Organometallics **1996,** *15,* 5678−5686

Perfluorobenzyl Complexes of Cobalt and Rhodium. Unusual Coupling between Pentafluorophenyl and Pentamethylcyclopentadienyl Rings

Russell P. Hughes* and Danielle C. Lindner

Department of Chemistry, Burke Chemistry Laboratory, Dartmouth College, Hanover, New Hampshire 03755-3564

Arnold L. Rheingold and Glenn P. A. Yap

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received August 22, 1996⊗

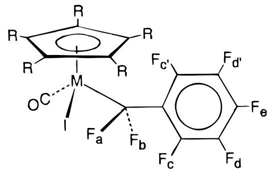
Oxidative addition of perfluorobenzyl iodide to [M(η^5-C_5R_5)(CO)$_2$] (M = Co, R = H, Me; M = Rh, R = Me) in benzene affords the perfluorobenzyl complexes [M(η^5-C_5R_5)($CF_2C_6F_5$)I(CO)] (M = Co, R = H (**1a**), Me (**2a**); M = Rh, R = Me (**2b**)). Further reaction of **1a** or **2a** with PMe_3 in benzene results in a substitution reaction to give complexes [Co(η^5-C_5R_5)($CF_2C_6F_5$)I(PMe_3)] (R = H (**3a**), Me (**4a**)) . While the reaction of (pentamethylcyclopentadienyl)cobalt complex **2a** with PMe_3 in benzene gives **4a**, the analogous reaction in THF results in alkyl C−H activation and aryl C−F activation, with coupling of the pentamethylcyclopentadienyl ligand and the perfluorobenzyl ligand, to give **9a**. Similarly, the reaction of **2a** with PMe_2Ph in THF affords the analogous ring-coupled complex **9b**, while reaction of the cyclopentadienyl analogue **1a** with PMe_2Ph affords the simple substitution product **5a**. In contrast to the reactions of the (pentamethylcyclopentadienyl)cobalt complexes, reaction of the rhodium analogue **2b** with PMe_3 or PMe_2Ph result in a simple substitution to give [Rh(η^5-C_5Me_5)($CF_2C_6F_5$)I(L)] (L = PMe_3 (**5a**) PMe_2Ph (**5b**)). Attempts to purify complexes **9** result in facile hydrolysis of the CF_2 group to give acyl complexes **10**. A mechanism is proposed for this coupling reaction, and an analogue **13** of a proposed cationic intermediate has been isolated and shown to react with iodide to afford **10**, via **9a**. Heating of **2a** results in a different coupling reaction to afford the organic cyclopentadiene **14**. The solid state structures of **3a**, **5b**, and **10b** were determined by X-ray crystallography.

Introduction

The recent commercial availability of perfluorobenzyl iodide prompted us to explore the synthesis and chemistry of perfluorobenzyl complexes of the transition metals. Except for the (perfluorobenzyl)cadmium and (perfluorobenzyl)copper reagents prepared by Burton and co-workers,[1] no (perfluorobenzyl)metal complexes appear to have been reported thus far. Here we describe the synthesis and structure of some cobalt and rhodium perfluorobenzyl complexes of the general formula [M(η^5-C_5R_5)($CF_2C_6F_5$)I(L)] (M = Co, Rh; R = H, Me; L = CO, PMe_3, PMe_2Ph). While *intra*molecular and *inter*molecular activation of aryl C−F bonds by transition metal centers has been observed in a number of systems,[2] activation of saturated C−F bonds has proven to be more difficult and seems to require a strongly reducing environment.[3] Similarly, while the hydrolysis of transition metal-CF_3 groups to give carbonyl ligands has been observed in several systems,[4−6] the reaction usually requires the presence of a strong Lewis acid like BF_3,[4a] SbF_5,[4b] or $SiMe_3$,[5] although there are some indications that H^+ can act as the initial fluoride acceptor in some instances. In contrast to the usual requirements for such hydrolysis reactions, we have observed an unusually facile hydrolysis reaction of benzylic C−F bonds in some of these complexes, and in one cobalt system, an unusually facile activation of an aryl C−F bond has been observed.

Results and Discussion

Perfluorobenzyl compounds of cobalt (**1a**, **2a**) and rhodium (**2b**) were readily prepared by the oxidative addition of perfluorobenzyl iodide to [M(η^5-C_5R_5)(CO)$_2$] (M = Co, R = H, Me; M = Rh, R = Me) in benzene at room temperature, in the manner previously reported for oxidative addition of fluoroalkyl iodides to [M(η^5-C_5H_5)(CO)$_2$] (M = Co,[7] Rh[8]). The reactions were monitored by solution IR and ^{19}F NMR spectroscopies to ensure that the complete reaction had occurred. The structures of compounds **1** and **2** were confirmed by ^1H



1a M = Co, R = H
2a M = Co, R = Me
2b M = Rh, R = Me

⊗ Abstract published in *Advance ACS Abstracts*, December 1, 1996.

[1] Burton, D. J.; Yang, Z. Y.; Platonov, V. *J. Fluorine Chem.* **1994**, *66*, 23−24.

[2] Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373−431.

[3] Harrison, R. G; Richmond, T. G. *J. Am. Chem. Soc.* **1993**, *115*, 5303−5304. Kiplinger, J. L.; Richmond, T. G. *Ibid.* **1996**, *118*, 1805−1806. Burdeniuc, J.; Crabtree, R. H. *Ibid.* **1996**, *118*,2525−2526.

S0276-7333(96)00725-X CCC: $12.00

Table 1. Infrared Stretching Frequencies (ν_{CO}) of CO Ligands in Perfluorobenzyl and Other Perfluoroalkyl Complexes of Cobalt and Rhodium

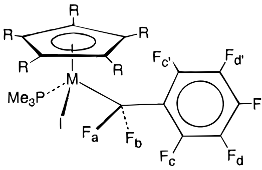
	ν_{CO} (cm^{-1}) (CH_2Cl_2)	ref
$Co(C_5H_5)(CF_2C_6F_5)(I)(CO)$ (**1a**)	2080	
$Co(C_5H_5)(CF_3)(I)(CO)$	2073	7a
$Co(C_5H_5)(C_2F_5)(I)(CO)$	2080^a	7a
$Co(C_5Me_5)(CF_2C_6F_5)(I)(CO)$ (**2a**)	2044	
$Co(C_5Me_5)(CF(CF_3)_2)(I)(CO)$	2062	7b
$Rh(C_5Me_5)(CF_2C_6F_5)(I)(CO)$ (**2b**)	2056	
$Rh(C_5H_5)(C_2F_5)(I)(CO)$	2098^a	8

[a] Infrared reported in CS_2.

and ^{19}F NMR spectroscopy, IR spectroscopy, and elemental analysis. The ^{19}F NMR spectra of all perfluorobenzyl complexes are similar, showing a characteristic AB splitting pattern for the diastereotopic fluorines of the α-CF_2 group located downfield of the 2:1:2 pattern of the three aromatic fluorine resonances between −140 and −160 ppm. The α-CF_2 resonances exhibit a large geminal coupling constant, J_{AB}, ranging from 205 to 250 Hz, and each shows a triplet coupling to the two ortho fluorines of the aromatic ring. As an example, the ^{19}F NMR spectrum of **1a** exhibits an AB splitting pattern, at δ −25.6 (dt, F_a) and −31.5 (dt, F_b) with the fluorine atoms on the aromatic ring appearing at δ −137.0, −153.7, and −162.5 in the expected 2:1:2 ratio. The pentafluorophenyl ring rotates freely about the $CF_2-C_6F_5$ bond on the NMR time scale, as evidenced from the NMR equivalence of the two ortho fluorines, even on cooling to −60 °C, and their triplet coupling to each of the CF_2 fluorines. That this triplet coupling is of a different magnitude to each CF_2 fluorine suggests (not unexpectedly) that the conformational ground state of the molecule does not have the plane of the fluoroaryl group bisecting the CF_2 group. In the rhodium analogue **1,c** any ^{103}Rh coupling to the CF_2 fluorines is too small to be resolved.

The infrared spectra of **1** and **2** each show a single high-frequency band characteristic of a single CO ligand bound to Co(III) or Rh(III), and the results are listed in Table 1 with those of other perfluoroalkyl analogues for comparison.

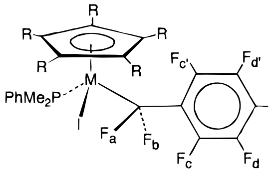
Reactions of **1** and **2** with 1 equiv of PMe_3 in *benzene* solution result in simple CO substitution to give **3** and **4**, respectively, in good yield. As expected for fluoroalkyl ligands,[9] no products resulting from the migratory insertion of CO into the fluoroalkyl−metal bond were observed. Complexes **3** and **4** were characterized spectroscopically and by elemental analysis. The solid state structure of **3a** was also obtained by X-ray diffraction. Crystallographic information for the structure determination of **3a** is given in Table 2, and a list of selected bond lengths and angles is provided in Table 3. An ORTEP plot with atom labeling scheme is shown in Figure 1. Discussion of the solid state structure is deferred until later.



3a M = Co, R = H
4a M = Co, R = Me
4b M = Rh, R = Me

The spectroscopic data obtained for the solution structure are consistent with the solid state structure. The presence of PMe_3 is manifested in the ^{19}F NMR spectrum as an additional doublet, ^{31}P coupling to the AB resonances of the diastereotopic CF_2 fluorines. In these substitution products (**3**, **4**, and **5**), one of the CF_2 fluorine atoms couples to ^{31}P more strongly than the other. The ^{31}P{^{1}H} NMR resonances corresponding to the cobalt substitution complexes are very broad, presumably as a result of the quadrupolar ^{59}Co isotope ($I = {}^7/_2$),[10] whereas those of the analogous rhodium complexes appear as the expected doublet of doublets, due to coupling with ^{103}Rh and one fluorine of the CF_2 group.

The preparations of complexes **5** by reaction of **1a** or **2b** with PMe_2Ph were similar to those of **3** and **4**, and the characterization methods were analogous. As expected, the methyl groups of the PMe_2Ph ligand are diastereotopic in complexes **5**, each methyl group appearing as a doublet in the ^{1}H NMR spectrum [J_{HP} =



5a M = Co, R = H
5b M = Rh, R = Me

Table 2. Crystallographic Data for 3a, 5b, and 10b

	3a	**10b**	**5b**
formula	$C_{15}H_{14}CoF_7IP$	$C_{25}H_{25}CoF_4IOP$	$C_{25}H_{26}F_7IPRh$
formula weight	544.1	634.3	720.2
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a, Å	10.422(3)	11.188(5)	8.778(3)
b, Å	11.830(3)	17.405(7)	14.170(2)
c, Å	14.573(4)	12.651(5)	21.145(4)
β, deg	100.160(2)	94.16(4)	100.05(4)
V, Å^3	1768.5(8)	2457(2)	2590(1)
Z	4	4	4
cryst color	brown	black	red
D (calc), g cm^{-3}	2.043	1.715	1.847
μ (Mo Kα), cm^{-1}	28.71	20.66	19.76
temp, K	293	296	296
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
$R(F)$, %^{a}	3.94	3.76	4.46
$R(wF)$, %^{a}	4.80	4.51	5.16

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

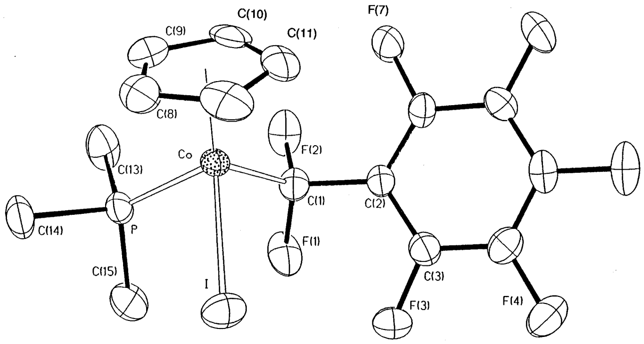


Figure 1. ORTEP drawing and labeling scheme for **3a**. Ellipsoids are drawn at 35% probability.Hydrogens have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3a

Co−I	2.583(1)	Co−P	2.204(2)
Co−C(1)	1.990(7)	Co−C(8)	2.118(10)
Co−C(9)	2.074(8)	Co−C(10)	2.059(8)
Co−C(11)	2.105(8)	Co−C(12)	2.129(9)
P−C(13)	1.815(8)	P−C(14)	1.813(9)
P−C(15)	1.811(9)	F(1)−C(1)	1.376(9)
F(2)−C(1)	1.390(7)	F(3)−C(3)	1.343(9)
F(4)−C(4)	1.342(8)	F(5)−C(5)	1.358(9)
F(6)−C(6)	1.343(9)	F(7)−C(7)	1.335(8)
C(1)−C(2)	1.536(10)	C(2)−C(3)	1.388(9)
C(2)−C(7)	1.392(9)	C(3)−C(4)	1.379(11)
C(4)−C(5)	1.358(11)	C(5)−C(6)	1.363(10)
C(6)−C(7)	1.368(10)	C(8)−C(9)	1.395(12)
C(8)−C(12)	1.406(13)	C(9)−C(10)	1.402(12)
C(10)−C(11)	1.402(11)	C(11)−C(12)	1.397(12)

I−Co−P	90.5(1)	I−Co−C(1)	97.5(2)
P−Co−C(1)	92.4(2)	I−Co−C(8)	97.6(2)
P−Co−C(8)	99.8(3)	C(1)−Co−C(8)	160.5(3)
I−Co−C(9)	135.3(3)	P−Co−C(9)	89.0(3)
C(1)−Co−C(9)	127.2(3)	C(8)−Co−C(9)	38.8(3)
I−Co−C(10)	151.4(2)	P−Co−C(10)	114.8(2)
C(1)−Co−C(10)	94.5(3)	C(8)−Co−C(10)	66.6(3)
C(9)−Co−C(10)	39.7(3)	I−Co−C(11)	113.0(2)
P−Co−C(11)	152.8(2)	C(1)−Co−C(11)	97.4(3)
C(8)−Co−C(11)	65.2(4)	C(9)−Co−C(11)	64.9(3)
C(10)−Co−C(11)	39.4(3)	I−Co−C(12)	86.8(2)
P−Co−C(12)	137.1(3)	C(1)−Co−C(12)	130.4(3)
C(8)−Co−C(12)	38.7(4)	C(9)−Co−C(12)	64.5(3)
C(10)−Co−C(12)	65.8(3)	C(11)−Co−C(12)	38.5(3)
Co−P−C(13)	114.5(3)	Co−P−C(14)	111.9(3)
C(13)−P−C(14)	104.6(4)	Co−P−C(15)	120.7(3)
C(13)−P−C(15)	101.3(4)	C(14)−P−C(15)	101.8(4)
Co−C(1)−F(1)	114.8(5)	Co−C(1)−F(2)	110.0(4)
F(1)−C(1)−F(2)	102.6(5)	Co−C(1)−C(2)	116.5(5)
F(1)−C(1)−C(2)	105.6(5)	F(2)−C(1)−C(2)	106.2(5)
C(1)−C(2)−C(3)	122.8(6)	C(1(−C(2)−C(7)	122.3(6)
C(3)−C(2)−C(7)	114.8(6)	F(3)−C(3)−C(2)	121.1(6)
F(3)−C(3)−C(4)	116.4(6)	C(2)−C(3)−C(4)	122.5(7)
F(4)−C(4)−C(3)	119.3(7)	F(4)−C(4)−C(5)	120.8(7)
C(3)−C(4)−C(5)	119.9(7)	F(5)−C(5)−C(4)	119.1(7)
F(5)−C(5)−C(6)	120.9(7)	C(4)−C(5)−C(6)	120.0(7)
F(6)−C(6)−C(5)	119.9(7)	F(6)−C(6)−C(7)	120.6(6)
C(5)−C(6)−C(7)	119.5(7)	F(7)−C(7)−C(2)	120.7(6)
F(7)−C(7)−C(6)	116.0(6)	C(2)−C(7)−C(6)	123.2(6)

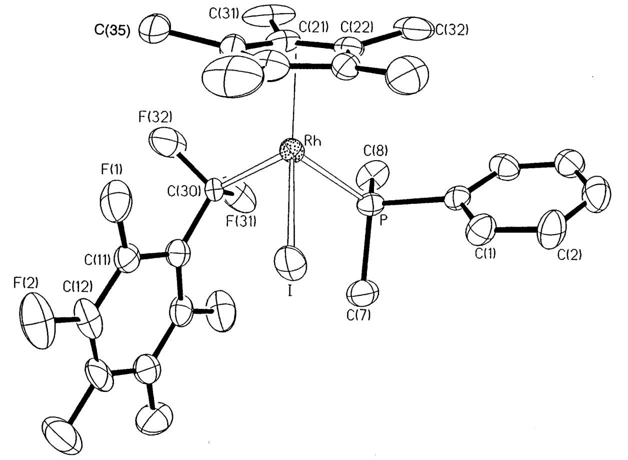


Figure 2. ORTEP drawing and labeling scheme for **5b**. Ellipsoids are drawn at 35% probability.Hydrogens have been omitted for clarity.

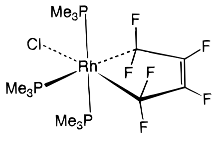
Table 4. Selected Bond Lengths (Å) and Angles (deg) for 5b

Rh−I	2.706(1)	Rh−P	2.305(3)
Rh−C(30)	2.190(11)	Rh−C(21)	2.153(10)
Rh−C(22)	2.217(9)	Rh−C(23)	2.251(10)
Rh−C(24)	2.255(11)	Rh−C(25)	2.251(11)
P−C(7)	1.804(10)	P−C(8)	1.804(12)
P−C(6)	1.815(10)	C(30)−C(16)	1.486(14)
C(30)−F(31)	1.257(14)	C(30)−F(32)	1.327(12)
C(1)−C(2)	1.374(15)	C(1)−C(6)	1.386(15)
C(2)−C(3)	1.361(18)	C(3)−C(4)	1.365(18)
C(4)−C(5)	1.348(17)	C(5)−C(6)	1.389(14)
C(11)−C(12)	1.356(15)	C(11)−C(16)	1.405(16)
C(11)−F(1)	1.334(13)	C(12)−C(13)	1.334(23)
C(12)−F(2)	1.327(17)	C(13)−C(14)	1.373(21)
C(13)−F(3)	1.331(15)	C(14)−C(15)	1.350(17)
C(14)−F(4)	1.329(15)	C(15)−C(16)	1.392(15)
C(15)−F(5)	1.334(15)		

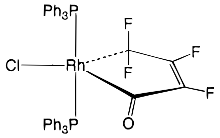
I−Rh−P	91.3(1)	I−Rh−C(30)	97.1(3)
P−Rh−C(30)	89.7(3)	I−Rh−C(21)	151.8(3)
P−Rh−C(21)	112.3(3)	C(30)−Rh−C(21)	98.2(4)
I−Rh−C(22)	130.2(3)	P−Rh−C(22)	94.0(3)
C(30)−Rh−C(22)	132.3(4)	C(21)−Rh−C(22)	37.4(4)
I−Rh−C(23)	96.5(3)	P−Rh−C(23)	109.6(3)
C(30)−Rh−C(23)	156.1(4)	C(21)−Rh−C(23)	61.9(4)
C(22)−Rh−C(23)	35.8(4)	I−Rh−C(24)	91.0(3)
P−Rh−C(24)	146.9(3)	C(30)−Rh−C(24)	122.7(5)
C(21)−Rh−C(24)	60.7(4)	C(22)−Rh−C(24)	60.3(4)
C(23)−Rh−C(24)	37.4(4)	I−Rh−C(25)	117.7(3)
P−Rh−C(25)	149.6(3)	C(30)−Rh−C(25)	95.1(4)
C(21)−Rh−C(25)	37.3(5)	C(22)−Rh−C(25)	61.1(4)
C(23)−Rh−C(25)	61.2(4)	C(24)−Rh−C(25)	35.0(5)
Rh−P−C(7)	117.2(4)	Rh−P−C(8)	115.7(4)
C(7)−P−C(8)	102.2(5)	Rh−P−C(6)	114.6(3)
C(7)−P−C(6)	101.0(5)	C(8)−P−C(6)	104.0(5)
Rh−C(30)−C(16)	117.2(7)	Rh−C(30)−F(31)	111.6(7)
C(16)−C(30)−F(31)	110.0(9)	Rh−C(30)−F(32)	105.9(7)
C(16)−C(30)−F(32)	105.9(8)	F(31)−C(30)−F(32)	105.3(9)
C(2)−C(1)−C(6)	121.1(10)	C(1)−C(2)−C(3)	120.4(12)
C(2)−C(3)−C(4)	119.2(12)	C(3)−C(4)−C(5)	120.7(11)
C(4)−C(5)−C(6)	121.8(11)	P−C(6)−C(1)	119.6(8)
P−C(6)−C(5)	123.7(8)	C(1)−C(6)−C(5)	116.6(9)
C(12)−C(11)−C(16)	123.2(11)	C(12)−C(11)−F(1)	118.0(11)
C(16)−C(11)−F(1)	118.8(9)	C(11)−C(12)−C(13)	121.0(13)
C(11)−C(12)−F(2)	118.4(13)	C(13)−C(12)−F(2)	120.5(11)
C(12)−C(13)−C(14)	119.2(12)	C(12)−C(13)−F(3)	121.7(13)
C(14)−C(13)−F(3)	119.1(14)	C(13)−C(14)−C(15)	119.4(12)
C(13)−C(14)−F(4)	120.4(12)	C(15)−C(14)−F(4)	120.0(13)
C(14)−C(15)−C(16)	124.4(12)	C(14)−C(15)−F(5)	115.6(10)
C(16)−C(15)−F(5)	120.0(9)		

11.1 (**5a**) and 10.5 (**5b**) Hz]. Curiously, the benzylic CF_2 resonances of **5b** appear as a broad singlet. Rapid inversion of configuration at the metal center is precluded by the observation of diastereotopic Me groups for the PMe_2Ph ligand (vide supra); the CF_2 fluorines are likely to have approximately coincidental chemical shifts. To confirm its identity, the solid state structure of **5b** was also determined by X-ray diffraction. Crystallographic information for the structure determination of **5b** is given in Table 2, and a list of selected bond lengths and angles is given in Table 4. An ORTEP plot with atom labeling scheme is presented in Figure 2.

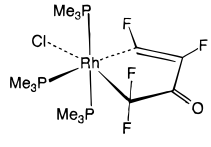
The solid state structures of **3a** and **5b** show some similarities and some significant differences. In both complexes, the metal has a pseudooctahedral geometry with the cyclopentadienyl ligand occupying three *fac* coordination sites. Interligand bond angles I−Co−P, I−Co−C(1), and P−Co−C(1) for **3a** and I−Rh−P, I−Rh−C(30), and P−Rh−C(30) for **5b** are approximate 90°. For cobalt complex **3a**, the Co−C(1) distance (1.990(7) Å) is similar to the Co−CF_2 distances in the cobalt *n*-perfluoropropyl complexes reported by Jablonski and co-workers: [Co(η^5-indenyl)(n-C_3F_7)I($Ph_2PNHCH(CH_3)$-(Ph))] = 1.962(2) Å,[11] [Co(η^5-indenyl)(n-C_3F_7)I(PMe_3)-(P(O)($OMe)_2$)] = 1.972(4) Å, [Co(η^5-indenyl)(n-C_3F_7)I(PMe_3)(P(O)Ph(OMe))] = 1.987(7) Å, [Co(η^5-indenyl)(n-C_3F_7)I(PMe_2Ph)(P(O)Ph(OMe))] = 1.979(5) Å, and [Co-(η^5-C_5H_5)(n-C_3F_7)I(PMe_3)(P(O)Ph(OMe))] = 1.968(4) Å.[12] The Co−P distance in **3a** (2.210(2) Å) is also similar to the Co−P distances in the (*n*-perfluoropropyl)cobalt complexes mentioned above.[12] In contrast, the Rh−CF_2 distance in **5b** is significantly longer than that in [Rh-(C_5H_5)(C_2F_5)I(CO)][13] (2.190(11) vs 2.08(3) Å) and longer than those in the metallacyclic complexes **6** (2.075(6), 2.024(6) Å), **7** (2.013(5) Å), and **8** (2.034(4) Å).[14] On the other hand, the Rh−P bond distance in **5b** (2.305(3) Å) is significantly shorter than those in **6** (2.386(2), 2.400(2), 2.378(2) Å) or **8** (2.362(1), 2.379(1), 2.367(1) Å).[14] The expected higher p-character in the carbon orbitals to fluorine is reflected in the typically acute bond angles[15,16] in the CF_2 groups of **3a** (102.6(5)°) and **5b** (105.3(5)°), with correspondingly more obtuse angles between the metal−CF_2−C_{ipso} found in **3a** (116.5(5)°) and **5b** (117.2(7)°). Further manifestation of the high p-character inthe carbon orbitals to fluorine and the correspondingly high s-character in the carbon orbital to the metal is provided in a comparison of the structure of **3a** with a different complex, described below.



6



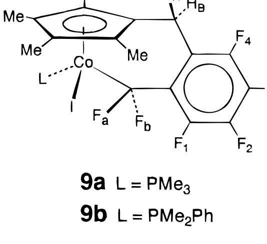
7



8

Comparison of **3a** and **5b** also reveals some differences in their solid state structures. The C−F distances in the CF_2 group in **5b** (1.257(14), 1.327(12) Å) are significantly shorter than those in **3a** (1.376(9), 1.390(7) Å). The conformation of the perfluorobenzyl ligand is also quite different. In **3a**, the pentafluorophenyl ring is directed away from the trimethylphosphine ligand, as expected, but also tilts toward the cyclopentadienyl ring, with F(7) being particularly close. While the H-atoms on the cyclopentadienyl carbons of **3a** were not located crystallographically, assumption of a reasonable C−H bond length of 1.00 Å for the H-atoms bound to C(10) and C(11) brings these H-atoms within 2.53 and 2.59 Å, respectively, of F(7), distances less than the sum of the van der Waals' radii (2.67 Å), indicative of weak intramolecular hydrogen bonding.[17] This interaction is far too weak to have any effect on the conformational dynamics of the pentafluorophenyl ring in solution, where it rotates freely on the NMR time scale (vide supra), but it may be a factor in favoring the solid state conformation. In contrast, and not unexpectedly, the perfluorobenzyl ligand in **5b** adopts a conformation in which the pentafluorophenyl ring tilts away from the much bulkier pentamethylcyclopentadienyl (Cp*) ligand. Even so, there are some necessarily close H···F contacts in this structure; making analogous assumptions as to the positions of the H-atoms, the ortho fluorine F(1) must be within 2.60 Å of a H-atom on C(35), the benzylic fluorine F(32) must be within 2.27 Å of the very same H-atom, and the other benzylic fluorine, F(31), is within 2.25 Å of a H-atom on the phosphorus methyl carbon C(8). Thus, weak hydrogen bonding interactions may be important in defining thepreferred conformations of these molecules; certainly H−F distances of this magnitude have been interpreted similarly in organic systems.[18]

While the cobalt complex **2a** reacts with PMe_3 in *benzene* to give **4a**, the corresponding reaction in *THF* results in a completely different pathway, in which a coupling of one methyl group of the pentamethylcyclopentadienyl ligand with one ortho position of the perfluorobenzyl ligand has occurred, affording **9a**. Hydrogen fluoride is evolved and was identified in the volatiles trapped from the reaction mixture by ^{19}F NMR (THF) at δ −194.2 (J_{HF} = 438 Hz).[19] The structural assignment for **9a** is based on the spectroscopic evidence and on the X-ray structure of a derivative described below.



9a L = PMe_3
9b L = PMe_2Ph

The ^{19}F NMR spectrum of **9a** shows diastereotopic CF_2 fluorines but only four aromatic fluorine resonances of

---

(4) (a) Richmond, T. G.; Crespi, A. M.; Shriver, D. F. *Organometallics* **1984**, *3*, 314−319. (b) Reger, D. L.; Dukes, M. D. *J. Organomet. Chem.* **1978**, *153*, 67.

(5) Koola, J. D.; Roddick, D. M.*Organometallics* **1981**, *10*, 591−597.

(6) Michelin, R. A.; Ros, R.; Guadalupi, G.; Bombieri, G.; Benetollo, F.; Chapius, G. *Inorg. Chem.* **1989**, *28*, 840−846.

(7) (a) King, R.; Treichel, P.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3593. (b) King, R. B.; Efraty, A.; Douglas, W. M. *J. Organomet. Chem.* **1973**, *56*, 345−355.

(8) McCleverty, J.; Wilkinson, G. *J. Chem. Soc.* **1964**,4200−4203.

(9) Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166. Calderazzo, F. *Angew. Chem.* **1977**, *89*, 305.

(10) Friebolin, H. *Basic One-and Two-Dimensional NMR Spectroscopy*; VCH Verlagsgesellschaft: Weinheim, FRG, 1991, p 344.

(11) Jablonski, C.; Zhou, Z.; Bridson, J. N. *J. Organomet. Chem.* **1992**, *429*, 379−389.

(12) Zhou, Z.; Jablonski, C.; Bridson, J. *Organometallics* **1994**, *13*, 781−794.

(13) Churchill, M. R. *Inorg. Chem.* **1965**, *4*, 1734−1739.

(14) Hughes, R. P.; Rose, P. R.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3109−3117.

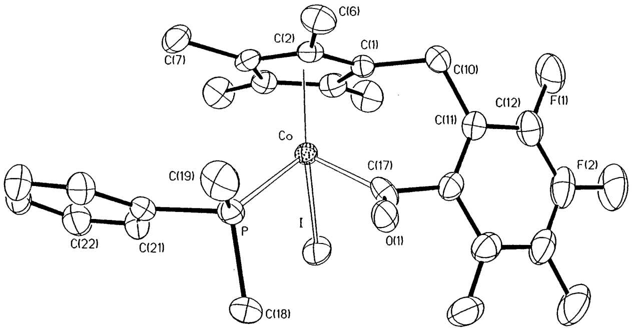


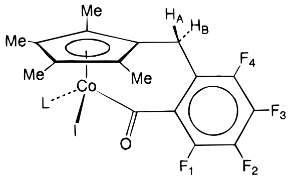
Figure 3. ORTEP drawing and labeling scheme for **10b**. Ellipsoids are drawn at 35% probability. Hydrogens have been omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 5b

Co−I	2.595(1)	Co−P	2.210(2)
Co−C(1)	2.071(4)	Co−C(2)	2.067(4)
Co−C(3)	2.168(4)	Co−C(4)	2.182(5)
Co−C(5)	2.128(5)	Co−C(17)	1.972(5)
P−C(18)	1.824(6)	P−C(19)	1.817(6)
P−C(26)	1.822(6)	O(1)−C(17)	1.118(6)
F(1)−C(12)	1.367(7)	F(2)−C(13)	1.356(8)
F(3)−C(14)	1.322(7)	F(4)−C(15)	1.343(7)
C(1)−C(2)	1.418(7)	C(1)−C(5)	1.408(7)
C(1)−C(10)	1.507(7)	C(2)−C(3)	1.431(6)
C(2)−C(6)	1.498(7)	C(3)−C(4)	1.405(7)
C(3)−C(7)	1.505(7)	C(4)−C(5)	1.434(7)
C(4)−C(8)	1.507(7)	C(5)−C(9)	1.511(8)
C(10)−C(11)	1.513(7)	C(11)−C(12)	1.372(8)
C(11)−C(16)	1.387(7)	C(12)−C(13)	1.390(9)
C(13)−C(14)	1.351(9)	C(14)−C(15)	1.391(9)
C(15)−C(16)	1.375(7)	C(16)−C(17)	1.520(7)
I−Co−P	93.8(1)	I−Co−C(1)	120.3(1)
P−Co−C(1)	145.8(1)	I−Co−C(2)	157.5(1)
P−Co−C(2)	106.9(1)	C(1)−Co−C(2)	40.1(2)
I−Co−C(3)	132.4(1)	P−Co−C(3)	94.2(1)
C(1)−Co−C(3)	65.4(2)	C(2)−Co−C(3)	39.4(2)
I−Co−C(4)	97.9(1)	P−Co−C(4)	115.6(1)
C(1)−Co−C(4)	65.4(2)	C(2)−Co−C(4)	65.5(2)
C(3)−Co−C(4)	37.7(2)	I−Co−C(5)	91.2(1)
P−Co−C(5)	154.4(1)	C(1)−Co−C(5)	39.2(2)
C(2)−Co−C(5)	66.3(2)	C(3)−Co−C(5)	64.5(2)
C(4)−Co−C(5)	38.8(2)	I−Co−C(17)	90.5(1)
P−Co−C(17)	89.8(1)	C(1)−Co−C(17)	87.8(2)
C(2)−Co−C(17)	98.1(2)	C(3)−Co−C(17)	136.4(2)
C(4)−Co−C(17)	152.5(2)	C(5)−Co−C(17)	115.3(2)
Co−P−C(18)	116.8(2)	Co−P−C(19)	115.6(2)
C(18)−P−C(19)	101.6(3)	Co−P−C(26)	113.8(2)
C(18)−P−C(26)	102.6(3)	C(19)−P−C(26)	104.7(3)
Co−C(1)−C(2)	69.8(2)	Co−C(1)−C(5)	72.6(3)
C(2)−C(1)−C(5)	108.6(4)	Co−C(1)−C(10)	125.4(3)
C(2)−C(1)−C(10)	126.4(4)	C(5)−C(1)−C(10)	124.9(4)
Co−C(2)−C(1)	70.1(2)	Co−C(2)−C(3)	74.1(2)
C(1)−C(2)−C(3)	107.2(4)	Co−C(2)−C(6)	128.7(3)
C(1)−C(2)−C(6)	126.4(4)	C(3)−C(2)−C(6)	125.7(4)
Co−C(3)−C(2)	66.5(2)	Co−C(3)−C(4)	71.7(3)
C(2)−C(3)−C(4)	108.5(4)	Co−C(3)−C(7)	133.7(3)
C(2)−C(3)−C(7)	125.4(4)	C(4)−C(3)−C(7)	125.6(4)
Co−C(4)−C(3)	70.6(3)	Co−C(4)−C(5)	68.5(3)
C(3)−C(4)−C(5)	107.7(4)	Co−C(4)−C(8)	130.5(3)
C(3)−C(4)−C(8)	126.5(4)	C(5)−C(4)−C(8)	125.6(5)
Co−C(5)−C(1)	68.2(3)	Co−C(5)−C(4)	72.6(3)
		Co−C(5)−C(9)	131.1(4)

equal intensity; the doublet of doublets of doublets pattern for one of the CF_2 resonances indicates that only one ortho fluorine atom is coupling to the α-CF_2 group . The ^1H NMR spectrum shows four inequivalent methyl groups for the tetramethylcyclopentadienyl ligand, two inequivalent, strongly coupled (J_{AB} = 15.6 Hz) methylene hydrogens, and a doublet at δ 1.30 for the PMe_3 ligand. An analogous product **9b** is observed in the reaction of **2a** and PMe_2Ph in *THF* and has been characterized similarly spectroscopically. No evidence for any ring-coupling products was obtained in the reactions of the rhodium analogue **2b**.

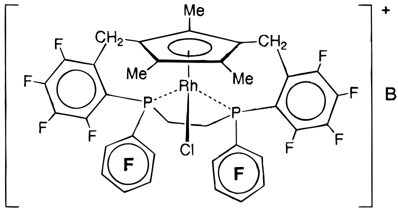
Complexes **9** were difficult to purify owing to rapid conversion to new compounds **10** via hydrolysis of the CF_2 group to a ketone; notably, this hydrolysis reaction proceeded even under "anhydrous" conditions, but could be inhibited by adding excess $CaCO_3$ to the reaction mixtures. The slightly more stable **9a** could be crystallized for microanalysis, whereas **9b** converted too rapidly to **10b** in solution. In contrast to progenitors **9**, the solution IR spectra of **10** reveal bands at ca. 1610 cm^{-1} for the acyl group and the ^{19}F NMR spectra lack resonances due to the CF_2 group. The solid state structure of **10b** was also obtained and confirms the structure indicated by the solution data. The crystallographic information for the structure determination of **10b** is given in Table 2, and a list of selected bond lengths and angles is given in Table 5. An ORTEP plot with atom labeling scheme is presented in Figure 3.



10a L = PMe_3
10b L = PMe_2Ph

Once again, the metal has a pseudooctahedral geometry with the Cp ligand occupying three *fac* coordination sites and interligand bond angles I−Co−P, I−Co−C(17), and P−Co−C(17) of approximately 90°. The distance from the metal to the three-coordinate acyl carbon in **10b**, Co−C(17) (1.972(5) Å), is identical within experimental error to that between cobalt and the four-coordinate fluorobenzylic carbon in **3a**, Co−C(1) (1.990(7) Å). This perhaps emphasizes the increased s-character expected in the carbon orbital to cobalt in **3a**, induced by the presence of two fluorines.

Compounds **10** represent the products of an unusual, but not unprecedented, coupling of a methyl group of Cp* with a pentafluorophenyl ring. Saunders and coworkers[20] recently reported a similar intramolecular coupling in the reaction of $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ with 1,2-bis[bis(pentafluorophenyl)phosphino]ethane to give **11**, crystallographically characterized as its BF_4^- salt. This product is the result of coupling of two methyl groups with two fluoroaryl carbon atoms, resulting in two new



11

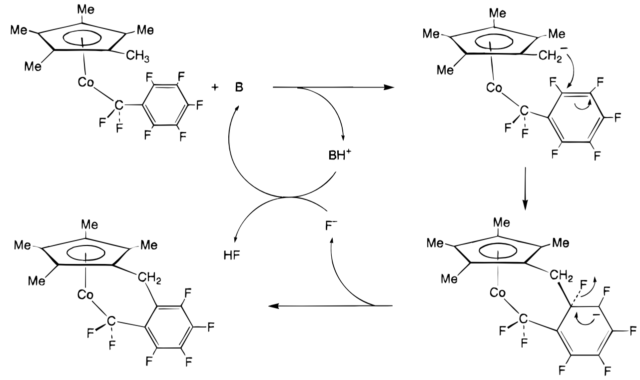
---

(15) Smart, B. E. In *The Chemistry of Functional Groups, Supplement D:* Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1983; Chapter 14.

(16) Bernett, W. A. *J. Org. Chem.* **1969**, *34*, 1772. Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(17) Smart, B. E. *Organofluorine Chemistry*; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum Press: New York, 1994; p 69.

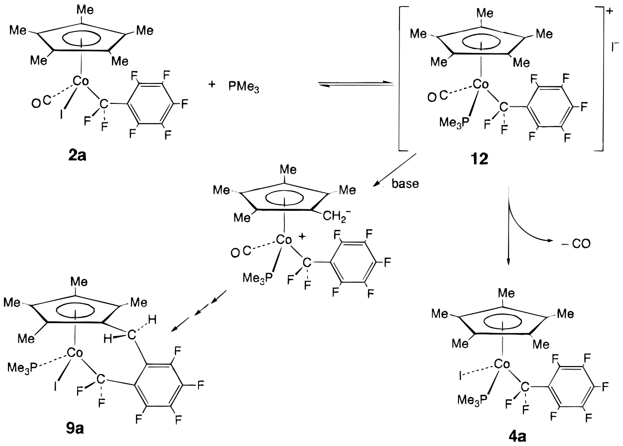
Scheme 1

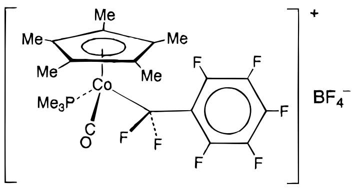


C−C bonds between the respective ortho aryl carbon atoms and the exocyclic carbons of Cp*. The HF which presumably must also accompany this coupling reaction was not identified. The authors suggest an electron transfer initiated mechanism involving the initial transfer of an electron from the Cp* ring to the fluoroarene;[20] an analogous pathway has been proposed for the C−F activation observed in the reaction of C_6F_6 with IrMe-$(PEt_3)_3$.[21] However, the latter reaction involves an Ir(I) precursor, whereas the metal center in the precursors for **11** or **9** are formally in the M(III) oxidation state and would be less likely to reduce a fluoroarene. A more likely pathway available in our system would involve deprotonation of a methyl group on the Cp* ring to give a fulvene intermediate, followed by nucleophilic addition−elimination of fluoride from the ortho-position of the pentafluorophenyl ring as shown in Scheme 1. However, as noted by the authors who prepared **11**,[20] deprotonation of the Cp* ligand to give fulvene−rhodium complexes requires a strong base[22] and it is not obvious what that base may be in their system; a similar concern pertains to formation of complexes **9**. We speculate in Scheme 1 that a trace of base (B) can initiate the reaction, and then the fluoride ion that is produced can act as a base giving HF, which we have observed (vide supra), thereby propagating the reaction. Surprisingly, treatment of either the starting material **2a** or the simple substitution product **4a** with bases such as LDA, $N(^iPr)_2Et$, or ^tBuLi did not result in coupling of the two rings, indicating that if deprotonation of the pentamethylcyclopentadienyl ligand is indeed a crucial step, it must occur at some intermediate stage in the overall substitution reaction rather than directly from starting material **2a** or substitution product **4a**.

A reasonable intermediate in the substitution reaction would result from substitution of phosphine for I^- in **2a** to give cation **12** as shown in Scheme 2. Indeed, Jablonski and co-workers[12] have investigated the reactions of $[Co(\eta^5\text{-}C_5H_5)(n\text{-}C_3F_7)(I)(L)]$ ($L = P(OMe)_3$, PMe_3) with $PR(OMe)_2$ ($R = OMe$, Ph) which afford analogous ionic species. We expect the methyl protons in cation **12** to be more acidic than those in starting material **2a** or product **4a** deprotonatation occurs more easily, and the resultant carbanion can then initiate the observed coupling reaction. Although attempts to isolate **12**, or to observe it during the course of the reaction, were unsuccessful, the BF_4^- analog **13** was readily synthesized from reaction of **4a** with $AgBF_4$ in the presence of CO. The solution IR spectrum of **13** shows a carbonyl band at 2060 cm^{-1} compared to starting complex **2a** (2044 cm^{-1}), consistent with a cationic cobalt center in **13**, and the NMR spectra are very similar to others described herein. In support of our hypothesis, the treatment of **13** with bis(triphenylphosphine)nitrogen(1+) iodide $[PPN^+I^-]$ in attempts to give **12** instead affords the ring coupling to give **10a** as the major product, presumably via **9a**, as well as small amounts of **2a** and **4a**. Apparently iodide can act as either the nucleophile or the initiating base in this reaction.

Scheme 2





13

Why is there no observed ring coupling during the substitution reactions of the rhodium analogue **2b**, especially in view of the facility of an analogous coupling in the related system to afford **11**? In the putative progenitor for rhodium complex **11**, one pentafluorophenyl group on each phosphorus must be in close proximity to the Cp* ligand, with a restricted conformational flexibility being imposed by coordination of the chelating diphosphine. In complex **2a**, the smaller cobalt center is also expected to be sterically congested, with the Cp* and pentafluorophenyl group spending some of their time in close proximity. In the rhodium derivatives, the larger metal center means a longer distance between Cp* and the pentafluorophenyl ring, without significant conformational restraints imposed on the perfluorobenzyl ligand. So, even if deprotonation of a methyl group can occur during the substitution mechanism of **2b**, any

---

(18) Huang, J.; Hedberg, K. *J. Am. Chem. Soc.* **1989**, *111*, 6909.

(19) Muenter, J. S.; Klemperer, W. *J. Chem. Phys.* **1970**, *52*, 6033.

(20) Atherton, M. J.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Karacar, A.; Russell, D. R.; Saunders, G. C. *J. Chem. Soc., Chem. Commun.* **1995**, 191−192. Atherton, M. J.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Karacar, A.; Russell, D. R.; Saunders, G. C. *J. Chem. Soc., Dalton Trans.* **1996**, 3215−3220.

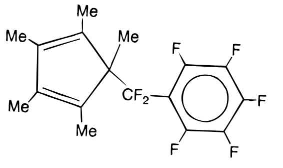
(21) Blum, O.; Frolow, F.; Milstein, D. *J Chem. Soc., Chem. Commun.* **1991**, 258.

(22) Gusev, O. V.; Sergeev, S.; Saez, I. M.; Maitlis, P. M. *Organometallics* **1994**, *13*, 2059. Miguel-Garcia, J. A.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1472−1473. Glueck, D. S.; Bergman, R. G. *Organometallics* **1990**, *9* , 2862−2863.

resultant nucleophilic attack on the pentafluorophenyl ring is likely to be entropically disfavored compared to **2a**.

The facility of hydrolysis of the CF_2 group in complexes **9** is also remarkable when compared to the lack of hydrolytic reactivity of the CF_2 groups in complexes **1**−**5**. By analogy with previously studied reactions of this type, we assume that such hydrolysis requires the presence of a fluoride acceptor (a Lewis or protic acid) and, of course, the adventitious moisture as the source of the oxygen atom in the final product. The pathway by which compounds **9** are formed also yields HF as a reaction product, and we suggest that this can initiate the hydrolysis mechanism in a manner similar to those suggested in the literature.[4,23] Traces of HF act as the initial fluoride acceptor to give a carbocation that is stabilized by π-back-bonding from the metal. Nucleophilic attack on carbon by adventitious water, followed by loss of 2 equiv of HF, affords the final ketone product and generates more HF to act as a fluoride abstractor. We have shown previously[14] that even glass surfaces that have been flame dried can still infuse sufficient water as a reagent to a reactive center, especially on the small scales on which these reactions are performed. Protection of the glass surface by silylation, or some other method of isolating the contained solution from the surface, is essential to exclude such moisture. A more detailed study on the role of trace protic acids, fluoride acceptors, and surface moisture on the hydrolysis reactions of saturated fluorocarbons is underway in our laboratories and will be published in due course.

Finally we have observed that heating **2a** at 80 °C for prolonged periods in benzene solution results in a direct coupling reaction of the perfluorobenzyl and pentamethylcyclopentadienyl ligands to give cyclopentadiene **14** in 20% yield. The diene was characterized by ^1H and ^{19}F NMR spectroscopy and gas chromatography/mass spectrometry (GC/MS). The ^1H NMR (C_6D_6)-spectrum reveals three singlets in a 1:2:2 ratio corresponding to the methyl groups, and the ^{19}F NMR (C_6D_6) reveals the expected four different types of fluorine resonances. The CF_2 resonance in **14** is shifted upfield from its position in the starting material. The three resonances due to the aromatic fluorine substituents appeared in positions similar to those of complexes described previously. GC/MS data reveal that the highest molecular weight ion peak corresponded to the molecular weight of the coupled organic fragment.



14

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 Hz. ^1H NMR chemical shifts were recorded in deuteriobenzene as ppm downfield from tetramethylsilane, unless otherwise stated, and referenced to the solvent. ^{19}F NMR chemical shifts were recorded in deuteriobenzene, unless otherwise stated, as ppm and internally referenced to $CFCl_3$. Chemical shifts for $^{31}P\{^1H\}$ NMR were recorded in deuteriobenzene, unless otherwise stated, 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. PMe_3 (Aldrich), $C_6F_5CF_2I$ (PCR), PMe_2Ph, $Co_2(CO)_8$, and pentamethylcyclopenta-1,3-diene (Strem), $[Co(C_5H_5)(CO)_2]$ (Aldrich or Strem), 1, 3-cyclohexadiene (Lancaster), $AgBF_4$ [Ato-Chem (North America)], and CO (Matheson) were purchased commercially. $[Co(C_5Me_5)(CO)_2]$,[24] $[Co(C_5R_5)(CO)(PMe_2Ph)]$ (R = H, Me),[25] and $[Rh(C_5Me_5)(CO)_2]$[26] were prepared according to literature methods. $(Ph_3P{=}N{=}PPh_3)^+I^-$ $[PPN^+I^-]$ was prepared by anion exchange from the corresponding chloride, which was obtained from Johnson-Matthey. Hydrocarbon and ethereal solvents were distilled under dinitrogen from sodium or sodium/potassium alloy and benzophenone ketyl, and halogenated solvents were distilled from calcium hydride. Deuterated solvents were purchased from ISOTEC, Inc., or Cambridge Isotope Laboratories.

(η^5-Cyclopentadienyl)iodo(perfluorobenzyl)carbonylcobalt(III) (1a). $[Co(C_5H_5)(CO)_2]$ (641 mg, 3.56 mmol) was dissolved in benzene (35 mL), $C_6F_5CF_2I$ (930 mg, 2.70 mmol) was added, and the reaction mixture was stirred at room temperature (46 h). Volatiles were removed under vacuum leaving behind a green-black solid, which was dissolved in diethyl ether. The solution was filtered via cannula, and the filtrate was concentrated. The product crystallized from ethyl ether at −78 °C as dark brown crystals (1.02 g, 76%). Mp: 118−119 °C. ^1H NMR (C_6D_6) δSPCLN 4.49 (s, 5H, C_5H_5). ^{19}F NMR (C_6D_6) δSPCLN −25.6 (dt, $J_{F_aF_b} = 207$, $J_{F_aF_{cc'}} = 30$, 1F, F_a), −31.5 (dt, $J_{F_aF_b} = 207$, $J_{F_bF_{cc'}} = 33$, 1F, F_a), −137.0 (m, 2F, $F_{cc'}$), −153.7 (t, $J_{FF} = 21$, 1F, F_e), −162.5 (m, 2F, $F_{dd'}$). IR (CH_2Cl_2): $\nu_{CO} = 2080\ cm^{-1}$. Anal. Calcd for $C_{13}H_5CoF_7IO$: C, 31.48; H, 1.02. Found: C, 31.55; H, 1.10.

(η^5-Pentamethylcyclopentadienyl)iodo(perfluorobenzyl)carbonylcobalt(III) (2a). A solution of $[Co(C_5Me_5)(CO)_2]$ (2.70 g, 10.8 mmol) in benzene (70 mL) was treated with $C_6F_5CF_2I$ (3.82 g, 11.1 mmol), and the mixture was stirred at room temperature (1 h). Similar workup gave the product as black crystals (5.70 g, 93%). Mp: 126−128 °C. ^1H NMR (C_6D_6) δ: 1.49 (15H, C_5Me_5). ^{19}F NMR (C_6D_6) δ: −50.6 (d, $J_{F_aF_b} = 217$, $J_{F_aF_{cc'}} = 27$, 1F, F_a), −58.4 (d, $J_{F_aF_b} = 217$, $J_{F_bF_{cc'}} = 36$, 1F, F_b), −136.1 (m, 2F, $F_{cc'}$), −155.1 (t, $J_{FF} = 21$, 1F, F_e), −163.3 (m, 2F, $F_{dd'}$). IR (CH_2Cl_2): $\nu_{CO} = 2044\ cm^{-1}$. Anal. Calcd for $C_{18}H_{15}CoF_7IO$: C, 38.19; H, 2.67. Found: C, 38.59; H, 2.62.

(η^5-Pentamethylcyclopentadienyl)iodo(perfluorobenzyl)carbonylrhodium(III) (2b). A solution of $[Rh(C_5Me_5)(CO)_2]$ (162 mg, 0.551 mmol) in benzene (10 mL) was treated with $C_6F_5CF_2I$ (232 mg, 0.673 mmol), and the mixture was stirred at room temperature (14 h). Volatiles were removed under vacuum, and the resultant red-orange solid was dissolved in CH_2Cl_2. The solution was filtered via cannula and concentrated, and hexane was layered gently on top of the CH_2Cl_2. The product crystallized at −20 °C as deep red crystals (284 mg, 85%). Mp: 146−147 °C. ^1H NMR (C_6D_6) δ: 1.53 (15H, C_5Me_5). ^{19}F NMR (C_6D_6) δ: −44.1 (dt, $J_{F_aF_b} = 211$, $J_{F_aF_{cc'}} = 23$, 1F, F_a), −53.6 (dt, $J_{F_aF_b} = 211$, $J_{F_bF_{cc'}} = 35$, 1F, F_b), −136.6 (m, 2F, $F_{cc'}$), −155.2 (t, $J_{FF} = 20$, 1F, F_e), −163.1 (m, 2F, $F_{dd'}$).

---

(23) Clark, G. R.; Hoskins, S. V.; Roper, W. R. *J. Organomet. Chem.* **1982**, *234*, C9−C12.

(24) Frith, S. A.; Spencer, J. L. *Inorg. Syn.* **1990**, *28*, 273−285.

(25) Werner, H.; Heiser, B.; Klingert, B.; Dolfel, R. *J. Organomet. Chem.* **1982**, *240*, 179−190.

(26) Maitlis, P. M.; Kang, J. W. *J. Organomet. Chem.* **1971**, *26*, 393−399.

IR (CH_2Cl_2): ν_{CO} = 2056 cm^{-1}. Anal. Calcd for $C_{18}H_{15}F_7IORh$: C, 35.44; H, 2.48. Found: C, 35.36; H, 2.66.

(η^5-Cyclopentadienyl)iodo(perfluorobenzyl)(trimethylphosphine)cobalt(III) (3a). A solution of **1a** (500 mg, 1.01 mmol) in benzene (30 mL) was treated with PMe_3 (105 μL, 1.01 mmol), and the mixture was stirred at room temperature (6 h). The reaction mixture was filtered via cannula, and the volatiles were removed under vacuum leaving behind a green-black solid (390 mg, 71%). Crystals for X-ray diffraction were obtained from an ethyl ether solution which was cooled to 10 °C. Mp: 136−137 °C. ^1H NMR (C_6D_6) δ: 1.24 (9H, J_{HP} = 11.4, PMe_3), 4.50 (5H, C_5H_5). ^{19}F NMR (C_6D_6) δ: −35.9 (dtd, $J_{F_aF_b}$ = 240, $J_{F_aF_{cc'}}$ = 22, J_{F_aP} = 7, 1F, F_a), −50.5 (ddt, $J_{F_aF_b}$ = 240, J_{F_bP} = 60, $J_{F_bF_{cc'}}$ = 30, 1F, F_b), −138.5 (m, 2F, $F_{cc'}$), −157.3 (t, J_{FF} = 20, 1F, F_e), −163.6 (m, 2F, $F_{dd'}$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 17.37 (br s, PMe_3). Anal. Calcd for $C_{15}H_{14}CoF_7IP$: C, 33.11; H, 2.59. Found: C, 33.09; H, 2.64.

(η^5-Pentamethylcyclopentadienyl)iodo(perfluorobenzyl)(trimethylphosphine)cobalt(III) (4a). A solution of **2a** (4.20 g, 7.60 mmol) in benzene (50 mL) was treated with PMe_3 (0.789 mL, 7.60 mmol), and the mixture was stirred at room temperature (6 h). Volatiles were removed under vacuum to leave a dark solid, which was dissolved in CH_2Cl_2 and filtered, and the filtrate was layered with hexanes. The product crystallized at −60 °C to afford dark orange crystals (3.87 g 83%). Mp: 149−152 °C. ^1H NMR (C_6D_6) δ: 1.28 (d, J_{HP} = 10.2, 9H, PMe_3), 1.41 (s, C_5Me_5). ^{19}F NMR (C_6D_6) δ: −49.5 (d, $J_{F_aF_b}$ = 260, F_a), −54.9 (ddt, $J_{F_aF_b}$ = 260, J_{F_bP} = 76, $J_{F_bF_{cc'}}$ = 37, F_b), −138.1 (m, 2F, $F_{cc'}$), −158.6 (t, J_{FF} = 20, 1F, F_e), −165.0 (m, 2F, $F_{dd'}$). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 13.24 (br s, PMe_3). Anal. Calcd for $C_{20}H_{24}CoF_7IP$: C, 39.11; H, 3.94. Found: C, 39.00; H, 4.16.

(η^5-Pentamethylcyclopentadienyl)iodo(perfluorobenzyl)(trimethylphosphine) rhodium(III) (4b). A solution of **2b** (52 mg, 0.085 mmol) in benzene (1 mL) was treated with PMe_3 (8.8 μL, 0.085 mmol), and the mixture was stirred at room temperature (1 h). Volatiles were removed under vacuum to afford the product as a red-orange solid (47 mg, 84%). Mp: 168−170 °C. If necessary, this compound can be recrystallized from CH_2Cl_2 and hexanes at −20 °C. ^1H NMR (C_6D_6) δ: 1.31 (d, J_{HP} = 10.8, 9H, PMe_3), 1.53 (d, J_{HRh} = 3.3, 15H, C_5Me_5). ^{19}F NMR (C_6D_6) δ: −44.6 (d, $J_{F_aF_b}$ = 248, F_z), −52.6 (ddtd, $J_{F_aF_b}$ = 248, J_{F_bP} = 87, $J_{F_bF_{cc'}}$ = 35, J_{F_bRh} = 12, 1F, F_b), −139.3 (m, 2F, $F_{cc'}$), −158.4 (t, J_{FF} = 23, 1F, F_e), −164.7 (m, 2F, $F_{dd'}$). $^{31}P\{^1H\}$NMR (C_6D_6) δ: 8.70 (dd, J_{PRh} = 151, J_{PF} = 76, PMe_3). Anal. Calcd for $C_{20}H_{24}F_7IPRh$: C, 36.50; H, 3.68. Found: C, 36.48; H, 3.98.

(η^5-Cyclopentadienyl)iodo(perfluorobenzyl)(dimethylphenylphosphine)cobalt(III) (5a). A solution of **1a** (200 mg, 0.402 mmol) in benzene (5 mL) was treated with PMe_2Ph (57 μL, 0.402 mmol), and the mixture was stirred at room temperature (2 h). Volatiles were removed under vacuum, and the resultant black solid was dissolved in a minimal amount of CH_2Cl_2 and then filtered via cannula. Hexane was gently layered on top of the CH_2Cl_2 solution. The product crystallized at −78 °C as black needles (184 mg, 75%). ^1H NMR (C_6D_6) δ: 1.58 (d, J_{HP} = 11.1, 3H, P*Me*$_2$Ph), 1.76 (d, J_{HP} = 11.1, 3H, P*Me*$_2$Ph), 4.44 (s, 5H, C_5H_5), 7.05 (m, 3H, PMe$_2$*Ph*), 7.62 (m, 2H, PMe$_2$*Ph*). ^{19}F NMR (C_6D_6) δ: −34.6 (dt, $J_{F_aF_b}$ = 236, $J_{F_aF_{cc'}}$ = 22, 1F, F_a), −49.3 (ddt, $J_{F_aF_b}$ = 236, J_{F_bP} = 61, $J_{F_bF_{cc'}}$ = 33, 1F, F_b), −137.4 (m, 2F, $F_{cc'}$), −157.2 (t, J_{FF} = 21, 1F, F_e), −163.6 (m, 2F, $F_{dd'}$). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 21.42 (br s, *P*Me$_2$Ph). Anal. Calcd for $C_{20}H_{16}CoF_7IP$: C, 39.63; H, 2.66. Found: C, 39.41; H, 2.65.

(η^5-Pentamethylcyclopentadienyl)iodo(perfluorobenzyl)(dimethylphenylphosphine)rhodium(III) (5b). A solution of **2b** (50 mg, 0.085 mmol) in benzene (1 mL) was treated with PMe_2Ph (11.7 μL, 0.345 mmol), and the mixture was stirred at room temperature (6 h). Removal of the volatiles under vacuum left behind a red-orange solid which was recrystallized from CH_2Cl_2 and methanol at −20 °C to yield deep red crystals (30 mg, 51%). Mp: 147−149 °C. ^1H NMR (C_6D_6) δ: 1.37 (d, J_{HRh} = 3.3, 15H, C_5Me_5), 1.71(d, J_{HP} = 10.5, 3H, C_5Me_5), 1.81 (d, J_{HP} = 10.5, 3H, C_5Me_5), 7.04 (m, 3H, PMe_2Ph), 7.72 (m, 3H, PMe_2Ph). ^{19}F NMR (C_6D_6) δ: −45.7 (br s, 2F, F_a, F_b), −139.7 (m, 2F, $F_{cc'}$), −159.0 (t, 1F, F_e), −165.1 (m, 2F, $F_{dd'}$). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 15.40 (dd, J_{PRh} = 160, J_{PF} = 73, PMe_2Ph). Anal. Calcd for $C_{25}H_{26}F_7IPRh$: C, 41.69; H, 3.64. Found: C, 41.62; H, 3.66.

Reaction of 2a with PMe$_3$ in THF To Give 9a. A solution of **2a** (1.00 g, 1.77 mmol) in THF (40 mL) was treated with PMe_3 (0.185 mL, 1.77 mmol), and the mixture was stirred at room temperature (20 h). Volatiles were removed under vacuum and trapped in a Schlenk flask that was cooled with liquid nitrogen. A ^{19}F NMR spectrum of the volatiles showed a resonance at δ −194.2 (d, J_{FH} = 438), consistent with the presence of HF. The residual green-black solid was dissolved in CH_2Cl_2 and filtered, and the filtrate was layered with hexanes. The product crystallized at −78 °C to afford **9a** (462 mg, 44%). ^1H NMR (C_6D_6) δ: 0.92 (s, 3H, C$_5$*Me*$_4$CH$_2$), 0.96 (s, 3H, C$_5$*Me*$_4$CH$_2$), 1.30 (d, J_{HP} = 9.9, 9H, P*Me*$_3$), 1.48 (s, 3H, C$_5$*Me*$_4$CH$_2$), 1.56 (d, J_{HP} = 3.3, 3H, C$_5$*Me*$_4$CH$_2$), 2.88 (d, J_{AB} = 15.6, H_A, C$_5$Me$_4$*CH$_2$*), 3.23 (d, J_{AB} = 15.6, H_B, C$_5$Me$_4$*CH$_2$*). ^{19}F NMR (C_6D_6) δ: −45.6 (d, $J_{F_aF_b}$ = 211, F_a), −58.3 (ddd, $J_{F_aF_b}$ = 211, $J_{F_bF_1}$ = 92, J_{F_bP} = 31, F_b), −139.4 (dm, $J_{F_1F_b}$ = 91, F_1), −147.3 (dd, $J_{F_4F_3}$ = 23, $J_{F_4F_1}$ = 12, F_4), −157.5 (t, $J_{F_2F_3}$ = 22, F_2), −158.3 (t, $J_{F_3F_2}$ = 21, F_3). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 16.31 (br s, PMe_3). Anal. Calcd for $C_{20}H_{23}CoF_6IP$: C, 40.43; H, 3.90. Found: C, 40.82; H, 3.96.

Hydrolysis of 9a To Give 10a. An NMR sample of **9a** (23 mg, 0.040 mmol) was dissolved in C_6D_6 (0.7 mL) and monitored by ^{19}F and ^1H NMR. The compound slowly but completely hydrolyzed to the acyl complex **10a** over 5 days. ^1H NMR (C_6D_6) δ: 0.82 (s, 3H, C$_5$*Me*$_4$CH$_2$), 1.02 (s, 3H, C$_5$*Me*$_4$CH$_2$), 1.28 (d, J_{PH} = 10.2, 9H, P*Me*$_3$), 1.53 (s, 3H, C$_5$*Me*$_4$CH$_2$), 1.87 (s, C$_5$*Me*$_4$CH$_2$), 2.11 (d, J_{AB} = 15.9, 1H, C$_5$Me$_4$*CH$_2$*), 3.21 (d, J_{AB} = 15.9, 1H, C$_5$Me$_4$*CH$_2$*). ^{19}F NMR (C_6D_6) δ: −145.1 (dd, $J_{F_1F_2}$ = 24, $J_{F_1F_4}$ = 14, F_1), −149.9 (dd, $J_{F_4F_3}$ = 22, $J_{F_4F_1}$ = 14, F_4), −157.9 (t, $J_{F_2F_3}$ = 22, F_2), −159.1 (t, $J_{F_3F_2}$ = 22, F_3). $^{31}P\{^1H\}$NMR (C_6D_6) δ: 23.41 (br s, PMe_2Ph). IR (CH_2Cl_2): $\nu_{C=O}$ = 1610 cm^{-1}.

Reaction of 2a with PMe$_2$Ph To Give 9b. A solution of **2a** (1.00 g, 1.77 mmol) in THF (50 mL) was treated with PMe_2Ph (380 μL, 2.66 mmol), and the mixture was stirred at room temperature (19 h). Volatiles were removed under vacuum leaving behind **9b** as a green-black solid (1.14 g, 98%). ^1H NMR (C_6D_6) δ: 0.39 (d, J_{HP} = 2.4, 3H, C$_5$*Me*$_4$CH$_2$), 0.73 (s, 3H, C$_5$*Me*$_4$CH$_2$), 1.40 (s, 3H, C$_5$*Me*$_4$CH$_2$), 1.58 (d, J_{HP} = 3.6, 6H, P*Me*$_2$Ph, C$_5$*Me*$_4$CH$_2$), 1.80 (d, J_{HP} = 9.9, 3H, P*Me*$_2$Ph), 2.90 (d, J_{AB} = 15.9, 1H, C$_5$Me$_4$*CH$_2$*), 3.21 (d, J_{AB} = 15.9, 1H, C$_5$Me$_4$*CH$_2$*), 7.07 (m, PMe$_2$*Ph*, 3H), 7.70 (m, PMe$_2$*Ph*, 2H). ^{19}F NMR (C_6D_6) δ: −44.9 (d, $J_{F_aF_b}$ = 206, 1F, F_a), −59.3 (ddd, $J_{F_aF_b}$ = 206, $J_{F_bF_1}$ = 91, J_{F_bP} = 37, 1F, F_b), −139.1 (dm, $J_{F_1F_b}$ = 91, 2F, F_1), −147.3 (dd, $J_{F_4F_3}$ = 22, $J_{F_4F_1}$ = 13, 1F, F_4), −157.5 (t, $J_{F_2F_3}$ = 21, 2F, F_2), −158.2 (t, $J_{F_3F_2}$ = 21, 2F, F_3). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 23.58 (br s, PMe_2Ph). Satisfactory microanalysis could not be obtained for this complex due to facile hydrolysis of the CF_2 group.

Hydrolysis of 9b To Give 10b. A solution of **9b** (125 mg, 0.190 mmol) in CH_2Cl_2 (50 mL) was stirred at room temperature (14 h). The volatiles were removed under vacuum leaving **10b** as a black solid in quantitative yield. The solid was recrystallized from CH_2Cl_2 and hexanes to afforded black cubic crystals. ^1H NMR (C_6D_6) δ: 0.58 (d, J_{HP} = 3.3, 3H, C$_5$*Me*$_4$CH$_2$), 0.66 (s, 3H, C$_5$*Me*$_4$CH$_2$), 1.46 (s, 3H, C$_5$*Me*$_4$CH$_2$), 1.69 (d, J_{HP} = 10.2, 3H, P*Me*$_2$Ph), 1.70 (d, J_{PH} = 10.2, 3H, P*Me*$_2$Ph), 1.81 (d, J_{HP} = 3.3, 3H, C$_5$*Me*$_4$CH$_2$), 2.17 (d, J_{AB} = 16.3, 1H, C$_5$Me$_4$*CH$_2$*), 3.19 (d, J_{AB} = 16.3, 1H, C$_5$Me$_4$*CH$_2$*), 7.08 (m, 3H PMe$_2$*Ph*), 7.90 (m, 2H, PMe$_2$*Ph*). ^{19}F NMR (C_6D_6) δ: −143.5 (dd, $J_{F_1F_2}$ = 24, $J_{F_1F_4}$ = 14, F_1), −149.9 (dd, $J_{F_4F_3}$ = 21, $J_{F_4F_1}$ = 14, F_4), −157.5 (t, $J_{F_2F_3}$ = 22, F_2), −158.4 (t, $J_{F_3F_2}$ = 21, F_3). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 26.83 (br s, *P*Me$_2$Ph). IR(CH_2Cl_2): $\nu_{C=O}$ = 1617 cm^{-1}. Anal. Calcd for $C_{25}H_{25}CoF_4IOP$: C, 47.34; H, 3.97. Found: C, 47.41; H, 3.91.

(η^5-Pentamethylcyclopentadienyl)(perfluorobenzyl)carbonyl(trimethylphosphine)cobalt(III) tetrafluoroborate (13). A Schlenk flask containing a solution of **4a** (1.50 g, 2.44 mmol) in CH_2Cl_2 (80 mL) was flushed with CO for 3 min. After CO was bubbled through the solution for another 5 min, $AgBF_4$ (475 mg, 2.44 mmol) was added, and the mixture was stirred (7 min) with continued bubbling of CO. The mixture was then stirred at room temperature (4 h) with no further CO passage. The reaction mixture was transferred to a glass frit by cannula and filtered to give a clear red-yellow solution. Volatiles were removed, the residue was dissolved in CH_2Cl_2 (25 mL), and the product was precipitated by adding ether (70 mL). The yellow-orange mixture was filtered via cannula, and the product was washed with ether (3 × 5 mL), dried under a flow of N_2, and then dried under vacuum to yield 1.23 g (84%) of a yellow-orange powder. ^{1}H NMR ($CDCl_3$) δ: 1.68 (s, C_5Me_5), 1.78 (d, $J_{PH} = 11.1$, PMe_3). ^{19}F NMR ($CDCl_3$) δ: −29.6 (dm, $J_{F_aF_b} = 236$, F_a), −52.9 (ddt, $J_{F_aF_b} = 236$, $J_{FbP} = 47$, $J_{F_bF_{cc'}} = 43$, F_b), −140.2 (m, 2F, $F_{cc'}$), −151.3 (t, $J_{FF} = 23$ 1F, F_e), −151.6 (s, BF_4), −160.4 (m, 2F, $F_{dd'}$). ^{31}P{^{1}H} NMR (C_6D_6) δ: 24.80 (s, *P*Me_3). IR(CH_2Cl_2): $\nu_{CO} = 2060$ cm^{-1}. Anal. Calcd for $C_{21}H_{24}BCoF_{11}P$: C, 41.89; H, 4.02. Found: C, 41.60; H, 4.04.

Reaction of 13 with PPN$^+$I$^-$. A cloudy yellow-orange suspension of **13** (115 mg, 0.191 mmol) in THF (10 mL) was treated with PPN$^+$I$^-$ (500 mg, 0.751 mmol). The reaction mixture changed color to yellow-green. After 16 h, the mixture was filtered, the filtrate evaporated to dryness, and the residue redissolved in CH_2Cl_2. Unreacted starting material was precipitated with ether, the mixture was filtered, and the filtrate was evaporated to dryness under vacuum. The ^{19}F NMR spectrum of the residue showed the three major products **10a**, **2a**, and **4a** in an 18:3:1 ratio.

Thermolysis of 2a To Give 14. A solution of **2a** (1.00g, 1.77 mmol) in benzene (40 mL) was stirred at reflux (60 h). The solution was filtered via cannula, and volatiles were removed under vacuum. The crude residue (200 mg) was purified by chromatography (silica gel, 1.5 × 20 cm, −40 °C) to yield 40 mg (20%) of white solid **14**. ^{1}H NMR (C_6D_6) δ: 1.26 (s, 3H), 1.33 (s, 6H), 1.88 (s, 6H). ^{19}F NMR (C_6D_6) δ: −90.9 (t, $J_{FF} = 27$ Hz, 2F, CF_2), −138.1 (m, $2F_{ortho}$), −152.3 (t, $J = 23$ Hz, $1F_{para}$), −163.4 (m, $2F_{meta}$). GC/MS *m*/*z* 352.10 M$^+$ ($C_{11}H_{15}F_7$).

Crystallographic Studies. Crystal data collection and refinement parameters are given in Table 2. 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. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL PLUS (4.2) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Acknowledgment. R.P.H. acknowledges generous financial support from the U.S. Air Force Office of Scientific Research and the Petroleum Research Fund, administered by the American Chemical Society. D.C.L. acknowledges support via the Department of Defense Augmentation Award for Scientific and Engineering Research Training Program. A loan of rhodium chloride from Johnson-Matthey Aesar/Alfa is also gratefully acknowledged.

Supporting Information Available: Tables of fractional atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, H-atom coordinates, and isotropic displacement coefficients for complex **3a, 5b,** and **10b** (21 pages). Ordering information is given on any current masthead page.

OM9607255