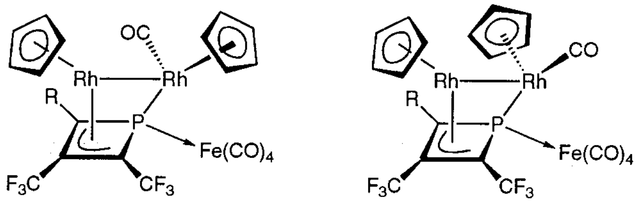


Figure 3. Possible isomers of complexes **6** and **7** in solution.

spectrum shows not two but *four* multiplets, i.e., two pairs within a narrow bracket of 4 ppm. The NMR spectra of the related complex **7** reveal a similar situation, although the ^{1}H and ^{13}C spectra are somewhat less informative because of the complex multiplets arising from the adamantyl groups. On the basis of these observations, we suggest that in solution complexes **6** and **7** exist in two isomeric forms in an approximately 1:1 ratio (Figure 3). It is clear that these isomers do not cocrystallize, since the X-ray structure of **7** (vide infra) shows the presence of only one isomer. The two isomers have slightly differing environments for the C_5H_5, Bu^t or Ad, CF_3, and P sites. That only one signal is seen in the ^{31}P{^{1}H} spectra of both complexes is believed to be entirely coincidental.

The X-ray structure of **7** and relevant bond lengths and angles are shown in Figure 4 and Table 3, respectively. The molecular structure of **7** consists of a phosphacyclobutenyl group bridging a rhodium−rhodium moiety in an unusual η^1: η^3 fashion. Each rhodium bears a η^5-cyclopentadienyl group, and a terminal CO group is bound to Rh(2). The η^1-P ligation is in the form of a σ bond between P(1) and Rh(2) (P(1)−Rh(2) = 2.282(3) Å), while the η^3 attachment arises from the interaction of Rh(1) with the allylic system defined by C(11), C(12), and C(13). The long phosphorus−carbon distances in the phosphacyclobutenyl ring (P(1)−C(11) = 1.858(9) Å, P(1)−C(13) = 1.878(8) Å) correspond to single bonds and clearly indicate that there is no delocalization over the C(11)−P(1)−C(13) region of the ring. The individual distances between the allylic carbons and the rhodium center Rh(1) differ significantly (Rh(1)−C(11) = 2.20(1) Å, Rh(1)−C(12) = 2.08(1) Å, Rh(1)−C(13) = 2.14(1) Å) but span a range similar to that for the analogous distances seen in a related rhodium−phosphacyclobutenyl complex reported by Binger et al. (mean Rh−C distance = 2.221 Å)[8] and in other rhodium allyl systems, e.g. $[RhCl_2(Ph_3As)_2(\eta^3\text{-}C_4H_7)]$ (mean Rh−C distance 2.246 Å).[22] The carbon−carbon bond lengths of the allylic system (C(11)−C(12) = 1.40(1) Å, C(12)−C(13) = 1.47(1) Å) are both intermediate between carbon−carbon single- and double-bond lengths, even though they are marginally different. The Rh−Rh distance of 2.7457(9) Å is longer than that in the previous two systems but is still within the range seen for Rh−Rh single bonds (ca. 2.617−2.842 Å).[21]

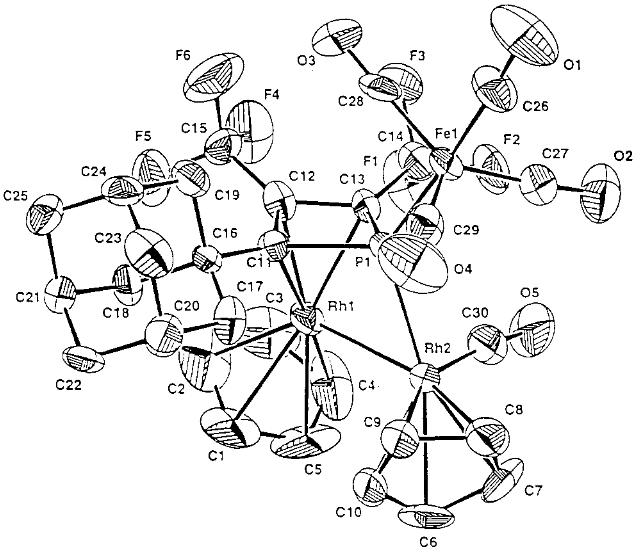


Figure 4. Molecular structure of complex **7**.

Table 3. Selected Bond Distances (Å) and Angles (deg) in Complex 7

Distances			
Rh(1)−C(13)	2.14(1)	Rh(2)−C(6)	2.29(1)
Rh(1)−C(12)	2.08(1)	Rh(2)−C(7)	2.19(1)
Rh(1)−C(11)	2.20(1)	Rh(2)−C(8)	2.25(1)
P(1)−C(11)	1.858(9)	Rh(2)−C(9)	2.26(1)
C(11)−C(12)	1.40(1)	Rh(2)−C(10)	2.31(1)
C(12)−C(13)	1.47(1)	Rh(1)−C(1)	2.27(2)
C(13)−P(1)	1.878(8)	Rh(1)−C(2)	2.221(2)
P(1)−Rh(1)	2.683(3)	Rh(1)−C(3)	2.18(1)
P(1)−Rh(2)	2.282(3)	Rh(1)−C(4)	2.20(2)
P(1)−Fe(1)	2.255(3)	Rh(1)−C(5)	2.19(2)
Rh(2)−Rh(1)	2.7457(9)		

Angles			
P(1)−C(11)−C(12)	92.9(6)	Rh(2)−P(1)−Fe(1)	123.0(1)
C(11)−C(12)−C(13)	101.6(7)	Rh(2)−P(1)−C(11)	105.4(4)
C(12)−C(13)−P(1)	90.0(5)	Fe(1)−P(1)−C(13)	115.5(4)
C(13)−P(1)−C(11)	73.3(4)	P(1)−Rh(2)−C(30)	90.4(4)
P(1)−Rh(2)−Rh(1)	63.7(4)	Rh(1)−Rh(2)−C(30)	81.1(5)

The formation of both **6** and **7** can possibly be attributed to the displacement of the CpRh(CO) fragment from **2** or **3** by an $Fe(CO)_4$ fragment. This would allow the generated rhodium fragment to form a rhodium−rhodium bond and the final products. A compound similar to **6** but with a coordinated $W(CO)_5$ moiety instead of an $Fe(CO)_4$ group may be viewed as a possible intermediate to **5**. Such an intermediate could rearrange to **5** by ring cleavage and the formation of a bond

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(22) Hewitt, T. G.; de Boer, J. J.; Anzenhofer, K. *Acta Crystallogr.* **1970**, *B26*, 1244.

between the CF_3-substituted ring carbon adjacent to the phosphorus center and the rhodium center coordinated to the allyl fragment. Elimination of the CO group would be necessary to maintain the electron count at each rhodium center.

Experimental Section

General Considerations. All procedures were conducted using conventional Schlenk or glovebox techniques under an atmosphere of high-purity argon or dinitrogen in flame-dried glassware. Hexane and diethyl ether were refluxed over sodium−potassium alloy under nitrogen for at least 12 h before being distilled and freeze−thaw-degassed before use. NMR spectra were recorded in dry degassed C_6D_6 on a Bruker WM-250 or AC-400 spectrometer. $^{31}P\{^1H\}$ and ^{19}F NMR spectra were referenced to 85% H_3PO_4 and $CFCl_3$, respectively, as external references. ^1H and ^{13}C spectra were referenced to the residual solvent resonances (128 ppm for ^{13}C; 7.14 ppm for ^1H). Mass spectra were recorded on a VG-Autospec FAB instrument (Cs^+ ions, 25 kV, 3-nitrobenzyl alcohol matrix). Melting points were recorded in capillaries sealed under argon. Infrared spectra were recorded on a Perkin-Elmer 1725-X Fourier transform instrument. A reproducible elemental analysis of **6** proved difficult to obtain, as its high solubility in all organic solvents made it difficult to purify by recrystallization. Although compounds **5** and **7** have relatively high melting points, they appear to slowly decompose at room temperature. As a result, accurate elemental analyses on these compounds proved difficult to obtain, but those which were are included below. $[Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C{\equiv}CCF_3)]$ (**1**) and the phosphaalkyne $P{\equiv}CAd$ were prepared according to the published procedures.[23,24] $P{\equiv}CBu^t$ was prepared by a modification[25] of the literature procedure.[26] $Fe_2(CO)_9$ was purchased from Aldrich and used without further purification.

Synthesis of $[Rh(\eta^5\text{-}C_5H_5)\{\mu\text{-}\eta^4{:}\eta^1\text{-}PC_3Bu^t(CF_3)_2\}\{Rh(CO)(\eta^5\text{-}C_5H_5)\}]$ (2). To a stirred solution of $[Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C{\equiv}CCF_3)]$ (**1**; 0.1 g, 0.19 mmol) in hexane (5 mL) at −20 °C was added the phosphaalkyne $P{\equiv}CBu^t$ (0.02 g, 32.3 μL, 0.2 mmol). When it was warmed, the initial green solution became cloudy with a yellow precipitate which disappeared upon reaching room temperature to leave a clear red solution. The resulting solution was stirred at room temperature for 24 h. Volatiles were then removed in vacuo, and the residue was recrystallized from hexane to afford **2** as large red crystals (0.06 g from two crops, 0.1 mmol, 50.4%); mp 128−130 °C. NMR (C_6D_6, 298 K): ^1H (400 MHz) δ 1.07 (s, 9H, Bu^t), 5.09 (s, 5H, $C_5\boldsymbol{H}_5$), 5.18 (s, 5H, $C_5\boldsymbol{H}_5$); ^{13}C (100.6 MHz) δ 30.8 (d, $C(\boldsymbol{C}H_3)_3$, $^3J_{PC} = 6.5$ Hz), 32.7 (d, $\boldsymbol{C}(CH_3)_3$, $^2J_{PC} = 6.5$ Hz), 86.5 (s, $\boldsymbol{C}_5H_5$), 88.0 (s, $\boldsymbol{C}_5H_5$), 195 (dd, $\boldsymbol{C}O$, $^2J_{PC} = 32$ Hz, $^1J_{RhC} = 83$ Hz), $\boldsymbol{C}F_3$ and $P\boldsymbol{C}_3Bu^t(CF_3)_2$ ring carbons unobserved; ^{19}F (376.4 MHz) δ −52.6 (quartet, $C\boldsymbol{F}_3$, $^5J_{FF} = 5.6$ Hz), −54.0 (m, $C\boldsymbol{F}_3$, $^3J_{PF} \approx {}^5J_{FF} \approx 6$ Hz); $^{31}P\{^1H\}$ (101.4 MHz) δ 23.5 (ddq, $^1J_{PRh} = 251$ and 42.9 Hz, $^3J_{PF} = 7.6$ Hz). FAB mass spectrum (25 kV): 626 ($[M]^+$, 22%), 598 ($[M - CO]^+$, 55%). IR: (ν/cm^{-1}): 1974 (m), 1964 (m). Anal. Found: C, 38.42; H, 2.97. Calcd for $C_{20}H_{19}Rh_2PF_6O$: C, 38.4; H, 3.06.

Synthesis of $[Rh(\eta^5\text{-}C_5H_5)\{\mu\text{-}\eta^4{:}\eta^1\text{-}PC_3Ad(CF_3)_2\}\{Rh(CO)(\eta^5\text{-}C_5H_5)\}]$ (3). To a stirred solution of $[Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C{\equiv}CCF_3)]$ (**1**; 0.1 g, 0.19 mmol) in hexane (5 mL) at −20 °C was added a solution of the phosphaalkyne $P{\equiv}CAd$ (0.0338 g, 0.19 mmol) in hexane (5 mL). Upon warming, the initial green solution became cloudy with a yellow precipitate, which disappeared upon reaching room temperature to leave a clear red solution. The resulting solution was stirred at room temperature for 24 h. Volatiles were then removed in vacuo and the residue recrystallized from hexane to afford **3** as large red crystals (0.07 g, 0.1 mmol, 52%); mp 100−103 °C. NMR (C_6D_6, 298 K): ^1H (400 MHz) δ 1.6−2.0 (m, 15H, Ad-$\boldsymbol{H}$), 5.2 (s, 5H, $C_5\boldsymbol{H}_5$), 5.3 (s, 5H, $C_5\boldsymbol{H}_5$); ^{13}C (100.6 MHz) δ 28.5 (s, Ad-$\boldsymbol{C}H$), 36.2 (s, Ad-$\boldsymbol{C}H_2$), 42.7 (s, Ad-$\boldsymbol{C}H_2$), 82.6 (s, $\boldsymbol{C}_5H_5$), 87.9 (s, $\boldsymbol{C}_5H_5$), 194.9 (dd, $\boldsymbol{C}O$, $^2J_{PC} = 32$ Hz, $^1J_{RhC} = 83.9$ Hz), $\boldsymbol{C}F_3$ and $P\boldsymbol{C}_3Bu^t(CF_3)_2$ ring carbons unobserved; ^{19}F (376.4 MHz) δ −52.2 (quartet, $C\boldsymbol{F}_3$, $^5J_{FF} = 6.5$ Hz), −53.9 (m, $C\boldsymbol{F}_3$, $^3J_{PF} \approx {}^5J_{FF} \approx 8$ Hz); $^{31}P\{^1H\}$ (101.4 MHz) δ 22.5 (ddq, $^1J_{PRh} = 251$ and 43.1 Hz, $^3J_{PF} = 7.6$ Hz). FAB mass spectrum (25 kV): 704 ($[M]^+$, 44%), 676 ($[M - CO]^+$, 69%). IR (ν/cm^{-1}): 1976 (s). Anal. Found: C, 44.43; H, 3.50. Calcd for $C_{26}H_{25}Rh_2PF_6O$: C, 44.34; H, 3.58.

Synthesis of $[Rh_2(\eta^5\text{-}C_5H_5)_2\{\mu\text{-}(1,2,4\text{-}\eta){:}(1,3,4\text{-}\eta)\text{-}PC_3Bu^t(CF_3)_2\}\{W(CO)_5\}]$ (5). $[W(CO)_6]$ (0.09 g, 0.256 mmol) in THF (40 mL) was irradiated (254 nm) for 6 h. Compound **2** (0.08 g, 0.128 mmol) in THF (10 mL) was added to the resulting yellow solution of $[W(CO)_5(THF)]$ and the mixture stirred for 48 h. Volatiles were then removed in vacuo, and the residue was extracted with hexane and filtered. The filtrate was evaporated and the residue chromatographed (Kieselgel, hexane/Et_2O 95%/5%). Compound **5** was collected as an orange fraction (0.03 g, 0.033 mmol, 25%); mp 168 °C dec. NMR (C_6D_6, 298 K): ^1H (400 MHz) δ 1.10 (s, 9H, Bu^t), 5.09 (s, 5H, $C_5\boldsymbol{H}_5$), 5.11 (s, 5H, $C_5\boldsymbol{H}_5$); ^{13}C (100.6 MHz) δ 29 (s, $C(\boldsymbol{C}H_3)_3$), 38.8 (s, $\boldsymbol{C}(CH_3)_3$), 88.2 (s, $\boldsymbol{C}_5H_5$), 88.7 (s, $\boldsymbol{C}_5H_5$), 197.4 (d, W($\boldsymbol{C}$O), cis-$^2J_{PC} = 6.1$ Hz), 200.0 (d, W($\boldsymbol{C}$O), trans-$^2J_{PC} = 29$ Hz), $\boldsymbol{C}F_3$ and $P\boldsymbol{C}_3Bu^t(CF_3)_2$ phosphabutadienyl carbons unobserved; ^{19}F (376.4 MHz) δ −53.0 (quartet, $\boldsymbol{C}F_3$, $^5J_{FF} \approx 6.5$ Hz), −57.3 (quartet, $\boldsymbol{C}F_3$, $^5J_{FF} \approx 6.5$ Hz no P−F coupling observed); $^{31}P\{^1H\}$ (101.4 MHz) δ 189.5 (dd, $^1J_{PRh} = 63.7$ and 44.4 Hz). FAB mass spectrum (25 kV): 922 ($[M]^+$, 1%), 865 ($[M - 2CO]^+$, 3%), 781 ($[M - 5CO]^+$, 5%), 597 ($[M - W(CO)_5]^+$, 5%); IR (ν/cm^{-1}): 1942.9 (s), 1959.8 (s), 2067.8 (m). Anal. Found: C, 29.24; H, 1.6. Calcd for $C_{24}H_{19}Rh_2PF_6O_5W$: C, 31.26; H, 2.08.

Synthesis of $[Rh_2(\eta^5\text{-}C_5H_5)_2(CO)\{\mu\text{-}\eta^1{:}\eta^3\text{-}PC_3Bu^t(CF_3)_2\}\{Fe(CO)_4\}]$ (6). To a stirred solution of compound **2** (0.143 g, 0.23 mmol) in THF (2 mL) was added $[Fe_2(CO)_9]$ (0.089 g, 0.24 mmol). The resulting mixture was stirred for 24 h, during which time a clear red solution formed. Volatiles were removed in vacuo, the residue was chromatographed (Kieselgel, hexane/Et_2O 1/3), and the two isomers of **6** (see Results and Discussion) were collected as a purple-red fraction (0.046 g, 0.058 mmol, 25%). The compound proved difficult to recrystallize because of its high solubility; mp 116−119 °C. NMR (C_7D_8, 298 K): ^1H (400 MHz) δ 1.21 (s, 9H, Bu^t), 1.13 (s, 9H, Bu^t), 5.03 (s, 5H, $C_5\boldsymbol{H}_5$), 5.05 (s, 5H, $C_5\boldsymbol{H}_5$), 5.06 (s, 5H, $C_5\boldsymbol{H}_5$), 5.11 (s, 5H, $C_5\boldsymbol{H}_5$); ^{13}C (100.6 MHz) δ 31.9 (s, $C(\boldsymbol{C}H_3)_3$), 32.2 (s, $C(\boldsymbol{C}H_3)_3$), 32.8 (d, $\boldsymbol{C}(CH_3)_3$, $^2J_{PC} = 6$ Hz), 33.5 (d, $\boldsymbol{C}(CH_3)_3$, $^2J_{PC} = 6$ Hz), 86.6 (s, $\boldsymbol{C}_5H_5$), 87.3 (s, $\boldsymbol{C}_5H_5$), 92.0 (s, $\boldsymbol{C}_5H_5$), 92.3 (s, $\boldsymbol{C}_5H_5$), 215.5 (dd, Fe$\boldsymbol{C}$O, $J = 33$ and 19 Hz); ^{19}F (376.4 MHz) δ −49.1 (m, $C\boldsymbol{F}_3$, $J \approx 6$ Hz), −50.7 (m, $C\boldsymbol{F}_3$, $J \approx 7$ Hz), −52.3 (quartet, $C\boldsymbol{F}_3$ $^5J_{FF} \approx 7$ Hz), −53.0 (quartet, $C\boldsymbol{F}_3$, $^5J_{FF} \approx 7$ Hz); $^{31}P\{^1H\}$ (101.4 MHz) δ 53.8 (dd, $^1J_{PRh} = 171.8$ Hz, $^2J_{PRh} = 81.2$ Hz). FAB mass spectrum (25 kV): 794 ($[M]^+$, 4%), 766 ($[M - CO]^+$, 13%), 710 ($[M - 3CO]^+$, 46%), 682 ($[M - 4CO]^+$, 16%), 654 ($[M - 5CO]^+$, 5%), 626 ($[M - Fe(CO)_4]^+$, 14%), 598 ($[M - Fe(CO)_5]^+$, 14%). IR (ν/cm^{-1}): 2036 (m), 2014 (w), 2000 (w), 1936 (s), 1926 (s).

Synthesis of $[Rh_2(\eta^5\text{-}C_5H_5)_2(CO)\{\mu\text{-}\eta^1{:}\ \eta^3\text{-}PC_3Ad(CF_3)_2\}\{Fe(CO)_4\}]$ (7). To a stirred solution of compound **3** (0.07 g, 0.099 mmol) in hexane (10 mL) was added $[Fe_2(CO)_9]$ (0.036 g, 0.099 mmol). The resulting mixture was stirred at room temperature for 24 h. Volatiles were then removed in vacuo, and the residue was extracted with Et_2O and filtered to give a red solution. Concentration of the filtrate followed by slow cooling to −30 °C afforded two isomers of compound **7** as red crystals (0.054 g, 0.062 mmol, 62.3%); mp 131−133 °C. NMR (C_6D_6, 298 K): ^1H (400 MHz) δ 1.55−2.1 (m, 30 H, Ad-$\boldsymbol{H}$), 5.06

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(s, 5H, $C_5\boldsymbol{H}_5$), 5.07 (s, 5H, C_5H_5), 5.09 (s, $C_5\boldsymbol{H}_5$), 5.13 (s, $C_5\boldsymbol{H}_5$); ^{13}C (100.6 MHz) δ 28.5 (s, Ad-CH), 28.9 (s, Ad-$\boldsymbol{C}$H), 35.9 (s, Ad-$\boldsymbol{C}H_2$), 36.2 (s, Ad-$\boldsymbol{C}H_2$), 42.1 (s, Ad-$\boldsymbol{C}H_2$), 42.6 (s, Ad-$\boldsymbol{C}H_2$), 85.8 (s, $\boldsymbol{C}_5H_5$), 86.5 (s, $\boldsymbol{C}_5H_5$), 91.6 (s, $\boldsymbol{C}_5H_5$), 92.1 (s, $\boldsymbol{C}_5H_5$); 215 (dd, Fe$\boldsymbol{C}$O, J = 39 and 17 Hz); ^{19}F (376.4 MHz) δ −50.2 (m, $C\boldsymbol{F}_3$, $J \approx 7$ Hz), −51.7 (m, $C\boldsymbol{F}_3$, $J \approx 7$ Hz), −52.8 (quartet, $C\boldsymbol{F}_3$, $^5J_{FF} = 6.9$ Hz), −53.5 (quartet, $C\boldsymbol{F}_3$, $^5J_{FF} = 7.6$ Hz); ^{31}P-{^{1}H} (101.4 MHz) δ 51 (dd, $^1J_{PRh} = 194$ Hz, $^2J_{PRh} = 83$ Hz). FAB mass spectrum (25 kV): 872 ($[M]^+$, 3%), 844 ($[M - CO]^+$, 10%), 788 ($[M - 3CO]^+$, 42%), 760 ($[M - 4CO]^+$, 15%), 732 ($[M - 5CO]^+$, 8%), 704 ($[M - Fe(CO)_4]^+$, 7%), 676 ($[M - Fe(CO)_5]^+$, 24%); IR (ν/cm^{-1}): 2041 (m), 1992 (w), 1937 (s), 1926 (m). Anal. Found: C, 42.8; H, 2.03. Calcd for $C_{30}H_{25}FeO_5PRh_2F_6$: C, 41.3; H, 2.89.

X-ray Structure Determinations. Crystals of **2** and **5** suitable for X-ray structure determination were mounted in silicone oil. Intensity data were measured on a FAST[27] area detector diffractometer using Mo Kα radiation. Both structures were solved by heavy-atom methods (SHELXS-86[28]) and refined by least squares using the SHELXL-93[29] program. The structures were refined on F^2 using all data. Neutral-atom complex scattering factors were employed.[30] Empirical absorption corrections were carried out by the DIFABS method.[31] A crystal of **7** was mounted on a glass fiber, and X-ray data were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. The structure was solved and refined using the Xtal 3.4 program system.[32] Crystal data and details of data collections and refinement are given in Table 4. Molecular structures are shown in Figures 1, 2, and 4. Anisotropic thermal parameters were refined for all non-hydrogen atoms. The hydrogen atoms in all structures were included in calculated positions (riding model).

Table 4. Crystallographic Data for Complexes 2, 5, and 7

	2	**5**	**7**
formula	$C_{20}H_{19}F_6OPRh_2$	$C_{24}H_{19}F_6O_5PRh_2W$	$C_{30}H_{25}O_5F_6PFeRh_2$
M_r	626.14	922.03	872.2
a, Å	10.043(2)	9.5180(11)	9.246(1)
b, Å	10.484(1)	18.1260(9)	10.07(1)
c, Å	11.271(1)	16.118(2)	17.881(1)
α, deg	109.03(1)	90	91.70(1)
β, deg	104.89(2)	101.940(11)	99.12(1)
γ, deg	91.27(1)	90	110.34(3)
V, Å^3	1076.9(3)	2820.6(5)	1534.9(3)
cryst syst	triclinic	monoclinic	triclinic
λ, Å	0.710 69	0.710 69	0.710 73
T, K	150(2)	150(2)	296(2)
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Z	2	4	2
size	0.25 × 0.35 × 0.30	0.25 × 0.20 × 0.30	0.42 × 0.52 × 0.44
color	red	orange	red
μ, cm^{-1}	16.66	55.50	16.6
2θ range, deg	1.99−24.98	2.25−25.04	2−50
no. of rflns collected	4353	9059	5743
no. of rflns obsd	2988	3943	3654
params varied	274	355	407
R ($I > 2\sigma(I)$)	0.0489	0.0339	0.075
R_w	0.1255	0.0681	0.085

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and bond angles and distances for **2**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990516V

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