Organometallics **2001,** *20,* 363−366

Conversion of Perfluorobenzyl Complexes of Rhodium to Fluorinated Oxarhodacycles

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Received September 21, 2000

*Summary: The perfluorobenzylrhodium complex [Cp*Rh(CO)($CF_2C_6F_5$)(I)],* ***1*** *(Cp* = C_5Me_5), reacts with N-methylmorpholine-N-oxide (NMO) with loss of CO_2 and formation of the iodo-bridged dimer [Cp*Rh(μ_2-I)($CF_2C_6F_5$)]$_2$,* ***5****, which has been characterized by X-ray crystallography. While attempts to prepare hydroxo complexes by reaction of [Cp*Rh(PMe_3)($CF_2C_6F_5$)(I)],* ***3****, with sources of hydroxide were unsuccessful, treatment of* ***3*** *with moist silver oxide affords the oxametallacycle [Cp*(PMe_3)RhO(C_6F_4)CF_2],* ***9****, which undergoes rapid hydrolysis of the α-CF_2 group by adventitious moisture to afford the crystallographically characterized analogue [Cp*(PMe_3)RhO(C_6F_4)C═O],* ***10****. A brief discussion of possible mechanisms is presented.*

We have previously described the synthesis of the perfluorobenzyl rhodium complexes **1**−**3**[1] and the reaction of **2** to afford the cationic water complex **4**.[2] The α-CF_2 group in **4** proved to be remarkably sensitive toward hydrolysis by the coordinated water ligand, and the role of the counterion in these hydrolysis reactions was shown to affect the rate of hydrolysis.[2] Here we report the structure of a dimer prepared from decarbonylation reaction of **1** and attempts to prepare hydroxo analogues of **4**, which lead to the unexpected formation of oxametallacycles.

Treatment of a methylene chloride solution of **1** with *N*-methylmorpholine-*N*-oxide (NMO) resulted in the expected loss of the CO ligand, presumably as CO_2, and clean formation (as monitored by NMR spectroscopy) of the stable iodide-bridged dimer **5**. The dimer was characterized in solution by ^{1}H and ^{19}F NMR spectroscopy and in the solid state by X-ray diffraction and elemental analysis. Crystallographic data can be found in Table 1. The ORTEP plot with atom-labeling scheme is depicted in Figure 1. The pairs of pentamethylcyclopentadienyl ligands and perfluorobenzyl ligands are mutually trans, as might be expected on the basis of steric effects. A major difference between the two sides of the dimer is the conformation of each of the perfluorobenzyl ligands, with one oriented with its perfluorophenyl ring tilted in toward the bridging ligands and the other tilted away from the core. The interligand bond angles show a constricted angle between I(1)−Rh(1)−I(2) [82.27(4)°] and I(1)−Rh(2)−I(2) [81.55(4)°] as a result of the four-membered ring core. As expected, slightly more obtuse angles are observed between the nonbridging ligands, C(11)−Rh(1)−I(1) [95.5(4)°], C(11)−Rh(1)−I(2) [94.2(4)°], C(28)−Rh(2)−I(1) [92.7(2)°], and

Table 1. Crystal Data and Summary of X-ray Data Collection

	5	**10**
formula	$C_{34}H_{30}F_{14}I_2Rh_2$	$C_{20}H_{24}F_4O_2PRh$
fw	1164.20	506.27
space group	P2(1)/c	P2(1)/n
a, Å	15.966(2)	8.6399(6)
b, Å	11.330(2)	21.296(2)
c, Å	20.031(3)	12.1241(9)
α, deg	90	90
β, deg	90.19(2)	108.286(9)
γ, deg	90	90
V, Å^3	3623.7(7)	2118.1(2)
Z	4	4
D(calcd), g/cm^3	2.134	1.588
abs coeff, mm^{-1}	2.712	0.928
temp, K	298(2)	
diffractometer	Siemens P4	
radiation	Mo Kα 0.71073 Å	
R(*F*), %[a]	4.23	3.29
R(*wF*^{2}), %[a]	8.39	7.79

[a] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$.

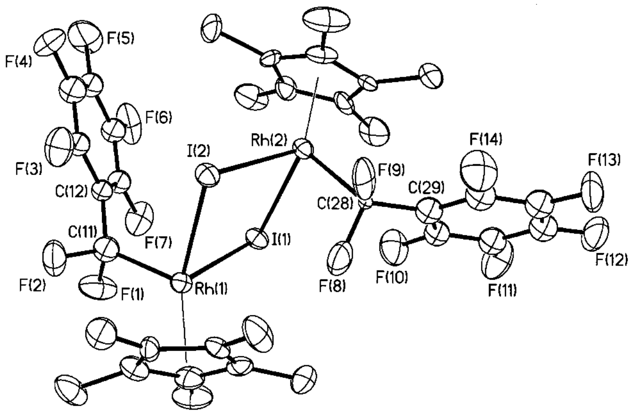

Figure 1. ORTEP drawing and atom-labeling scheme for **5**. Ellipsoids are drawn at 35% probability except for those of the phenyl rings (see Experimental Section). Hydrogens are omitted for clarity. Selected distances (Å) and angles (deg): Rh(1)−C(11) 2.079(13), Rh(2)−C(28) 2.214(10), Rh(1)−I(1) 2.7186(14), Rh(1)−I(2) 2.7322(13), Rh(2)−I(1) 2.7536(13), Rh(2)−I(2) 2.7368(14), C(11)−F(1) 1.43(2), C(11)−F(2) 1.349(15), C(28)−F(8) 1.355(12), C(28)−F(9) 1.189(11): F(1)−C(11)−F(2) 101.9(11), F(8)−C(28)−F(9) 107.6(10), Rh(1)−C(11)−C(12) 125.6(9), Rh(2)−C(28)−C(29) 119.3(7).

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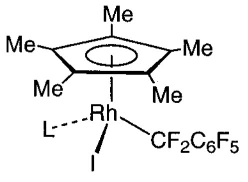
10.1021/om0008171 CCC: \$20.00
Publication on Web 12/14/2000

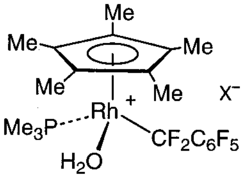
C(28)−Rh(2)−I(2) [89.0(3)°]. Interestingly, the bond lengths associated with the two perfluorobenzyl groups are considerably different. For example, the distance between Rh(1)−C(11) [2.079(13) Å] is significantly shorter than that for Rh(2)−C(28) [2.214(10) Å]. Comparison values are 2.190(11) Å in **3**,[1] 2.152(14) Å in the iridium analogue of **1**,[3] and 2.113(9) Å in the cation **4**.[2] The α-C−F distances in **5** are also different. One set exhibits a rather long C−F bond [C(11)−F(1) = 1.43(2) Å] and one normal [C(11)−F(2) = 1.349(15) Å], whereas the other set has one unusually short distance [C(28)−F(9) = 1.189(11) Å] and one normal [C(28)−F(8) = 1.355(12) Å]. The F−C−F bond angle which contains the longest C−F bond is consistent with greater p-character in that bond, as the angle is significantly more acute than that containing the unusually short C−F bond [F(1)−C(11)−F(2) = 101.9(11)° vs F(8)−C(28)−F(9) = 107.6(10)°]. Comparison values are 1.257(14) and 1.327(12) Å in **3** with an F−C−F angle of 105.3(9)°,[1] 1.375(16) and 1.319(17) Å with F−C−F of 105.6(12)° in the iridium analogue of **1**,[3] and 1.388(10) and 1.412(10) Å with F−C−F of 101.8(6)° in **4**.[2] The correspondingly obtuse Rh−CF$_2$−C(ipso) angles [Rh(1)−C(11)−C(12) = 125.6(9)° and Rh(2)−C(28)−C(29) = 119.3(7)°] appropriately reflect the degree of narrowing in the F−C−F angle; the smaller the F−C−F bond angle, the greater its corresponding Rh−CF$_2$−C(ipso) angle. On the other hand, the CF$_2$−C(ipso) bond lengths are the same [1.508(15) Å for C(11)−C(12) and 1.499(11) Å for C(28)−C(29)]. Once again comparison values can be found in the corresponding bond angles [and C−C distances] of 117.2(7)° [1.486(14) Å] in **3**,[1] 116.4(10)° [1.528(17) Å] in the iridium analogue of **1**,[3] and 116.0(5)° [1.542(9) Å] in **4**.[2] Acute F−C−F angles and obtuse M−CF$_2$R$_F$ angles are not unusual,[3] but the perfluorobenzyl ligand appears to be capable of accommodating quite a wide range of distances and angles internally and between itself and the metal.

The data obtained from solution are consistent with the solid-state structure of **5**, but the presence of symmetry equivalent benzylic fluorine substituents requires that the perfluorobenzyl groups rotate freely about their respective Rh−CF$_2$ bonds, each sampling an effective plane of symmetry, which bisects the two geminal fluorine atoms. In addition, the triplet coupling observed for the CF$_2$ resonance (J_{FF} = 29 Hz) suggests that the pentafluorophenyl ring rotates freely about the CF$_2$−C$_6$F$_5$ bond, affording an equal coupling with both ortho fluorine atoms. The 2:1:2 ratio of peaks upfield of the benzylic fluorines is also consistent with free rotation about the CF$_2$−C$_6$F$_5$ bond. Similar observations have been made for other perfluorobenzyl complexes.[1−3]

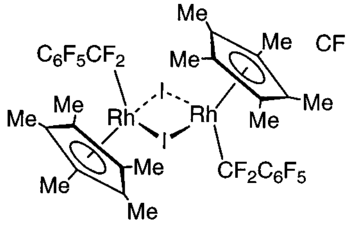
A similar complex was reported by Stone and co-workers.[4] They found that reaction of [Rh(η^5-C$_5$H$_5$)(C$_2$H$_4$)$_2$] and n-C$_3$F$_7$I affords the oxidative addition product [Rh(η^5-C$_5$H$_5$)(C$_2$H$_4$)(C$_3$F$_7$)I], which if heated to 50 °C, loses ethylene to give a halide dimer **6**, analogous to **5**. Our attempts to mimic this reaction by using [Rh(η^5-C$_5$Me$_5$)(C$_2$H$_4$)$_2$] and perfluorobenzyl iodide were unsuccessful. The lack of reactivity in the pentamethylcyclopentadienyl case may be attributable to steric blocking of the metal center by the Cp* ring, which has a greater cone angle than Cp (188° for Cp* vs 148° for Cp).[5,6]



1 L = CO
2 L = PMe$_3$
3 L = PMe$_2$Ph



4 X = BF$_4^-$



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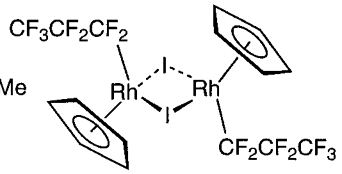

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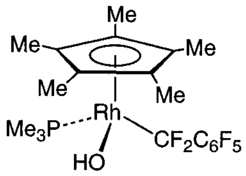

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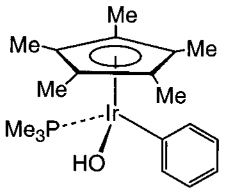

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We were interested in the preparation of hydroxo complex **7** because, in theory, it could be treated with a variety of proton sources to generate the aqua complex **4**, thereby allowing a more controlled entry to studying the rate of subsequent hydrolysis (vide supra) in the presence of various counterions.[2] Complexes containing hydroxo ligands are not common among late transition metals, presumably because of their tendency to donate a proton to another M−OH complex, resulting in the formation of bridging oxo complexes, which are often very stable.[7] Bergman and co-workers have been successful in obtaining and characterizing some late transition metal hydroxo complexes,[8] including the iridium complex **8**,[9] which allowed us hope that synthesis of **7** might be an achievable goal.

Attempts to effect the substitution of iodide in **2** using NaOH or CsOH in THF and water returned only starting material. On reflection, moist silver oxide was then considered as a potentially good reagent, combining a source of hydroxide with Ag$^+$ as a well-known[10] iodide abstracting agent in these systems. However, when **2** was treated with freshly prepared moist silver oxide, the desired hydroxo complex **7** was not observed, and a different product **9** was formed in quantitative yield.

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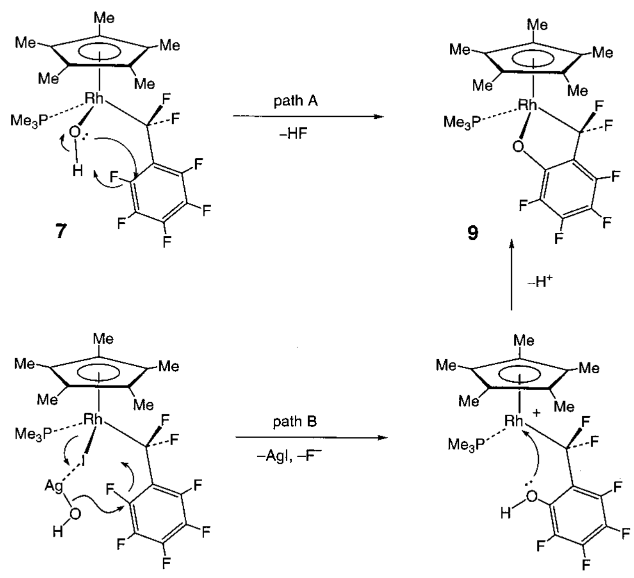
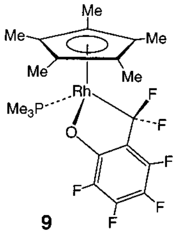
Scheme 1



Complex **9** was characterized in solution by ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR spectroscopy. The ^{1}H NMR spectrum showed the expected phosphorus coupled doublets for Cp* and PMe$_3$. The ^{31}P{^{1}H} NMR spectrum appeared as a doublet of doublets of doublets, with coupling to rhodium (J_{PRh} = 162 Hz) and each of the α-CF$_2$ fluorines (J_{PF} = 40, 27 Hz). In C$_6$D$_6$ the ^{19}F NMR spectrum of **9** was initially puzzling, as the CF$_2$ resonances are accidentally isochronous, but on changing the NMR solvent to acetone-d_6, the chemical shifts of the two geminal fluorine atoms appeared as the expected strongly coupled AB pattern with J_{FF} = 234 Hz. One CF$_2$ fluorine exhibited additional splitting to phosphorus and rhodium (J_{FP} = 40, J_{FRh} = 12) with an additional coupling to the ortho fluorine on the aromatic ring (J_{FF} = 12), while the second CF$_2$ fluorine exhibited a smaller coupling to phosphorus (J_{PF} = 27 Hz) and similar coupling (8 Hz) to rhodium and to the ortho fluorine. Only four fluorine peaks of equal intensity were observed corresponding to the substituents on the aryl ring.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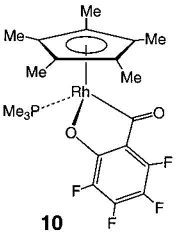
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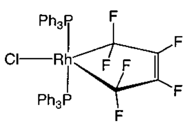
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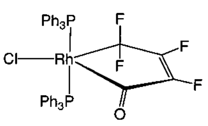
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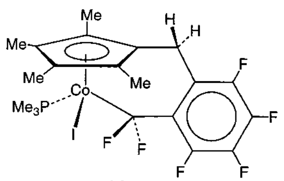
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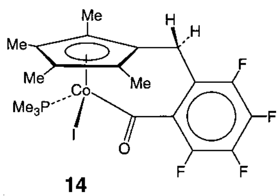
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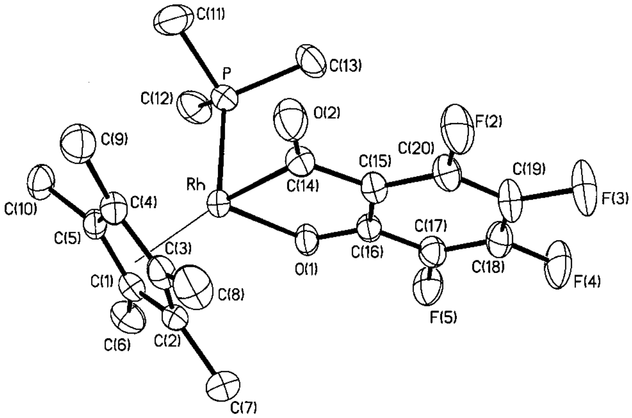

Figure 2. ORTEP drawing and atom-labeling scheme for **5**. Ellipsoids are drawn at 35% probability. Hydrogens are omitted for clarity. Selected distances (Å) and angles (deg): Rh–C(14) 2.010(4), Rh–O(1) 2.103(3), Rh–P 2.2728(13), C(14)–O(2) 1.203(5), C(14)–C(15) 1.472(6), C(15)–C(16) 1.412(6), C(16)–O(1) 1.326(5): C(14)–Rh–O(1) 82.61(15), Rh–O(1)–C(16) 110.4(3), Rh–C(14)–O(2) 124.8(3), O(2)–C(14)–C(15) 124.2(4), P–Rh–O(1) 90.05(9), P–Rh–C(14) 86.81(14).

Isolation of an adequate sample of **9** for elemental analysis was hampered by an unusually facile hydrolysis during recrystallization to give **10**. Formation of **10** results in the expected disappearance of the CF$_2$ resonances in the ^{19}F NMR spectrum and appearance in its IR spectrum of an additional band at ν 1658 cm^{-1} corresponding to the C=O stretch of the newly formed acyl. X-ray quality crystals were obtained of **10** for confirmation of the overall structure. Crystallographic data are presented in Table 1. An ORTEP plot with atom-labeling scheme is found in Figure 2. As expected, the distance from the metal to the sp^2-acyl carbon (Rh–C(14) = 2.011(4) Å) is shorter than that to the sp^3 carbon in **4** [2.113(9) Å] and is typical of a Rh–C(sp^2) distance [1.982 Å].[11] The Rh–O(1) [2.103(3) Å] distance is in the range for a typical rhodium–oxygen bond,[11] but is significantly shorter than that in **4** [2.164(7)].

Two possible mechanisms for the formation of the oxygen–carbon bond in **9** are presented in Scheme 1. Path A involves initial formation of the desired hydroxo complex **7**, followed by intramolecular attack of coordinated OH on the ortho position of the perfluorobenzyl ring, eliminating HF in an addition–elimination reaction, to give the observed product. The other possibility considers the formation of an initial silver–iodide complex (path B) which then directs the attack of hydroxide to the ortho position of the fluoroaryl ring without prior involvement of **7**. Several studies have shown that such silver–halide interactions are favorable and may be the first step in the mechanism of halide abstraction or substitution.[12,13] Clearly, if **7** could be prepared by an alternative route, its potential role in path A could be evaluated. Alas, attempts to produce **7** by deprotonation reactions of **5** have been uniformly unsuccessful; most bases either displace water or react by other pathways to produce hydrido complexes.[14]

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Finally, the unusual facility with which hydrolysis of the CF_2 group in **9** occurs is worthy of comment. Similar facile hydrolyses have been observed in the rhodium perfluorobenzyl complex **4** (vide supra),[2] in the transformation of metallacycle **11** to **12** under all but the most rigorous conditions of water exclusion,[15] and in the ring-linked complex **13**, which is rapidly transformed to **14** by even traces of adventitious moisture.[1] While the α-CF_2 hydrolysis in **4** has been shown unambiguously to involve the coordinated water molecule,[2] and that of **11** has been suggested to involve coordinated water,[15] the corresponding hydrolyses of **9** and **11** appear not to involve ligated water and may be a consequence of catalysis by traces of exogenous acid present, as observed for other systems.[16−18] The CF_2 groups in all these cases are unusually activated, with additional benzylic or allylic stabilization of the initially formed carbocation resulting from fluoride loss.

Experimental Section

General Considerations. All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of dinitrogen which had been deoxygenated over BASF catalyst and dried over Aquasorb, or in a Braun drybox. ^1H NMR (300 MHz), ^{19}F NMR (282.2 MHz), and ^{31}P NMR (121.4 MHz) spectra were recorded on a Varian Unity Plus 300 FT spectrometer at 23 °C; coupling constants were recorded in hertz. ^1H NMR chemical shifts were recorded as ppm downfield from tetramethylsilane and referenced to the solvent. ^{19}F NMR chemical shifts were recorded as ppm and internally referenced to $CFCl_3$. Chemical shifts for $^{31}P\{^1H\}$ NMR were recorded as ppm and externally referenced to 85% H_3PO_4. The infrared spectra were recorded on a Perkin-Elmer FTIR 1600 Series spectrometer. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Reagents. Hydrocarbon and ethereal solvents were distilled under dinitrogen from sodium or sodium/potassium alloy and benzophenone ketyl, and halogenated solvents from calcium hydride. Deuterated solvents were purchased from ISOTEC Inc. or Cambridge Isotope Laboratories. NMO (4-methylmorpholine-*N*-oxide) was purchased from Aldrich. Silver(I) oxide hydrate was prepared according to the literature method,[19] as were complexes **1** and **2**.[1]

[Rh(η^5-C_5Me_5)($CF_2C_6F_5$)I]$_2$ (5). Rh(η^5-C_5Me_5)($CF_2C_6F_5$)I(CO) (**1**; 250 mg, 0.410 mmol) was dissolved in methylene chloride (10 mL), and NMO (50 mg, 0.410 mmol) was added as a solid. The reaction mixture was stirred overnight. During the reaction a precipitate formed that was filtered via cannula. Washing the precipitate with benzene redissolved it, and it was added to the original solution. The ^{19}F NMR spectrum of the filtrate showed a single product (**5**), which was isolated after removal of the volatiles. Crystallization from methylene chloride and hexanes afforded deep red crystals (39%). ^1H NMR (C_6D_6): δ 1.28 (s). ^{19}F NMR (C_6D_6): δ −40.7 (t, J_{FF} = 29, 2F, $C_\alpha F_2$), −134.2 (m, 2F, ortho), −157.4 (t, J_{FF} = 22, 1F, para), −164.0 (m, 2F, meta). Anal. Calcd for $C_{34}H_{30}F_{14}I_2Rh_2$: C, 35.08; H, 2.60. Found: C, 34.59; H, 2.54.

Rh(η^5-C_5Me_5)($CF_2C_6F_4O$)(PMe_3) (9). Rh(η^5-C_5Me_5)($CF_2C_6F_5$)(I)(PMe_3) (**2**; 83 mg, 0.126 mmol) was dissolved in CH_2Cl_2 (5 mL) to give a orange-yellow solution. Freshly prepared $Ag_2O{\cdot}xH_2O$ (40 mg) was then added as a solid, and the solution turned a yellow color. The reaction mixture was stirred for 18 h and then filtered. The volatiles were removed under vacuum to give **9** as a yellow solid (52 mg, 78%). ^1H NMR (acetone-d_6): δ 1.73 (d, J_{HRh} = 3, 15H, C_5Me_5), 1.37 (d, J_{HP} = 11, 9H, PMe_3); (C_6D_6) δ 1.36 (d, J_{HRh} = 3, 15H, C_5Me_5), 0.84 (d, J_{HP} = 11, 9H, PMe_3); (CD_2Cl_2) δ 1.70 (d, J_{HRh} = 3, 15H, C_5Me_5), 1.33 (d, J_{HP} = 11, 9H, PMe_3). ^{19}F NMR (acetone-d_6): δ −47.3 (dm, J_{AB} = 234, J_{FP} = 27, J_{FF} = J_{FRh} = 8, 1F, $C_\alpha F_A$), −48.1 (ddt, J_{AB} = 234, J_{FP} = 40, J_{FF} = J_{FRh} = 12, 1F, $C_\alpha F_B$), −147.3 (m, 1F), −161.5 (t, J_{FF} = 20, 1F), −168.7 (m, 1F), −181.1 (m, 1F); (C_6D_6) δ −47.0 (m, 2F, CF_2), −146.5 (m, 1F), −159.9 (t, J_{FF} = 20, 1F), −168.4 (m, 1F), −179.3 (m, 1F); (CD_2Cl_2) δ −48.4 (m, 2F, CF_2), −148.2 (m, 1F), −161.1 (t, J_{FF} = 20, 1F), −169.1 (m, 1F), −180.3 (m, 1F). $^{19}F\{^{31}P\}$ NMR (acetone-d_6) δ −47.3 (dt, J_{AB} = 234, J_{FF} and J_{FRh} = 8, 1F, $C_\alpha F_A$), −48.1 (dt, J_{AB} = 234, J_{FF} and J_{FRh} = 12, 1F, $C_\alpha F_B$). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 6.4 (ddd, J_{PRh} = 160, J_{PF} = 40, J_{PF} = 27, PMe_3); (C_6D_6) δ 4.3 (ddd, J_{PRh} = 162, J_{PF} = 40, J_{PF} = 27, PMe_3); (CD_2Cl_2) δ 4.9 (ddd, J_{PRh} = 160, J_{PF} = 39, J_{PF} = 29, PMe_3). Accurate microanalysis was precluded by the facility of hydrolysis to **9** to give **10**.

Rh(η^5-C_5Me_5)(C(O)C_6F_4O)(PMe_3) (10). On standing in solution, under dinitrogen, compound **9** hydrolyzes quantitatively to the acyl **10**, which was isolated as yellow crystals from methylene chloride and hexanes. ^1H NMR (C_6D_6): δ 1.36 (d, J_{HRh} = 2.9, 15H, C_5Me_5), 0.70 (d, J_{HP} = 10.3, 9H, PMe_3). ^{19}F NMR (C_6D_6): δ −146.1 (m, 1F), −156.1 (t, J_{FF} = 21, 1F), −167.3 (m, 1F), −179.8 (m, 1F). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 2.9 (d, J_{PRh} = 166, PMe_3). The compound was also characterized by a single-crystal X-ray diffraction experiment.

Crystallographic Structural Determinations. Crystal, data collection, and refinement parameters for **5** and **10** are given in Table 1. The systematic absences in the diffraction data are uniquely consistent for the reported space groups. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Semiempirical absorption corrections were applied to the data sets. To maintain a better than 10:1 data-to-parameter ratio, the carbon atoms of the phenyl rings in **5** were isotropically refined. All other non-hydrogen atoms in **5** and all non-hydrogen atoms in **10** were refined with anisotropic displacement coefficients.

Acknowledgment. R.P.H. is grateful to the National Science Foundation and to the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support.

Supporting Information Available: Atomic fractional coordinates, bond distances and angles, and anisotropic thermal parameters for **5** and **10** are available free of charge via the Internet at http://pubs.acs.org.

OM0008171

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