Reactions of Perfluoroalkyl Iodides with $M(C_5H_5)(CO)(PMe_3)$ [M = Rh, Ir]; Evidence for Direct Fluoroalkylation at a CO Ligand

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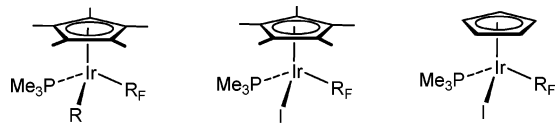
While reaction of n-C_3F_7I with $CpRh(PMe_3)(CO)$ gives the expected product of oxidative addition, $CpRh(PMe_3)(^nC_3F_7)(I)$, the analogous reaction of iso-C_3F_7I affords a mixture of $CpRh(PMe_3)(CF(CF_3)_2)(I)$ and the perfluoroacyl complex $CpRh(PMe_3)(COCF(CF_3)_2)(I)$. The latter compound is not formed from the former by a migratory insertion reaction. In further contrast, low-temperature reaction of $CpIr(CO)(PMe_3)$ with n-C_3F_7I gives the ionic complex $[CpIr(CO)(PMe_3)(^nC_3F_7)]^+I^-$, which is inert to thermal substitution; treatment with *N*-methylmorpholine-*N*-oxide (NMO) results in CO oxidation and iodide coordination to give $CpIr(PMe_3)(^nC_3F_7)(I)$. The same reaction at room temperature affords a mixture of four products, including small amounts of $[CpIr(CO)(PMe_3)(^nC_3F_7)]^+I^-$ and $CpIr(PMe_3)(^nC_3F_7)(I)$; the major components are the perfluoroacyl complex $CpIr(PMe_3)(CO^nC_3F_7)(I)$ and the perfluoroacyl(perfluoroalkyl) complex $CpIr(PMe_3)(CO^nC_3F_7)(^nC_3F_7)$. Crystallographic structure determinations of all these molecules are reported, and a mechanism involving direct fluoroalkylation at CO is proposed.

Introduction

For some time we have been interested in the scope and mechanism of activation of carbon−fluorine bonds by metals of group 9.[1−6] Our studies have focused mostly on iridium compounds of the general type **1** (R = H, CH_3; R_F = primary or secondary fluoroalkyl) containing the pentamethylcyclopentadienyl ligand, Cp*, for which the general precursor complex is **2**. Compounds **2** can be formed straightforwardly by oxidative addition of fluoroalkyl iodides, R_F−I, to $Cp^*Ir(CO)_2$ to give $Cp^*Ir(CO)(R_F)I$ followed by thermal substitution of CO by PMe_3 to give **2**.[7] To examine the role of the cyclopentadienyl ligand on these types of C−F bond activation processes, we sought the corresponding Cp complexes **3**, from which we could synthesize cyclopentadienyl analogues of compounds **1** to further our studies. Here we describe the less straightforward synthesis of compounds **3** and some unexpected alternate products formed in the oxidative addition reaction of fluoroalkyl iodides to low-valent precursors. A brief survey of oxidative addition reactions of fluoroalkyl iodides to compounds of general type $CpML_2$ [M = Co, Rh, Ir] is included here for the purpose of perspective.



Fluoroalkyl iodides are likely to undergo oxidative addition reactions by mechanisms different from their hydrocarbon counterparts due to the reverse polarity of the R_F−I bond, which provides a δ^+ iodine as a result of the strongly electronegative fluorines of the alkyl group.[8,9] Steric effects and lone pair repulsive forces associated with fluorine also shield the carbon atom of the R_F group from nucleophilic attack, and such fluoroalkyl iodides are resistant to displacement of iodide under S_N1 and S_N2 conditions.[10,11]

Notwithstanding this inverted polarity, straightforward oxidative additions of some primary fluoroalkyl

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(1) Hughes, R. P.; Laritchev, R. B.; Zakharov, L. N.; Rheingold, A. L. *J. Am. Chem. Soc.* **2005**, *127*, 6325−6334.
(2) Hughes, R. P.; Willemsen, S.; Williamson, A.; Zhang, D. *Organometallics* **2002**, *21*, 3085−3087.
(3) Hughes, R. P.; Lindner, D. C.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **2001**, *20*, 363−366.
(4) Hughes, R. P.; Zhang, D.; Zakharov, L. N.; Rheingold, A. L. *Organometallics* **2002**, *21*, 4902−4904.
(5) Hughes, R. P.; Smith, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 6084−6085.
(6) Hughes, R. P.; Lindner, D. C.; Rheingold, A. L.; Liable-Sands, L. M. *J. Am. Chem. Soc.* **1997**, *119*, 11544−11545.
(7) Hughes, R. P.; Smith, J. M.; Liable-Sands, L. M.; Concolino, T. E.; Lam, K.-C.; Incarvito, C.; Rheingold, A. L. *J. Chem. Soc., Dalton Trans.* **2000**, 873−879.
(8) Smart, B. E. Fluorocarbons. In *Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Ed.; Wiley: New York, 1983; Chapter 14, pp 603−655.
(9) Smart, B. E. *Mol. Struct. Eng.* **1986**, *3*, 141−191.

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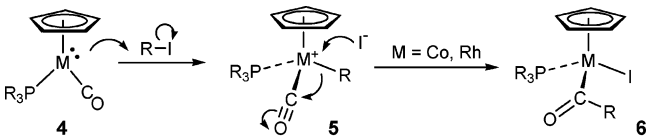
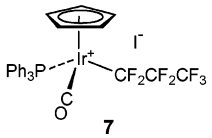
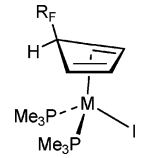
iodides to the metal center in $CpM(CO)_2$ [M = Co, Rh] to give $CpM(R_F)(CO)I$ were described some decades ago.[12,13] Primary and secondary fluoroalkyl iodides also react very straightforwardly with $Cp^*M(CO)_2$ [M = Co, Rh] analogues to give $Cp^*M(CO)(R_F)I$,[6,7,14] followed by thermal substitution of CO by PMe_3 to give **2**.[7] In some pioneering mechanistic work, oxidative addition reactions using primary alkyl and fluoroalkyl iodides were studied by Graham using mixed ligand systems such as $CpM(CO)L$ [**4**: M = Co, Rh, Ir; L = PPh_3, $PPhMe_2$].[15−18] The prototypical hydrocarbon example, methyl iodide, gave as the initial product the cationic complex **5**, which, when M was Co or Rh, underwent subsequent migratory insertion with coordination of iodide, to give the acyl products **6**. A mechanism involving nucleophilic attack by the metal center at carbon was consistent with detailed kinetic studies.[15,18] However, when the metal was Ir, the cation **5** was inert to migratory insertion or iodide coordination, and attempts to force matters thermally resulted in apparent nucleophilic attack by iodide at carbon to regenerate starting materials.[15,16] The corresponding reaction of $CpIr(CO)(PPh_3)$ with perfluoro-*n*-propyl iodide was performed at low temperature and reported to give the cationic complex **7**, but no comment on the mechanism of its formation or any subsequent chemistry was noted.[16] As will be seen shortly, the choice of low temperature for this reaction may have been a fortuitous one. No observations concerning any reactions of this substrate with fluoroalkyl iodides at room temperature were reported.





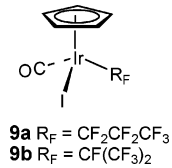
In subsequent work we noted that, while the dicarbonyl precursors $CpM(CO)_2$ [M = Co, Rh] react with both primary and secondary fluoroalkyl iodides to give products of formal oxidative addition at the metal center, use of the $CpM(PMe_3)_2$ [M = Co, Rh] analogues resulted in no metal-based fluoroalkylation, but instead in *exo*-fluoroalkylation at the Cp ring to give the unexpected products **8**, a reaction undesirable for our purposes.[19−21] Direct fluoroalkylation of ligands rather than at the metal was also observed in reactions of fluoroalkyl iodides with $Cp_2M(C_2H_4)$ [M = Mo, W].[22,23]



In an attempt to generate our target complexes **3** in a direct manner we have examined the reactions of various cyclopentadienyl-iridium precursors and, in some cases, their rhodium analogues with fluoroalkyl iodides. Here we describe reactions that are varied in complexity depending on reaction conditions and substrates, but which can in some cases be controlled to afford the desired products of fluoroalkylation at the metal center.

Results

Given the previous observations that reactions of $CpM(CO)_2$ [M = Co, Rh] with primary and secondary fluoroalkyl iodides afford simple oxidative addition to give $CpM(R_F)(CO)I$,[12,13,20,21] it came as no surprise to find that analogous reactions of $CpIr(CO)_2$ with perfluoro-*n*-propyl iodide or its isopropyl isomer afforded the corresponding products **9**. In contrast to the Co and Rh analogues in which substitution of CO by PMe_3 is clean and facile at room temperature, compounds **9** give complex mixtures on reaction with PMe_3 under ambient conditions. In attempts to circumvent this problem we turned to precursors, $CpM(CO)(PMe_3)$ [M = Rh, Ir], in which the phosphine was already in place.



We were initially encouraged to observe that treatment of the mixed ligand system $CpRh(PMe_3)(CO)$ with perfluoro-*n*-propyl iodide in CH_2Cl_2 at either room temperature or −78 °C resulted in clean formation of the metal-centered oxidative addition product $CpRh(PMe_3)(^nC_3F_7)(I)$, **10**, which could be crystallized from methylene chloride/hexanes as red needles. The complex was fully characterized by NMR, elemental analysis, and X-ray crystallography. Details of all crystallographic determinations are presented in Table 1; representative bond lengths and angles are provided in Tables 2 and 3, respectively. An ORTEP of compound **10** is shown in Figure 1.

(10) Wakselman, C.; Lantz, A. Perfluoroalkyl bromides and iodides. In *Organofluorine Chemistry*; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum: New York, NY, 1994; pp 177−194.
(11) Li, X.; Jiang, X.; Pan, H.; Hu, J.; Fu, W. *Pure Appl. Chem.* **1987**, *59*, 1015−1020.
(12) King, R. B.; Treichel, P. M.; Stone, F. G. A. *Proc. Chem. Soc.* **1961**, 69−70.
(13) McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1964**, 4200−4203.
(14) Hughes, R. P.; Lindner, D. C.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 5678−5686.
(15) Hart-Davis, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 2658−2663.
(16) Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 2653−2657.
(17) Oliver, A. J.; Graham, W. A. G. *Inorg. Chem.* **1970**, *9*, 243−247.
(18) Hart-Davis, A. J.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 1653−1657.
(19) Hughes, R. P.; Maddock, S. M.; Husebo, T. L.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **2002**, *21*, 243−246.
(20) Hughes, R. P.; Husebo, T. L.; Rheingold, A. L.; Liable-Sands, L. M.; Yap, G. P. A. *Organometallics* **1997**, *16*, 5−7.
(21) Hughes, R. P.; Husebo, T. L.; Holliday, B. J.; Rheingold, A. L.; Liable-Sands, L. M. *J. Organomet. Chem.* **1997**, *548*, 109−112.
(22) Hughes, R. P.; Maddock, S. M.; Guzei, I. A.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **2001**, *123*, 3279−3288.
(23) Hughes, R. P.; Maddock, S. M.; Rheingold, A. L.; Liable-Sands, L. M. *J. Am. Chem. Soc.* **1997**, *119*, 5988−5989.

Table 1. Details of the Crystallographic Structure Determinations

	10	**11**	**11/12**	**16**	**17**	**18**	**19**
formula	$C_{11}H_{14}F_7IPRh$	$C_{11}H_{14}F_7IPRh$	$C_{11.5}H_{14}F_7IO_{0.5}IPRh$	$C_{12}H_{14}F_7IIrOP$	$C_{11}H_{14}F_7IIrP$	$C_{12}H_{14}F_7IIrOP$	$C_{18}H_{17}F_{14}IrOP$
fw	540.00	540.00	554.01	657.30	593.26	657.30	738.49
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	7.3127(2)	14.313(2)	17.994(8)	14.108(4)	7.3279(14)	18.381(13)	10.5553(17)
b, Å	8.2671(2)	7.6318(12)	13.678(4)	8.2591(13)	8.2526(16)	14.036(4)	14.677(2)
c, Å	14.8748(2)	16.000(2)	14.561(7)	15.569(4)	14.832(3)	14.204(9)	14.816(2)
α, deg	79.631(1)				79.976(3)		
β, deg	78.185(1)	111.673(10)	109.22(3)	97.93(2)	77.998(3)	104.06(5)	92.241(3)
γ, deg	70.362(2)				70.441(3)		
V, Å^3	822.95(3)	1624(1)	3577(2)	1796.6(7)	821.4(3)	3555(3)	2293.7(6)
Z	2	4	4	2	2	8	4
D(calc), g cm^{-3}	2.179	2.208	2.175	2.430	2.399	2.456	2.139
μ(Mo Kα), cm^{-1}	30.68	31.09	29.90	93.02	101.54	94.02	60.13
temp, K	173	241(2)	246	244	213	243(2)	223(2)
diffractometer	Siemens P4 CCD	Siemens P4	Siemens P4 CCD	Siemens P4	Siemens P4 CCD	Siemens P4	Siemens P4 CCD
radiation	Mo Kα (λ = 0.71073 Å)						
no. of reflns collected	5095	2784	5102	4109	6123	5779	17 111
no. of unique reflns (R_{int})	3476(0.1164)	2113(0.1239)	4154(0.0444)	3160(0.0690)	3647(0.0151)	4615(0.0418)	5337(0.0323)
no. of obsd reflns	1551	1452	2808	2031	3336	3438	4424
$R(F)$, %[a]	7.90	5.41	6.22	4.51	5.09	5.25	4.20
$R(wF^2)$, %[b]	18.87	11.05[c]	14.74	9.47[c]	13.82	11.88[c]	12.49

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R(wF^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o,0)]/3$. [c] $R(wF) = \{\sum[w(|F_o| - |F_c|)^2]/\sum[wF_o^2]\}^{1/2}$; $w = 1/\sigma^2(F_o)$.

Table 2. Selected Bond Distances (Å)

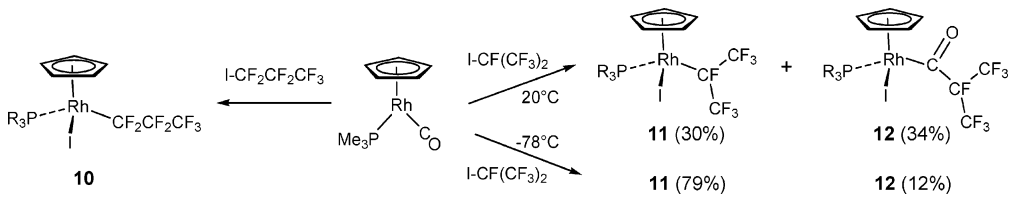
	M−P	M−C$_\alpha$	M−I	M−Ct
CpRh(PMe$_3$)(^{n}C$_3$F$_7$)(I), **10**	2.273(4)	2.06(2)	2.671(2)	1.875(2)
CpRh(PMe$_3$)(^{i}C$_3$F$_7$)(I), **11**	2.294(3)	2.135(13)	2.6937(12)	1.854(14)
CpRh(PMe$_3$)(^{i}C$_3$F$_7$)(I),[a] **11**	2.303(4)	2.13(2)	2.671(2)	1.872(2)
CpRh(PMe$_3$)(CO^{i}C$_3$F$_7$)(I),[a] **12**	2.271(4)	1.93(2)	2.662(2)	1.907(3)
[CpIr(CO)(PMe$_3$)(^{n}C$_3$F$_7$)]I, **16**[b]	2.320(3)	2.064(13)		1.904(12)
CpIr(PMe$_3$)(^{n}C$_3$F$_7$)(I), **17**	2.271(2)	2.066(10)	2.6790(7)	1.869(10)
CpIr(PMe$_3$)(CO^{n}C$_3$F$_7$)(I), **18**[c]	2.270(4)	2.00(2)	2.670(2)	1.904(2)
	2.268(4)	2.01(2)	2.678(2)	1.878(3)
CpIr(PMe$_3$)(CO^{n}C$_3$F$_7$)(^{n}C$_3$F$_7$), **19**[d]	2.228(3)	2.064(10)[d]		1.915(8)

[a] Cocrystal of **11** and **12**. [b] M−CO, 1.866(14) Å. [c] Data from two independent molecules in the asymmetric unit. [d] M−COR$_f$, 2.058(8) Å.

Table 3. Selected Bond Angles (deg)

	C$_\alpha$−M−P	C$_\alpha$−M−I	I−M−P	Ct−M−I	Ct−M−C$_\alpha$	Ct−M−P
CpRh(PMe$_3$)(^{n}C$_3$F$_7$)(I), **10**	95.6(4)	89.9(5)	89.59(14)	121.39(7)	126.12(7)	124.20(7)
CpRh(PMe$_3$)(^{i}C$_3$F$_7$)(I), **11**	95.5(3)	92.7(3)	88.58(9)	121.03(6)	126.38(7)	123.01(6)
CpRh(PMe$_3$)(^{i}C$_3$F$_7$)(I), **11**[a]	95.1(4)	93.0(4)	88.38(13)	119.99(6)	127.13(7)	123.53(6)
CpRh(PMe$_3$)(CO^{i}C$_3$F$_7$)(I), **12**	86.5(5)	98.8(5)	88.73(12)	121.57(12)	126.67(13)	124.14(13)
[CpIr(CO)(PMe$_3$)(^{n}C$_3$F$_7$)]I, **16**[b]	89.9(4)				126.01(6)	121.54(5)
CpIr(PMe$_3$)(^{n}C$_3$F$_7$)(I), **17**	94.81(2)	89.0(3)	89.28(7)	120.28(4)	127.01(4)	125.59(4)
CpIr(PMe$_3$)(CO^{n}C$_3$F$_7$)(I), **18**[c]	87.0(5)	87.9(5)	92.92(11)	120.49(7)	131.54(9)	125.39(7)
	88.5(5)	89.4(5)	91.21(12)	118.24(13)	131.95(13)	125.95(12)
CpIr(PMe$_3$)(CO^{n}C$_3$F$_7$)(^{n}C$_3$F$_7$), **19**[d]	92.8(3)				123.97(5)	124.20(3)

[a] Cocrystal of **11** and **12**. [b] C−M−CO, 89.0(5)°; C−M−P, 91.9(4)°. [c] Data from two independent molecules in the asymmetric unit. [d] R$_f$CO−M−P, 87.0(2)°; R$_f$CO−M−R$_f$, 89.1(4)°; Ct−Ir−COR$_f$ 128.44(4)°.



In contrast, treatment of CpRh(PMe$_3$)(CO) with perfluoro-isopropyl iodide at room temperature resulted in two principal products, which could be separated by Florisil column chromatography. The first fraction (eluted with 30% ether/hexanes) afforded the fluoroalkyl-metal compound CpRh(PMe$_3$)(CF(CF$_3$)$_2$)(I) (**11**) (30%), while elution with ether gave the perfluoroacyl complex CpRh(PMe$_3$)(COCF(CF$_3$)$_2$)(I) (**12**) (34%). Further elution afforded small amounts of an uncharacterized mixture of byproducts. The same reaction conducted at −78 °C afforded a cleaner result, with the perfluoroacyl complex **12** being significantly favored (79%) over the perfluoroalkyl analogue **11** (21%). Fortunately crystal structures of both derivatives were

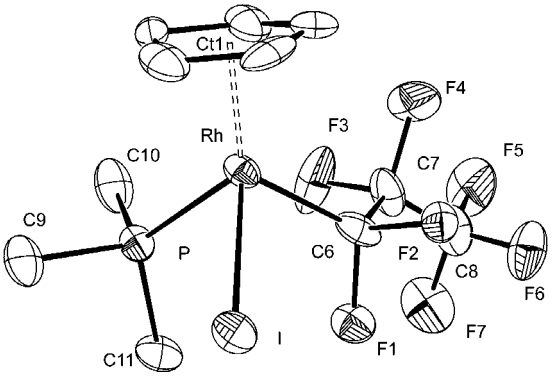


Figure 1. ORTEP diagram of the non-hydrogen atoms of $CpRh(PMe_3(^nC_3F_7)(I)$, **10**, showing the partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level.

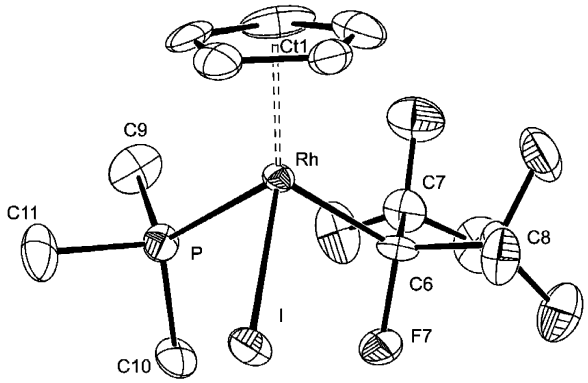


Figure 2. ORTEP diagram of the non-hydrogen atoms of $CpRh(PMe_3)(CF(CF_3)_2)(I)$, **11**, showing the partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level.

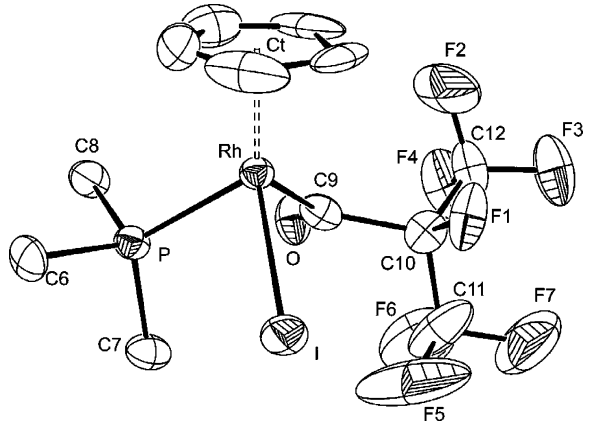


Figure 3. ORTEP diagram of the non-hydrogen atoms of $CpRh(PMe_3)(COCF(CF_3)_2)(I)$, **12**, from a cocrystal with **11**, showing the partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level.

obtained; perfluoroalkyl derivative **11** crystallized alone and also cocrystallized as a 1:1 mixture with perfluoroacyl complex **12**. Notably, once formed, compounds **11** and **12** were inert; in particular there was no evidence for conversion of **12** to **11** at room temperature or above. ORTEP diagrams of compounds **11** and **12** are shown in Figures 2 and 3.

Upon changing the metal from rhodium to iridium, these oxidative addition reactions became even more varied and complex. The perfluoro-isopropyl iodide system was particularly messy, with reaction of per-

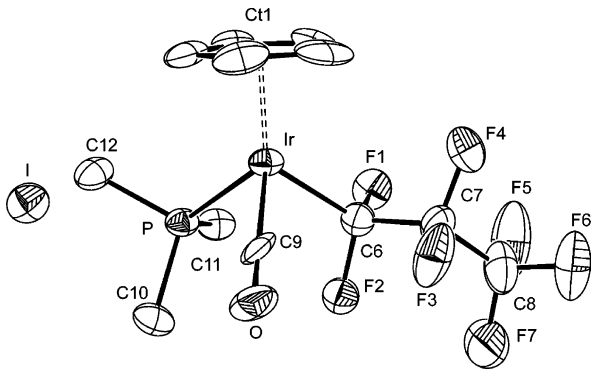
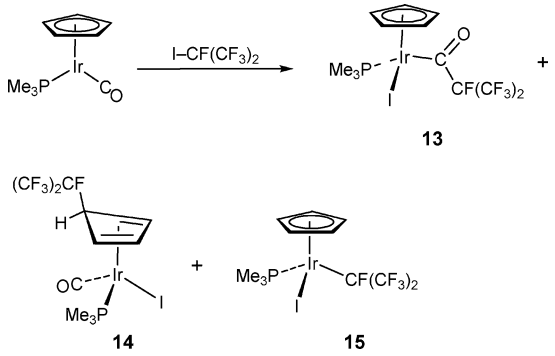
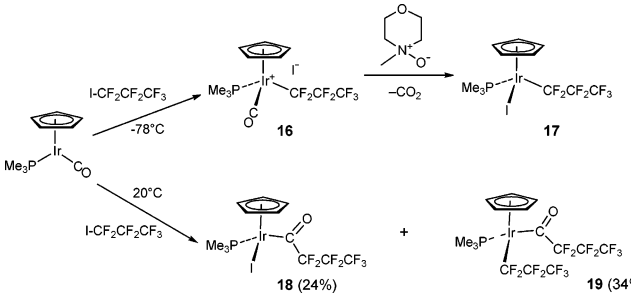


Figure 4. ORTEP diagram of the non-hydrogen atoms of $[CpIr(CO)(PMe_3)(^nC_3F_7)]I$, **16**, showing the partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level.

fluoro-isopropyl iodide with $CpIr(CO)(PMe_3)$ at −78 °C giving a complex mixture of products. Only partial separation was possible, but on the basis of comparison of IR and NMR data to the Rh analogues **11** and **12** (vide supra), analogues discussed below, and previously characterized complex **8**,[12,13,20,21] compounds **13**−**15** were tentatively identified as the principal components of the mixture, among other unidentified products.



Reactions of $CpIr(CO)(PMe_3)$ with perfluoro-*n*-propyl iodides were also complex, although at low temperatures a single product, the cationic complex **16**, was formed as an off-white solid, which was crystallographically characterized. An ORTEP representation of the structure is shown in Figure 4.



Consistent with previous reports of the inert behavior of analogous iridium cations of general structure **5**,[15,16] heating **16** at reflux in methylene chloride for 24 h gave no reaction whatsoever. There was no evidence for coordination of iodide or migration of the fluoroalkyl group to CO. Prolonged heating in toluene resulted in decomposition to unidentified materials. However, treatment of **16** with *N*-methylmorpholine-*N*-oxide (NMO)

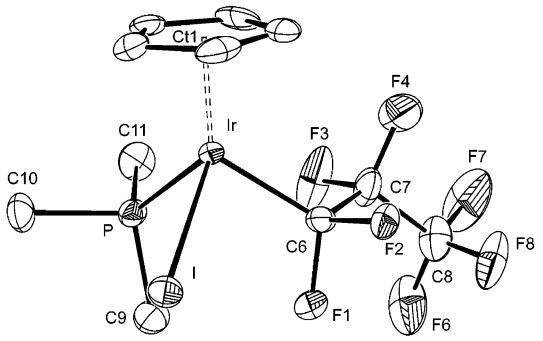


Figure 5. ORTEP diagram of the non-hydrogen atoms of $CpIr(PMe_3)(^nC_3F_7)(I)$, **17**, showing the partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level.

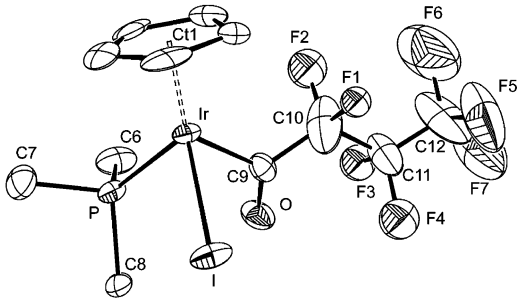


Figure 6. ORTEP diagram of the non-hydrogen atoms of $CpIr(PMe_3)(COCF_2CF_2CF_3)(I)$, **18**, showing the partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. The compound crystallizes with two independent molecules in the asymmetric unit. Only one is shown.

in THF at 0 °C resulted in chemical oxidation of coordinated CO,[3,24–27] freeing up a coordination site and allowing iodide coordination to afford our target compound **17**, which was also crystallographically characterized. An ORTEP diagram of **17** is presented in Figure 5.

When the reaction of either 1 or 2 equiv of perfluoro-*n*-propyl iodide with $CpIr(CO)(PMe_3)$ was performed at room temperature, four principal products were obtained, along with small amounts of unidentified materials. Small amounts of the iodide salt **16** could be identified and separated by virtue of its insolubility in ether. Of the ether-soluble products, **17** could be identified, though in low yield (~15%). Employment of column chromatography on neutral alumina separated the remaining products, which were identified by ^1H, ^{19}F, and ^{31}P NMR, IR, and X-ray crystallography. The second fraction off the column (eluting with hexanes/ether) was found to have an IR stretch at 1644 cm^{-1} (hexanes), consistent with formation of an acyl compound. X-ray crystallography confirmed this structure as **18**. An ORTEP is shown in Figure 6. The first fraction was more difficult to separate from **18** but was eventually shown to have an IR stretch at 1647 cm^{-1} (hexanes), also indicating the presence of an acyl ligand. The ^{19}F NMR spectrum showed the presence of two distinct perfluoro-*n*-propyl groups, and the structure **19** was finally confirmed by X-ray crystallography. An ORTEP

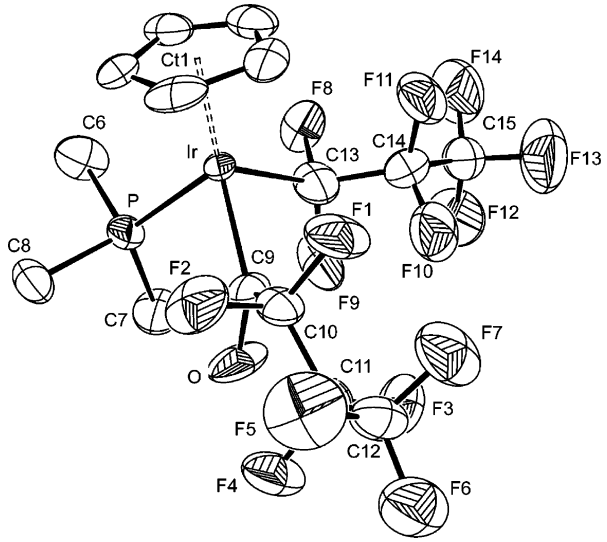


Figure 7. ORTEP diagram of the non-hydrogen atoms of $CpIr(PMe_3)(COCF_2CF_2CF_3)(CF_2CF_2CF_3)$, **19**, showing the partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. The compound crystallizes with a half molecule of benzene in the asymmetric unit, which is not shown.

is shown in Figure 7. Compound **19** does not arise from direct reaction of cationic compound **16** with excess perfluoropropyl iodide, either on heating or under the influence of UV light, which is known to generate fluoroalkyl radicals. Likewise reaction of $CpIr(CO)(PMe_3)$ and perfluoro-*n*-propyl iodide in the presence of cation **16** did not result in formation of more **19** than was produced in the absence of **16**. Clearly **19** is produced by reaction of perfluoropropyl iodide with some reactive intermediate.

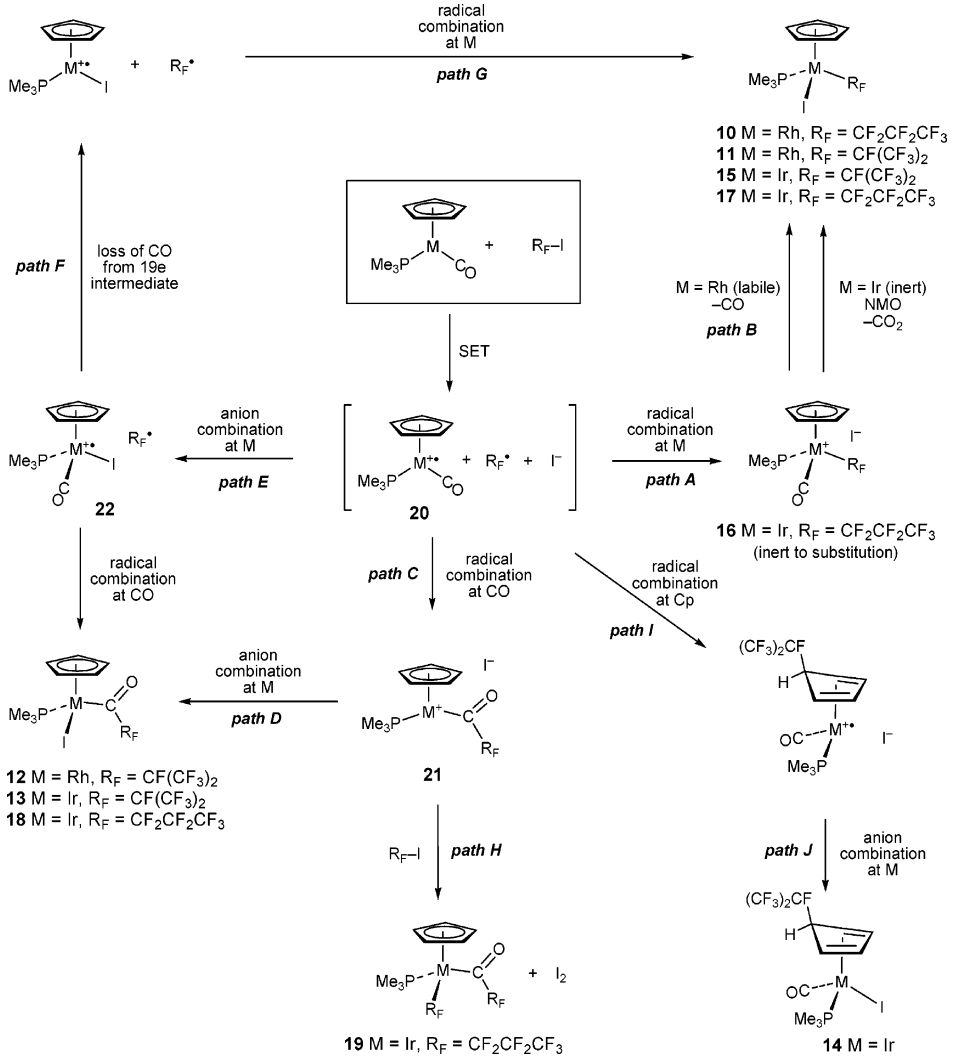
Discussion

In previous studies[19,22] we have probed the mechanism of reaction of various low-valent metal complexes with perfluoroalkyl iodides using a method pioneered by Toscano,[28] in which CH_3OD is used as a trap that differentiates between fluoroalkyl radicals,[29] which abstract from the weaker C–H bonds,[30] and fluoroalkyl carbanions,[31] which abstract from the more acidic O–D bond. Only in the cases of secondary perfluorinated substrates was definitive evidence provided for the intermediacy of fluoroalkyl carbanions.[19,22] In the situation most relevant to this paper, only the reaction of the very electron rich $CpRh(PMe_3)_2$ with perfluoroisopropyl iodide gave evidence for direct nucleophilic attack of the metal at iodine to afford an intermediate perfluoro-isopropyl anion;[19] no reactions involving $CpM(CO)_2$ species with primary or secondary fluoroalkyl substrates have provided definitive evidence either way; that is, no trapping was observed. The mixed ligand system clearly falls between the two systems studied so far, and we have likewise been unable to provide definitive evidence for a radical or carbanion pathway.

Accordingly, the pathways shown in Scheme 1 are proposed, based only on the nature of the products

(24) Hughes, R. P.; Tucker, D. S. *Organometallics* **1993**, *12*, 4736–4738.
(25) Koelle, U. *J. Organomet. Chem.* **1978**, *155*, 53–62.
(26) Koelle, U. *J. Organomet. Chem.* **1977**, *133*, 53–58.
(27) Jian Kun, S.; Yi-Ci, G.; Shi, Q. Z.; Basolo, F. *J. Organomet. Chem.* **1991**, *401*, 295–303.
(28) Toscano, P. J.; Brand, H.; Liu, S.; Zubieta, J. *Inorg. Chem.* **1990**, *29*, 2101–2105.
(29) Dolbier, W. R., Jr. *Chem. Rev.* **1996**, *96*, 1557–1584.
(30) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.
(31) Farnham, W. B. *Chem. Rev.* **1996**, *96*, 1633–1640.

Scheme 1

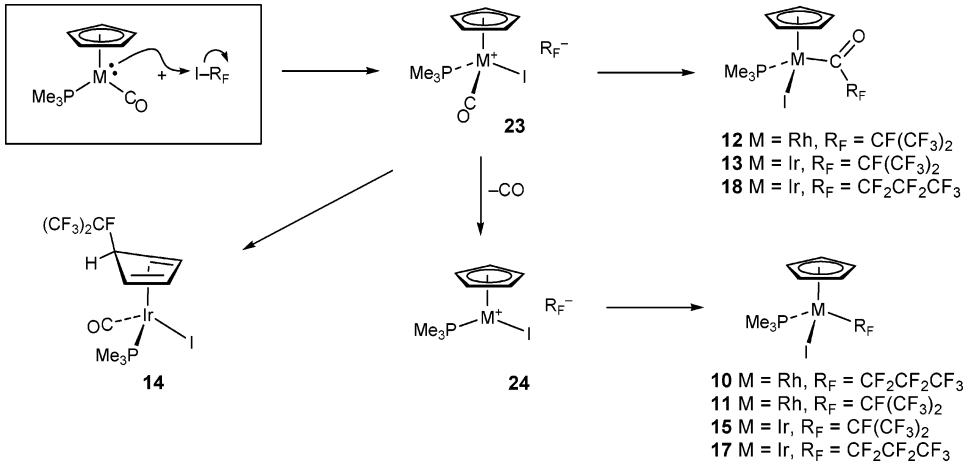


produced, some knowledge of their relative stability, and some understanding of the relative rates of reactions of Rh and Ir complexes from previous studies.[15−18] All products are assumed to evolve from initial SET from metal to R_F−I to produce the radical cation of the metal substrate (**20**), a known product of one-electron oxidation of such complexes,[32] together with iodide and the perfluoroalkyl radical, the known products of one-electron reduction of fluoroalkyl iodides.[33] Assuming that at low temperatures the opportunities for these species to escape the solvent cage are minimized, the low-temperature products should give some indication of the kinetically favored pathways. When M = Ir and $R_F = CF_2CF_2CF_3$, collapse to give **16** is clean, pointing to radical combination at the metal (*path A*) as the selective process. Compound **16** is inert to substitution, and conversion of **17** must be accomplished chemically using NMO. However, when M = Rh and $R_F = CF_2CF_2CF_3$ or $CF(CF_3)_2$, formation of the analogous cation would result in rapid CO substitution by iodide (*path B*) to give observed low-temperature products **10** and **11**, a reaction that is known to be fast. Notably no migrations of R_F to CO have been observed here. Consequently formation of the acyl product **12** concomitantly with **10** must arise from a competitive reaction of **20** involving direct fluoroalkylation at CO, shown as occurring by *path C* to give intermediate **21**, which then collapses to **12** (*path D*) by fast iodide coordination. Presumably this pathway is favored by a sterically more demanding secondary fluorinated radical, which would slow reaction at the metal, and by increased temperature, which may allow for more reorganization of the various fragments in the solvent cage before combination occurs. This represents a novel, though clearly not very selective, way to make metal-perfluoroacyl compounds, which have only been previously prepared using acylating agents such as a perfluoroacyl halide or acid anhydride.[34−38]

At higher temperatures reactions of the iridium substrate with perfluoro-*n*-propyl iodide are even more complex. Formation of **16** and **18** can arise by the same pathways used to explain the corresponding rhodium

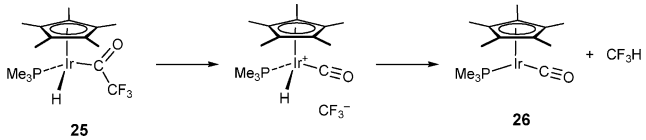
(32) Connelly, N. G.; Lucy, A. R.; Payne, J. D.; Galas, A. M. R.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 1879−1885.
(33) Andrieux, C. P.; Gelis, L.; Savéant, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 786−791.
(34) Mukhedkar, A. J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 947−951.
(35) Blake, D. M.; Shields, S.; Wyman, L. *Inorg. Chem.* **1974**, *13*, 1595−1600.
(36) Klabunde, K. J.; Low, J. Y. F.; Efner, H. F. *J. Am. Chem. Soc.* **1974**, *96*, 1984−1985.
(37) Hieber, W.; Lindner, E. *Ber.* **1962**, *95*, 2042−2048.
(38) Treichel, P. M.; Pitcher, E.; Stone, F. G. A. *Inorg. Chem.* **1962**, *1*, 511−517.

Scheme 2

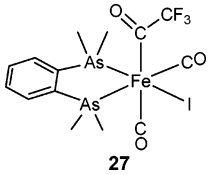


chemistry, but formation of compounds **17** and **19** clearly arises by more convoluted sequences of events. In particular, compounds **17** and **19** cannot arise via the intermediacy of **16**, which is inert under these conditions. Pathways leading to these products from intermediate **20** are depicted in Scheme 1 as *paths E, F,* and *G* to afford **17** and *paths C* and *H* to yield **19**. We put these forward only as suggestions to account for the observed products. Clearly the option of having **20** react by anion combination at the metal to give a 19-electron intermediate **22** (*path E*) provides alternative routes to perfluoroacyl complexes **12** and **18** and, by virtue of potentially higher substitutional lability of **22**, to perfluoroalkyl complexes **10** and **11**. At present we have no means of distinguishing between them, except to note that the clear kinetic mode of reactivity of **20** [M = Ir] at low temperatures appears to be formation of **16** (*path A*); the inertness of **16** seems to render implausible the likelihood that *path A* is reversible at higher temperatures. Finally the less well-defined products arising from reaction of CpIr(CO)-(PMe_3) with perfluoro-isopropyl iodide can be similarly accounted for: **13** (*paths C, D*), **15** *(paths E, F, G)*, and **14** (*paths I, J*).

A brief note on possible two-electron pathways is appropriate. Scheme 2 illustrates the formation of **23** as the product of an S_N2 displacement at iodine; clearly nucleophilic attack by R_F^- at CO or Cp provides a route to perfluoroacyl complexes or ring alkylated products, as shown. Indeed the microscopic reverse of one of these types of reaction, loss of CF_3^- from an acyl ligand, has been shown to be important in the thermal decomposition of **25** to give **26** and CF_3H.[39] However it is unclear how the intermediacy of **23** can account for formation of perfluoroalkyl compounds, as shown, except by dissociative loss of CO to give **24**; yet the proportion of acyl product is higher at higher temperatures, an observation inconsistent with this proposition. Furthermore, the role of intermediate **23** in production of compounds **16** and **19** is difficult to understand.



Finally, a comment on what appears to be the only report of an apparent migratory insertion reaction involving a CO and a fluoroalkyl ligand: the reaction of Fe(DIARS)$(CO)_3$ with CF_3I to give **27** as a mixture of stereoisomers.[40] The product **27** is assumed to arise via initial formation of an Fe−CF_3 species, followed by migration of CF_3 to CO. This is based on the admitted assumption that the reaction proceeds by nucleophilic attack of the metal at carbon, a reaction that now seems unlikely (vide supra). No difference in product was observed when the reaction was carried out in the presence of radical inhibitors,[40] although these would presumably only inhibit radical chain reactions, and not those involving radicals that remain within the solvent cage. The author wisely provides numerous appropriate cautions regarding the conclusions reached.[40] On the basis of our observations this result should perhaps be re-evaluated to consider direct fluoroalkylation at CO rather than formation of a metal-fluoroalkyl followed by migratory insertion.



Experimental Section

General Procedures. All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen that had been deoxygenated over BASF catalyst and dried over molecular sieves or in a Braun glovebox. Solvents were either distilled under nitrogen from K (ethers) and CaH_2 (pentane, hexanes, and chlorinated solvents) or deoxygenated and dried over activated alumina under nitrogen.[41] ^1H (300 MHz), ^{19}F (282 MHz), and ^{31}P (121.4 MHz) NMR spectra were recorded on a Varian Unity-300 spectrometer at 25 °C. Chemical shifts are reported as ppm downfield of TMS (^1H, referenced to solvent) or internal $CFCl_3$ (^{19}F) and external 85% H_3PO_4 (^{31}P). Coupling constants are reported in hertz. IR spectra were recorded on a Perkin-Elmer FTIR 1600 Series spectrophotometer. Melting points were

(39) Cordaro, J. G.; Bergman, R. G. *J. Am. Chem. Soc.* **2004**, *126*, 16912−16929.
(40) Jablonski, C. R. *Inorg. Chem.* **1981**, *20*, 3940−3947.
(41) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

obtained using an electrically heated capillary tube and are uncorrected. Elemental analyses were performed by Schwartzkopf (Woodside, NY) and X-ray crystallographic analyses at the University of Delaware (Wilmington) and University of California, San Diego.

$RhCl_3 \cdot 3H_2O$ and $IrCl_3 \cdot 3H_2O$ (Pressure Chemical Company), trimethylphosphine (Aldrich), and CO (Matheson) were obtained commercially and used as received. $I(CF_2)_2CF_3$ and $ICF(CF_3)_2$ (PCR, Synquest) were purified by washing with a solution of sodium thiosulfate to remove iodine, followed by washing with water and then drying over magnesium sulfate and deoxygenation by several cycles of freeze−pump−thaw. $CpRh(CO)(PMe_3)$[42−44] and $CpIr(CO)(PMe_3)$[45] were prepared by literature procedures.

X-ray Crystal Structure Determinations. Diffraction intensity data were collected with Siemens P4 (**11**, **16**, **18**) and Siemens P4/CCD (**10**, **11/12**, **17**, **19**) diffractometers. Crystallographic data and details of X-ray studies are given in Table 1. Absorption corrections were applied to all data by semiempirical psi-scans method for **11**, **16**, and **18** and by SADABS for **10**, **11/12**, **17**, and **19**. The structures were solved using the direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients except the atoms of disordered groups, which were refined with isotropic thermal parameters. Hydrogen atoms were treated as idealized contributions. There are two symmetrically independent molecules in the crystals of **11/12** and **18**. The $CF_3CF_2CF_2$ ligands in **18** are disordered over two positions and were refined with restrictions on the C−C and C−F bond distances. All software and sources of scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI).

CpIr(CO)(^{n}C$_3$F$_7$)(I) (9a). $CpIr(CO)_2$ (0.27 g, 0.612 mmol) was dissolved in methylene chloride (20 mL) to produce a clear yellow solution and cooled to 0 °C. $^nC_3F_7I$ (80 μL, 0.657 mmol) was added, and the clear orange solution was allowed to stir at 0 °C (4 h). The solvent was removed to yield a yellow-orange solid, which was recrystallized from methylene chloride/hexanes. Yield: 0.270 g (76%). Anal. Calcd for $C_9H_5F_7IOIr$: C, 18.60; H, 0.87. Found: C, 18.70; H, 0.88. IR (CH_2Cl_2): ν_{CO} 2067 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 5.98 (d, 5H, $J_{HF} = 0.6$, C_5H_5). ^{19}F NMR (CD_2Cl_2): δ −55.3 (dt, 1F, $J_{AB} = 265$ $J_{FF} = 10$, $C_\alpha F_A$), −62.1 (dt, 1F, $J_{AB} = 268$, $J_{FF} = 12$, $C_\alpha F_B$), −79.3 (t, 3F, $J_{FF} = 12$, CF_3), −113.9 (dd, 1F, $J_{AB} = 284$, $J_{FF} = 8$, $C_\beta F_A$), −116.4 (dt, 1F, $J_{AB} = 282$, $J_{FF} = 8$, $C_\beta F_B$).

CpIr(CO)(^{i}C$_3$F$_7$)(I) (9b). $CpIr(CO)_2$ (0.05 g, 0.160 mmol) was dissolved in methylene chloride (5 mL) and cooled to −78 °C. A solution of $(CF_3)_2CFI$ (50 μL, 0.35 mmol) in methylene chloride (5 mL) was added to the iridium solution slowly by cannula at −78 °C. The color of the solution changed from lemon yellow to yellow-orange. The solution was warmed to room temperature, and the volatiles were removed under vacuum, leaving behind an orange solid, which was crystallized from CH_2Cl_2/hexanes (0.06 g, 70%). Anal. Calcd for $C_9H_5F_7IIrO$; C, 18.60; H, 0.87. Found; C, 18.69; H, 1.07. IR (THF): ν_{CO} 2073 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 5.93 (s, 5H,Cp). ^{19}F NMR (CD_2Cl_2): δ −67.6 (dq, $J_{F-F} = 10$ Hz, $J_{F-F} = 2$ Hz, 3F, CF_3), −70.3 (dq, $J_{F-F} = 10$ Hz, $J_{F-F} = 2$ Hz, 3F, CF_3), −155.0 (bm, 1F, CF).

CpRh(PMe$_3$)(^{n}C$_3$F$_7$)(I) (10). To a solution of $CpRh(CO)(PMe_3)$ (20 mg, 0.074 mmol) in CD_2Cl_2 (2 mL), in a vial in the glovebox, was added a solution of $CF_3(CF_2)_2I$ (11 μL, 81 mmol) in CD_2Cl_2 (1 mL). The color of the solution immediately changed from yellow to red. The reaction was left to stir at room temperature overnight, by which time ^{1}H, ^{19}F, and ^{31}P NMR indicated only one product. Hexanes were added, and the product was left to crystallize by slow evaporation in the air, to give red needles. Yield: 24 mg, 61%. Anal. Calcd for $C_{11}H_{14}F_7IPRh$ (539.99): C, 24.47; H, 2.56. Found: C, 24.47; H, 2.61. ^{1}H NMR ($CDCl_3$): δ 5.53 (d, $J_{PH} = 1.5$, 5H, C_5H_5), 1.82 (d, $J_{PH} = 11.4$, 9H, $P(CH_3)_3$). ^{19}F NMR ($CDCl_3$): δ −55.5 (d, $J_{AB} = 253$, 1F, $C_\alpha F_A$), −66.2 (d, $J_{AB} = 253$, 1F, $C_\alpha F_B$), −79.0 (t, $J_{FF} = 11$, 3F, CF_3), −113.0 (d, $J_{AB} = 279$, 1F, $C_\beta F_A$), −115.2 (m, $J_{AB} = 279$, 1F, $C_\beta F_B$). ^{31}P NMR ($CDCl_3$): δ 12.3 (dm, $J_{RhP} = 146$, $P(CH_3)_3$).

Reaction of CpRh(PMe$_3$)(CO) with $(CF_3)_2$CFI at Room Temperature. To a solution of $CpRh(PMe_3)(CO)$ (50 mg, 0.184 mmol) in CH_2Cl_2 (10 mL) in a vial in the glovebox was added a solution of $(CF_3)_2CFI$ (30 μL, 0.21 mmol) in CH_2Cl_2 (2 mL). The color of the solution darkened from yellow to deep red. The reaction was stirred at RT overnight. ^{1}H NMR of the reaction mixture revealed three products. The volatiles were pumped off, and the residue was subjected to column chromatography (Florisil). Two main fractions were isolated:

CpRh(PMe$_3$)(^{i}C$_3$F$_7$)(I) (11) from a yellow-orange band (30% Et_2O/hexanes). ^{1}H NMR ($CDCl_3$): δ 5.47 (d, $J_{PH} = 1.5$, 5H, C_5H_5), 1.86 (d, $J_{PH} = 11.4$, 9H, $P(CH_3)_3$). ^{19}F NMR ($CDCl_3$): δ −65.5 (s, 3F, CF_3), −68.2 (s, 3F, CF_3), −172.2 (s, 1F, CF). ^{31}P{^{1}H} NMR ($CDCl_3$): 16.42 (d, $J_{RhP} = 148.3$, $P(CH_3)_3$).

CpRh(PMe$_3$)(CO^{i}C$_3$F$_7$)I (12) from an orange-red band (Et_2O), which crystallized as red plates (36 mg, 34%). Anal. Calcd for $C_{12}H_{14}F_7IOPRh$ (568.00): C, 25.37; H, 2.48. Found: C, 25.35; H, 2.49. Mp: 92−93 °C. IR (CH_2Cl_2): ν_{CO} 1651 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.54 (d, $J_{PH} = 1.5$, 5H, C_5H_5), 1.82 (dd, $J_{PH} = 11.4$, $J_{RhH} = 0.7$, 9H, $P(CH_3)_3$). ^{19}F NMR ($CDCl_3$): δ −70.8 (quintet, 3F, $J_{FF} = 8.1$, CF_3), −72.6 (quintet, 3F, $J_{FF} = 8.0$, CF_3), −160.0 (septet, $J_{FF} = 8.2$, 1F, CF). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 16.4 (d, $J_{RhP} = 148.4$, $P(CH_3)_3$).

Reaction of CpRh(PMe$_3$)(CO) with $(CF_3)_2$CFI at Low Temperature (−78 °C). A solution of $CpRh(PMe_3)(CO)$ (20 mg, 0.074 mmol) in CH_2Cl_2 (15 mL) in a Schlenk flask was cooled to −78 °C. A solution of $(CF_3)_2CFI$ (12 μL, 0.084 mmol) in CH_2Cl_2 (15 mL), cooled to −78 °C, was added via cannula. The color of the solution changed from yellow to yellow-brown. After 3 h, the dark orange-red solution was pumped down to give a brown-yellow solid, which was slowly warmed to RT with no change in color. ^{1}H, ^{19}F, and ^{31}P NMR spectra showed the same products as the room-temperature reaction, but with the perfluoroacyl complex **12** being the major product (79%) together with the perfluoroalkyl complex **11** (12%).

Reaction of CpIr(PMe$_3$)(CO) with $(CF_3)_2$CFI at Low Temperature (−78 °C). A solution of $CpIr(CO)(PMe_3)$ (0.05 g, 0.138 mmol) in THF (5 mL) was cooled to −78 °C, and a solution of $(CF_3)_2CFI$ (44 μL, 0.304 mmol) in THF (2 mL) was added to the iridium solution slowly by a cannula at −78 °C. The volatiles were removed under vacuum at this temperature, leaving behind an orange oil. This was dissolved in a minimum amount of methylene chloride, and a copious amount of hexanes was added to precipitate a tan-orange solid. NMR spectroscopy data indicated that the orange solid was mostly $CpIr(PMe_3)(^iC_3F_7)I$, **15**, and the filtrate contained mainly **13** and **14**. It was not possible to accomplish clean separation of the components, which were identified spectroscopically.

13: IR (CH_2Cl_2): ν_{CO} 1628 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 5.5 (s, 5H, Cp), 2.03 (d, $J_{PH} = 11$, 9H, PMe_3). ^{19}F NMR (CD_2Cl_2): δ −75.7 (d, $J_{FF} = 8$, 3F, CF_3), −76.0 (d, $J_{FF} = 12$, 3F, CF_3), −187.2 (m, 1F, CF). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ -49.23 (m, PMe_3).

14: IR (THF): ν_{CO} 2002 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 5.51 (br d, $J_{HP} = 1.2$ Hz, 2H, CH), 4.73 (d, $J_{H-F} = 26.4$ Hz, 1H, CH), 2.83 (br s, 2H, CH), 1.8 (d, $J_{P-H} = 11.4$ Hz, 9H PMe_3). ^{19}F NMR (C_6D_6): δ −79.3 (d, $J_{F-F} = 8.4$ Hz, 6F of 2 CF_3),

(42) van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1990**, *28*, 90−92.
(43) Werner, H.; Feser, R.; Harder, V.; Hofmann, W.; Neukomm, H. *Inorg. Synth.* **1990**, *28*, 280−285.
(44) Feser, R.; Werner, H. *J. Organomet. Chem.* **1982**, *233*, 193−204.
(45) Wang, D.; Angelici, R. J. *Inorg. Chem.* **1996**, *35*, 1321−1331.

−192.4 (d sept, J_{H-F} = 26.4 Hz, J_{F-F} = 7.6 Hz, 1F of CF). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −41.6 (s, PMe_3).

15: ^1H NMR (CD_2Cl_2): δ 5.60 (d, J_{H-P} = 1.2 Hz, 5H, Cp), 1.88 (d, J_{H-P} = 11.4 Hz, 9H, PMe_3). ^{19}F NMR (CD_2Cl_2): δ −74.6 (dq, $^3J_{F-F}$ = 8 Hz, $^4J_{F-F}$ = 8 Hz, 3F, CF_3), −76.1 (dq, $^3J_{F-F}$ = 8 Hz, $^4J_{F-F}$ = 8 Hz, 3F, CF_3), −162.4 (m, 1F, CF). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −33.9 (m).

[CpIr(PMe$_3$)(CO)(^{n}C$_3$F$_7$)]$^+$I$^-$ (16). A solution of CpIr(PMe$_3$)(CO) (0.05 g, 0.160 mmol) in methylene chloride (5 mL) was cooled to −78 °C. A solution of $CF_3(CF_2)_2I$ (50 μL, 0.35 mmol) in methylene chloride (5 mL) was added to the iridium solution slowly by a cannula at −78 °C. The color of the solution went from lemon yellow to yellow-orange. The reaction mixture was warmed to room temperature, the volatiles were removed under vacuum, and the residue was crystallized from methylene chloride/hexanes to yield a slightly off-white solid. Yield: 0.06 g, 70%. Anal. Calcd for $C_{12}H_{14}F_7IIrOP$ (657.16): C, 21.90; H, 2.15. Found: C, 21.93; H, 2.24. IR (CH_2Cl_2): ν_{CO} 2077 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 6.33 (s, 5H, C_5H_5), 2.27 (d, J_{PH} = 12.3, 9H, $P(CH_3)_3$). ^{19}F NMR (CD_2Cl_2): δ −57.9 (dm, J_{AB} = 265, 1F, $C_\alpha F_A$), − 68.5 (dm, J_{AB} = 268, 1F, $C_\alpha F_B$), −79.7 (t, J_{FF} = 13.8, CF_3), −113.6 (br d, J_{AB} = 289, 1F, $C_\beta F_A$), −117.1 (dt, J_{AB} = 282, J_{FF} = 10 Hz, 1F, $C_\beta F_B$). ^{31}P NMR (CH_2Cl_2): δ −30.0 (d, J_{PF} = 18.3 Hz, $P(CH_3)_3$).

CpIr(PMe$_3$)(^{n}C$_3$F$_7$)(I) (17). Method A: *N*-Methylmorpholine *N*-oxide (0.041 g, 0.350 mmol) in THF (5 mL) was added dropwise to a cloudy yellow-orange solution of **16** (0.230 g, 0.350 mmol) in THF (15 mL) at 0 °C. The solution turned clear yellow-orange and was allowed to stir at 0 °C (4 h). The solvent was removed under vacuum, and the residue was extracted with ether at −78 °C. The extract was filtered and the filtrate evaporated to yield a yellow solid. Recrystallization from CH_2Cl_2/hexanes at −40 °C yielded the product as yellow crystals. Yield: 0.15 g, 68%. Anal. Calcd for $C_{11}H_{14}F_7IIrP$ (629.29): C, 20.99; H, 2.24. Found: C, 21.27; H, 2.04. ^1H NMR (C_6D_6): δ 4.730 (s, 5H, C_5H_5), 1.275 (d, 9H, J_{PH} = 11, $P(CH_3)_3$). ^{19}F NMR (C_6D_6): δ −57.9 (doct, J_{AB} = 276, J_{FF} = 7, 1F, $C_\alpha F_A$), −65.3 (dm, J_{AB} = 277, 1F, $C_\alpha F_B$), −78.6 (t, J_{FF} = 12, 3F, CF_3), −112.3 (d, J_{AB} = 279, J_{FF} = 7, 1F, $C_\beta F_A$), −115.3 (dq, J_{AB} = 279, J_{FF} = 7, 1F, $C_\beta F_B$). ^{31}P NMR (C_6D_6): δ −39.349 (m, $P(CH_3)_3$).

Method B: Compound **16** (0.348 g, 0.5294 mmol) and *N*-methylmorpholine *N*-oxide (0.063 g, 0.538 mmol) were added as solids to a Schlenk flask equipped with a stir bar. THF (20 mL) was added, and the mixture was allowed to stir at 0 °C (4 h). A yellow solution was formed, and the solvent was removed to yield a yellow solid. Extraction in ether and recrystallization from methylene chloride/hexanes yielded the desired product as a yellow solid. Yield: 0.253 g (76%).

Reaction of CpIr(CO)(PMe$_3$) with CF$_3$CF$_2$CF$_2$I at Room Temperature. To a solution of CpIr(PMe$_3$)(CO) (0.083 g, 0.230 mmol) in methylene chloride (10 mL) was added neat $CF_3CF_2CF_2I$ (55 μL, 0.452 mmol). The solution slowly turned a darker orange color and was allowed to stir at room temperature (15 h). The solvent was removed to yield a dark oily solid. This was extracted into ether and the solvent removed to yield an orange oily solid (0.113 g). This was placed on a column of neutral alumina and eluted with 1:1 hexanes/ether.

CpIr(PMe$_3$)(COC$_3$F$_7$)(C$_3$F$_7$) (19) was obtained from the first, darker yellow-orange fraction. Solvent was removed to yield a very pale yellow powder, which was crystallized from hexanes at −78 °C to afford pure compound. Yield: 0.055 g, 34%. Anal. Calcd for $C_{15}H_{14}F_{14}IrOP$ (699.43): C, 25.76; H, 2.02. Found: C, 25.96; H, 2.14. IR (hexanes): ν_{CO} 1647 cm^{-1}. ^1H NMR (C_6D_6): δ 4.73 (s, 5H, C_5H_5), 1.27 (d, J_{HH} = 11, 9H, $P(CH_3)_3$). ^{19}F NMR (C_6D_6): δ −63.9 (doct, J = 274, J = 7, 1F, *alkyl*-$C_\alpha F_A$), −67.9 (d, J = 273, 1F, *alkyl*-$C_\alpha F_B$), −78.7 (t, J = 12, 3F, *alkyl*-CF_3), −80.5 (t, J = 9, 3F, acyl-CF_3), −107.4 (dsextet, J = 290, J = 8, 1F, *acyl*-$C_\alpha F_A$), −110.7 (d, J = 291, 1F, *acyl*-$C_\alpha F_B$), −113.3 (d, J = 278, 1F, *alkyl*-$C_\beta F_A$), −114.8 (dq, J = 279, J = 8, 1F, *alkyl*-$C_\beta F_B$), −124.3 (dt, J = 293, J = 6, 1F, *acyl*-$C_\beta F_A$), −125.3 (d, J = 294, 1F, *acyl*-$C_\beta F_B$). ^{31}P (C_6D_6): δ −30.28 (m, $P(CH_3)_3$).

CpIr(CO^{n}C$_3$F$_7$)(PMe$_3$)(I) (18) was obtained from the second bright yellow fraction. Solvent was removed to yield yellow powder, which was crystallized from hexanes at −78 °C to afford pure compound. Yield: 0.036 g, 24%. Anal. Calcd for $C_{12}H_{14}F_7IIrOP$ (657.16): C, 21.93; H, 2.15. Found: C, 22.29; H, 2.16. IR (CH_2Cl_2): 1636 cm^{-1}; ν_{CO} (hexanes): 1644 cm^{-1}. ^1H NMR (C_6D_6): δ4.78 (d, J_{HH} = 1.2, 5H, C_5H_5), 1.30 (d, J_{PH} = 11, 9H, $P(CH_3)_3$). ^{19}F NMR (C_6D_6): δ −80.5 (t, J_{FF} = 10, 3F, CF_3), −104.4 (dq, J_{AB} = 285, J_{FF} = 8, 1F, $C_\alpha F_A$), −109.8 (dq, J_{AB}=285, J_{FF} = 9, 1F, $C_\alpha F_B$), −124.5 (s, 2F, $C_\beta F_2$). ^{31}P NMR (C_6D_6): δ −34.37 (s, $P(CH_3)_3$).

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Supporting Information Available: CIF files for **10**−**12** and **16**−**19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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