Variable-Temperature NMR Determination of the Barriers to Rotation about the Ir−C σ-Bond in a Series of Primary Perfluoroalkyl Iridium Complexes $[IrCp^*\{(CF_2)_nCF_3\}(PMe_3)_2]^+X^-$ [n = 1, 2, 3, 5, 7, 9, 11; X = I, OT_f]

Cheryl J. Bourgeois,[#] Hui Huang,[#] Roman B. Larichev,[#] Lev N. Zakharov,[§] Arnold L. Rheingold,[§] and Russell P. Hughes*,[#]

Departments of Chemistry, 6128 Burke Laboratory, Dartmouth College, Hanover, New Hampshire 03755, and University of California, San Diego, California 92093-0358

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A series of primary perfluoroalkyl iridium complexes $[IrCp^*\{(CF_2)_nCF_3\}(PMe_3)_2]^+X^-$ [n = 1, 2, 3, 5, 7, 9, 11; X = I, OT_f] has been prepared. X-ray crystallographic studies of a representative example, $[IrCp^*\{(CF_2)_9CF_3\}(PMe_3)_2]^+I^-$, shows the ground state structure of the cation in the solid to be of C_1 symmetry, with the perfluoroalkyl ligand adopting a conformation in which the fluorines on each CF_2 group reside in different chemical environments. In solution the ^{19}F NMR spectra of all these compounds indicate that the α-CF_2 fluorines are diastereotopic at low temperatures, consistent with the solid state structure. On warming, these resonances coalesce, indicating a rotation or windshield-wiper motion of the perfluoroalkyl ligand that samples a conformation of C_s symmetry; Eyring plots of the rate constant/temperature data provide values of $\Delta H^‡$ of ∼33 ± 2 kJ/mol for each system; the values are independent of the counterion. While there is clearly a difference between $\Delta S^‡$ values for the perfluoroethyl compounds compared to longer chain analogues, the precision of the data is insufficient to quantify this effect. The barrier to perfluoroalkyl ligand rotation is ascribed to steric effects; changing the Cp* ligand to Cp or changing from PMe_3 ligands to the O atoms of acetylacetonate in $IrCp^*(R_F)$(acac) results in no decoalescence of CF_2 resonances at low temperatures, even though the X-ray structure of $IrCp^*(CF_2$-$CF_3)$(acac) shows an identical unsymmetrical ground state conformation for the perfluoroethyl ligand to that observed in the bis(trimethylphosphine) analogues.

Introduction

Barriers to rotation about single bonds are significant in determining conformational stereochemistry, which in turn may determine ground state structure. Many chemical reactions have a stereochemical requirement such that reaction cannot proceed directly from the ground state conformation, and the activation energy to achieve the required bond rotation must be part of the overall barrier for the chemical transformation.[1] While conformational analysis and measurement of rotational barriers have been used mainly for C−C bonds, analogous studies of a variety of compounds containing transition metal−carbon σ-bonds have also proven useful in predicting ground state conformations, reactivity patterns, and reaction stereoselectivities.[2−4] While early vibrational spectroscopic studies were used to estimate the barrier to rotation of ∼3 kcal/mol for the Mn−C bond in CH_3−$Mn(CO)_5$,[5] the most common techniques have been those of NMR spectroscopy. ^{13}C relaxation studies were used to define barriers for M−CH_3 rotation in a number of compounds, with sterically uncrowded CH_3−$Re(CO)_5$, CH_3−$Au(PPh_3)$, and $(CH_3)_2Os(CO)_4$ having negligibly small barriers and more crowded systems like $CpFe(CO)_2(CH_3)$, $CpMo(CO)_3$-(CH_3), and $Cp_2Zr(CH_3)_2$ having barriers of >6 kcal/mol.[6]

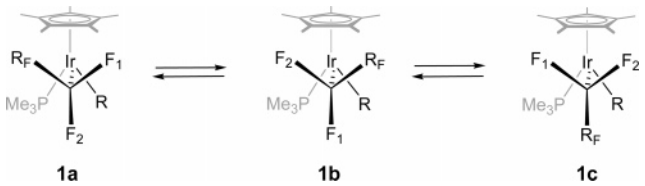

Figure 1. Staggered conformations, viewed down the C−Ir σ-bond, of the primary fluoroalkyl ligand in complexes of general type **1**, which have a stereocenter at Ir.

Analogous barriers to C−C σ-bond rotation in fluorinated organic compounds have been studied by variable-temperature ^{19}F NMR spectroscopy, the significantly larger chemical shift range allowing access to data not as easily achievable in hydrocarbons. For example, Weigert was able to observe the individual fluorine resonances within the trifluoromethyl groups of various fluorocarbons and measured barriers for C−C bond rotation between 5.2 and 8.5 kcal/mol.[7] Similarly in some organometallic haloalkyl complexes MCX_2CF_3 (M = $Re(CO)_5$, $Mn(CO)_5$, $CpMo(CO)_3$; X = Br, Cl, F), restricted rotation about

* Corresponding author. E-mail: rph@dartmouth.edu.
[#] Dartmouth College.
[§] University of California, San Diego.

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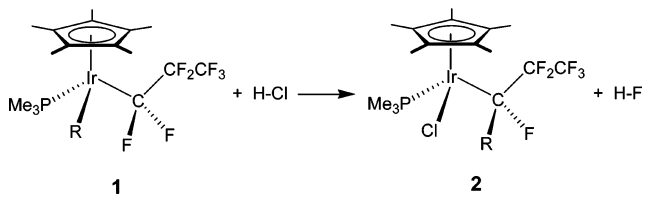
Table 1. Crystal, Data Collection, and Refinement Parameters

	4g	5g	7b
formula	$C_{23}H_{24}F_{21}IrP$	$C_{26}H_{37}F_{21}IrO_2P_2$	$C_{17}H_{22}F_5IrO_2$
fw	1049.49	1161.60	545.55
space group	*P*2(1)/*n*	*P*2(1)/*c*	*P*2(1)/*c*
a, Å	24.772(9)	21.236(3)	14.187(3)
b, Å	9.545(3)	8.7661(10)	8.6710(17)
c, Å	28.600(10)	20.491(2)	15.227(3)
α, deg			
β, deg	111.080(9)	94.160(2)	97.669(3)
γ, deg			
V, Å^3	6310(4)	3804.4(8)	1856.4(6)
Z	8	4	4
cryst color, habit	yellow, block	yellow, block	brown, block
D(calc), g cm^{-3}	2.209	2.028	1.952
μ(Mo Kα), mm^{-1}	5.401	4.534	7.247
temp, K	213(2)	208(2)	213(2)
diffractometer		Bruker Smart Apex CCD	
radiation		Mo Kα (0.71073 Å)	
no. of measd reflns	34 625	29 884	13 597
no. of indep reflns	9896 [R_{int} = 0.0409]	8934 [R_{int} = 0.0465]	4337 [R_{int} = 0.0254]
R (*F*), %[a]	7.22	5.55	2.6
R (*wF*^{2}), %[b]	19.33	9.7	6.6

the C−C bond was observed at low temperatures, and estimated barriers to C−C bond rotation between 5.1 and 12.2 kcal/mol were determined.[8] Rotational barriers for M−C bonds in fluoroalkyl complexes have been less easily achieved. Estimates of rotational barriers (between 5 and 10 kcal/mol) and conformational preferences in compounds of the type CpCo(L)(I)(R_F) and CpFe(L)(CO)(R_F) have been published.[9,10] These estimates were made on the basis of temperature dependence of chemical shift and coupling constant data and, as with analogous studies of corresponding alkyl analogues, have been subject to criticism, particularly in their predictions of conformational preferences.[2−4]

We have been interested in the structural features of fluoroalkyl−transition metal compounds for some time.[11−18] Recently we have found unusual reactivity patterns for compounds of type **1**, involving activation of α-C−F bonds by external protic sources, coupled with migration of hydride, methyl, phenyl, and other organic groups to give diastereoselective formation of compounds **2**.[19−23] Recently we have measured the overall activation barrier ($\Delta H^{\ddagger}$) for the conversion of **1** → **2** (R = H) to be between 73 and 86 kJ/mol, depending on the reaction solvent.[21] We have shown that the ground state conformation of the primary fluoroalkyl group in complexes **1** [R = CH_3] is the staggered conformation **1a** (Figure 1) in the solid state using X-ray crystallography and in solution using $^{19}F\{^1H\}$ HOESY experiments.[11,12] However, we have argued that protic activation and R-migration may not occur directly from ground state conformation **1a**, but rather from alternative staggered conformation **1b** or **1c**.[19−21] Clearly the accessibility of alternative conformations requires rotation about the M−C *σ*-bond, and we sought a means of estimating reliably the magnitude of the barrier for such rotation in order to assess what portion of the overall activation barrier for this reaction might possibly be assigned to a conformational change. As with previously studied compounds CpCo(L)(I)(R_F) and CpFe(L)(CO)(R_F) (vide supra),[9,10] the presence of a stereocenter in compounds of type 1 means the α-CF_2 fluorines are diastereotopic *in all conformations*. Consequently, unless site exchange can be observed between two or more conformational populations, M−C bond rotation cannot unambiguously be defined as having a high or low energy barrier, and attempts to define it using temperature dependence of *δ* or *J* values[9,10] may be subject to other interpretations.[2−4] In most cases only a single conformer is populated to any observable extent so there is no chemical site exchange resulting from any rotation about the M−C bond, and no rotation barrier can be estimated using typical NMR coalescence methods.



1 **2**

Here we report the synthesis and structures of some cationic and neutral iridium−fluoroalkyl compounds in which such

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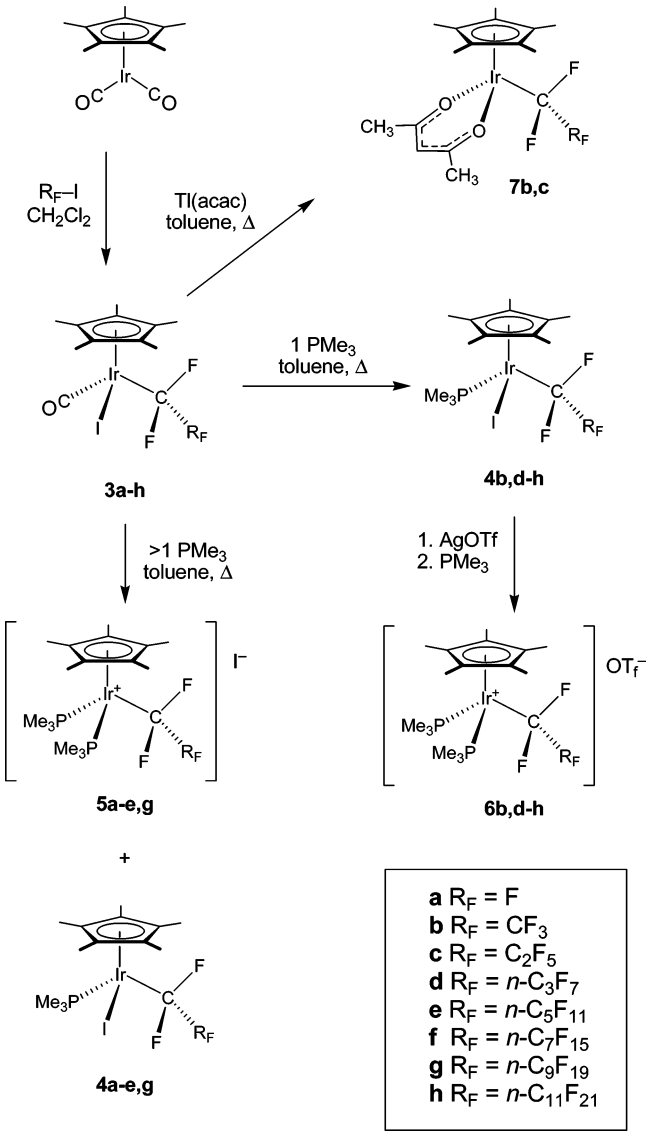
Scheme 1

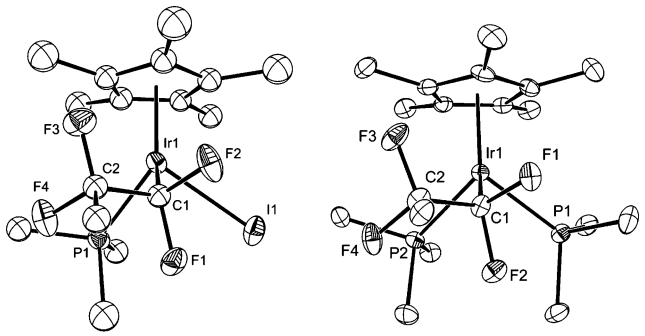


rotation barriers can be defined unambiguously using variable-temperature NMR spectroscopy.

Results and Discussion

Oxidative addition of various perfluoroalkyl iodides (R_FI) to $Cp^*Ir(CO)_2$ ($Cp^* = C_5Me_5$) according to the general method previously reported[17] produces $Cp^*Ir(CO)I(R_F)$ (**3a**−**h**), some of which were converted to the PMe_3-substituted derivatives **4b**,**d**−**h** by treatment with 1 equiv of PMe_3 in refluxing toluene (Scheme 1). When selected compounds **3** were refluxed with a slight excess (1.2−1.5 equiv) of PMe_3 in toluene, the bis(phosphine) complexes **5a**−**e**,**g** were obtained as iodo salts along with the monophosphine derivatives **4a**−**e**,**g**. Neutral compounds **4** were easily separated from the salts by washing with ether. Selected triflate salts **6b**,**d**−**h** were also prepared by sequential treatment of the monophosphine precursors with silver triflate followed by additional PMe_3. Additionally, two neutral acetylacetonato compounds **7b**,**c** were prepared by refluxing Tl(acac) (1.1 equiv) with **3b**,**c** in toluene.

Three representative complexes, **4g**, **5g**, and **7b**, were characterized by single-crystal X-ray diffraction studies. Details of the crystallographic determinations are compiled in Table 1. Compound **5g** crystallized with two molecules of water in the asymmetric unit.



A B

Figure 2. Truncated ORTEP representations of the structure of **4g** (A) and the cation of **5g** (B) showing only the first three carbons of the fluoroalkyl ligand, looking down the C1−Ir bond and showing the different environments of F_1 and F_2. All ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg) for **5g**: Ir(1)−C(1), 2.07(3); Ir−Ct01, 1.92(8); Ir(1)−P(1), 2.33(6); Ir(1)−P(2), 2.303; C(1)−F(1), 1.38(3); C(1)−F(2), 1.39(4); Ct01−Ir(1)−C(1), 125.4(1); Ct01−Ir(1)−P(1), 123.8(5); Ct01−Ir(1)−P(2), 122.8(3); Ir(1)−C(1)−C(2), 121.1(9); Ir(1)−C(1)−F(1), 110.0(7); Ir(1)−C(1)−F(2), 115.4(4); C(1)−Ir(1)−P(1), 87.0(2); C(1)−Ir(1)−P(2), 94.7(1); P(1)−Ir(1)−P(2), 93.3(3).

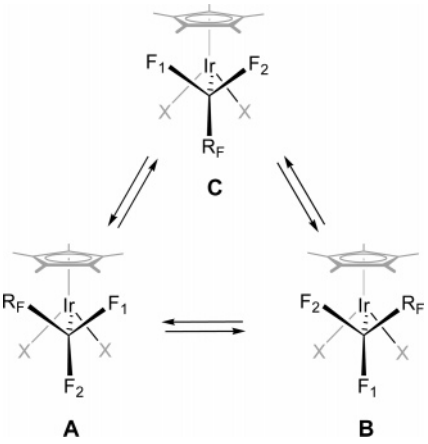


Figure 3. Staggered conformations for the primary fluoroalkyl ligand in cationic complexes **5** and **6** [X = PMe_3] and neutral **7** [X = O (acac)].

Figure 2 shows truncated ORTEP representations of the neutral complex **4g** and the cationic portion of its bis(phosphine) analogue **5g**, showing the local environment around iridium from a perspective analogous to a Newman projection looking down the C_1−Ir bond. The structures are remarkably consistent. The conformation of the fluoroalkyl ligand in **4g** is that shown as **1a** (Figure 1) and as found in many other analogues.[11,12,17] However, in the bis(phosphine) analogue **5g** the stereocenter is absent, and the three possible staggered conformations are shown in Figure 3: two equal energy and enantiomerically related conformations A and B of C_1 symmetry and conformation C of C_s symmetry. The solid state conformation found in **5g** clearly corresponds to a C_1 rotamer. As a consequence, the fluorines F_1 and F_2 are in inequivalent environments in the ground state structure, but are interchangeable by a simple rotation about the Ir−C_1 bond; the same is true of course for other pairs of geminally related fluorines along the fluoroalkyl chain.

Likewise the perfluoroethyl ligand in the acac complex **7b** adopts an analogous C_1 symmetric conformation in the ground state, as shown by the ORTEP in Figure 4.

In solution the ^{19}F NMR spectrum of **7b** showed only a single environment for F_1 and F_2 down to −80 °C, consistent with

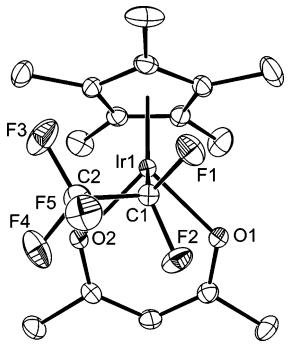


Figure 4. ORTEP representation of the structure of **7b**, with ellipsoids drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ir(1)−C1, 2.06(6); Ir(1)−Ct01, 1.79(4); Ir-(1)−O(1), 2.092; Ir(1)−O(2), 2.092; C(1)−F(1), 1.39(1); C(1)−F(2), 1.383; Ct01−Ir(1)−C(1), 133.2(1); Ct01−Ir(1)−O(1), 133.2-(1); Ct01−Ir(1)−O(2), 123.6(0); Ir(1)−C(1)−C(2), 119.5(0); Ir(1)−C(1)−F(1), 112.8(4); Ir(2)−C(1)−F(2), 114.6(0); C(1)−Ir(1)−O(1), 86.3(2); C(1)−Ir(1)−O(2), 88.2(9); O(1)−Ir(1)−O(2), 88.3(1).

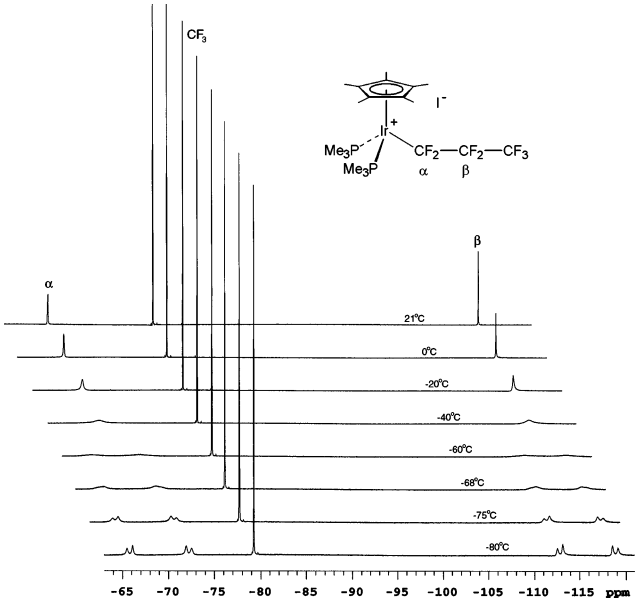


Figure 5. Variable-temperature ^{19}F NMR spectra of complex **5c** (480 MHz; CD_2Cl_2 solution).

either a different, symmetrical structure C (Figure 3) in solution from that in the solid state or a rapid interconversion of F_1 and F_2 environments by either a full rotation or partial windshield-wiper motion of the fluoroalkyl ligand between enantiomerically related conformations A and B (Figure 3), i.e., a fast (on the NMR time scale) rotation about the Ir−C_1 bond. The absence of any decoalescence of fluorine resonances makes these two options indistinguishable.

Similarly, cooling solutions of the trifluoromethyl complex **5a** to −80 °C resulted in slight broadening of the fluorine resonance, but no decoalescence. However, cooling solutions of other cationic bis(phosphine) compounds **5** and **6** containing primary fluoroalkyl ligands does indeed result in decoalescence of resonances for F_1 and F_2, along with other pairs of fluorines along the chain. This is illustrated for the perfluoropropyl compound **5c** in Figure 5 and can only be a result of slowing of site exchange between conformations A and B (Figure 3) in which F_1 and F_2 are inequivalent; the barrier to this process is most likely a good estimate of the maximum barrier to rotation about the Ir−C_1 bond. Rate constants were obtained by line

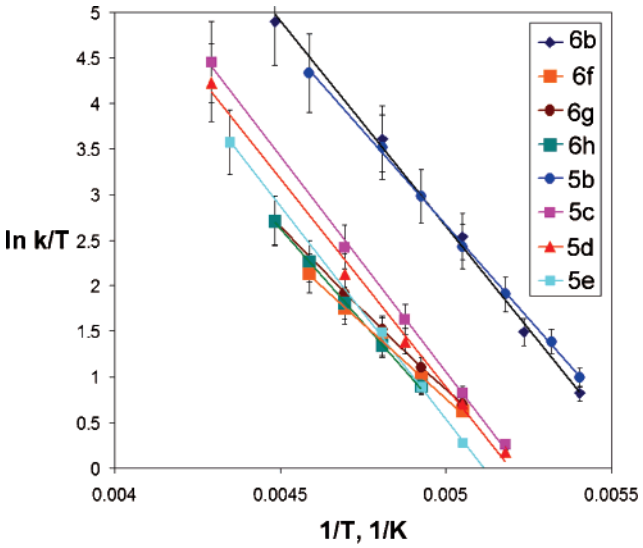


Figure 6. Eyring plots for the variable-temperature rate constants for the dynamic behavior of compounds **5** and **6**.

Table 2. Calculated Rotational Barriers by gNMR

compound	$\Delta G^{\ddagger}_{298K}$, kJ/mol	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, J/mol·K
6b $[Cp^*Ir(PMe_3)_2(C_2F_5)]^+OTf^-$	34 ± 2	38 ± 2	12 ± 20
5b $[Cp^*Ir(PMe_3)_2(C_2F_5)]^+I^-$	36 ± 2	34 ± 2	−5 ± 3
5c $[Cp^*Ir(PMe_3)_2(C_3F_7)]^+I^-$	38 ± 2	36 ± 2	−6 ± 5
5d $[Cp^*Ir(PMe_3)_2(C_4F_9)\ ]^+I^-$	38 ± 2	38 ± 2	−2 ± 5
5e $[Cp^*Ir(PMe_3)_2(C_6F_{13})\ ]^+I^-$	38 ± 2	39 ± 2	1 ± 4
6f $[Cp^*Ir(PMe_3)_2(C_8F_{17})]^+OTf^-$	43 ± 2	28 ± 2	−55 ± 20
6g $[Cp^*Ir(PMe_3)_2(C_{10}F_{21})]^+OTf^-$	42 ± 2	30 ± 2	−42 ± 20
6h $[Cp^*Ir(PMe_3)_2(C_{12}F_{25})]^+OTf^-$	41 ± 2	34 ± 2	−22 ± 20

shape analysis using gNMR;[24] Eyring plots are shown in Figure 6, and resultant values of the activation parameters are listed in Table 2.

The plots shown in Figure 6 illustrate that the slopes, and the values of $\Delta H^{\ddagger}$ obtained from them, are all approximately the same within experimental error. The enthalpic contribution to the bond rotation barrier appears to be independent of chain length and also of the counteranion. However, it is also clear that the two perfluoroethyl complexes **5b** and **6b** are distinct from those analogues of longer chain length; for plots of identical slope this must originate from differences in $\Delta S^{\ddagger}$. However the values of $\Delta S^{\ddagger}$ determined by these means are prone to significant error; the extrapolation to zero intercept is a long one, and small errors in the slope of these plots lead to big uncertainties in $\Delta S^{\ddagger}$, which propagates to corresponding values of $\Delta G^{\ddagger}$. Thus, while it seems apparent that there is a greater entropic contribution to the barriers for rotation in perfluoroalkyl chains of three carbons and higher compared to perfluoroethyl, and while this is perhaps quite understandable in terms of reorganizational requirements within the ligands, our data are insufficiently precise to allow quantification of these differences.

Finally the origin of the enthalpic, and most important, part of the barrier is clearly steric in nature. For the acac complexes **7**, with small O atoms *cis* to the fluoroalkyl ligand, the barrier is small enough that no decoalescence is observed; as expected, the larger PMe_3 ligands in compounds **5** and **6** result in a significantly higher barrier. As an obvious extension to this argument, replacement of the Cp* ligand with the smaller cone

(24) *gNMR* Ver. 5.0; Cherwell Scientific Ltd.: Oxford, UK, 2002.

angle[25] Cp ligand should result in a smaller barrier. Indeed, CpIr(PMe$_3$)$_2$(*n*-C$_3$F$_7$)]$^+$OT$_f^-$, prepared from CpIr(PMe$_3$)(*n*-C$_3$F$_7$)I[26] by the methodology shown in Scheme 1, showed only slight broadening of the ^{19}F resonances at −80 °C, consistent with a significantly lower barrier to rotation about the Ir−C bond than found in its pentamethylcyclopentadienyl analogues.

In summary, the barriers to rotation about the Ir−C bond in a series of sterically crowded perfluoroalkyl complexes of iridium are dominated by $\Delta H^{\ddagger}$ values of ∼33 ± 2 kJ/mol. While perfluoroethyl ligand rotation appears to have a smaller value of $\Delta S^{\ddagger}$ compared to longer chain perfluoroalkyls, as judged by the offset of the slopes of Eyring plots, the precision of our data is insufficiently good to allow a quantitative estimate of this difference to be made. For the conversion of **1** → **2** (R = H) the measured overall value of $\Delta H^{\ddagger}$ is 73 ± 5 kJ/mol in CD_2Cl_2.[21] Given the dominance of steric effects in determining rotation barriers in these compounds, it seems likely that in the hydrido starting material **1** (R = H) any contribution of fluoroalkyl rotation to the overall value of $\Delta H^{\ddagger}$ for the reaction is considerably less than 33 ± 2 kJ/mol, i.e., significantly less than half of the overall barrier.

Experimental Section

General Data. Air-sensitive reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen, which was deoxygenated over BASF catalyst and dried over Aquasorb, or in a Braun drybox. Methylene chloride, hexanes, diethyl ether, tetrahydrofuran, and toluene were dried over an alumina column under nitrogen.[27] NMR spectra were recorded on a Varian Unity Plus 300 or 500 FT spectrometer. ^{1}H NMR spectra were referenced to the protio impurity in the solvent: C_6D_6 (7.16 ppm), CD_2Cl_2 (5.32 ppm). ^{19}F NMR spectra were referenced to external $CFCl_3$ (0.00 ppm). ^{31}P{^{1}H} NMR spectra were referenced to 85% H_3PO_4 (0.00 ppm). Coupling constants are reported as absolute values in units of hertz. Elemental analyses were performed by Schwartzkopf (Woodside, NY).

$IrCl_3{\cdot}3H_2O$ (Pressure Chemical Company), Cp*H (Strem), *n*-C$_4$F$_9$I, *n*-C$_6$F$_{11}$I, *n*-C$_8$F$_{17}$I, *n*-C$_{10}$F$_{21}$I, and *n*-C$_{12}$F$_{25}$I (PCR), and PMe$_3$ (Aldrich) were obtained commercially and used as received.

The complexes Cp*Ir(CO)$_2$,[28] Cp*Ir(CO)(CF$_3$)I (**3a**),[29] Cp*Ir(CO)(*n*-C$_2$F$_5$)I (**3b**),[17] Cp*Ir(CO)(*n*-C$_4$F$_9$)I (**3c**),[17] Cp*Ir(PMe$_3$)(*n*-C$_2$F$_5$)I (**4b**),[17] Cp*Ir(PMe$_3$)(*n*-C$_3$F$_7$)I (**4c**),[17] and CpIr(PMe$_3$)(*n*-C$_3$F$_7$)(I)[26] were prepared according to literature procedures.

Cp*Ir(CO)(*n*-C$_4$F$_9$)I (3d). To a yellow solution of Cp*Ir(CO)$_2$ (100 mg, 0.260 mmol) in dry CH_2Cl_2 (10 mL) was added *n*-C$_4$F$_9$I (90 mg, 45 μL, 0.260 mmol) dropwise at room temperature. The mixture was stirred for 30 min, and then the solvent was removed on a rotary evaporator. The product was obtained as a yellow solid, which could be recrystallized from hexane/methylene chloride (181 mg, 99%). Anal. Calcd for $C_{15}H_{15}F_9IIrO$: C, 25.69; H, 2.16. Found: C, 25.77; H, 2.34. ^{1}H NMR ($CDCl_3$, 500 MHz, 21 °C): δ 2.11 (s, 15H, C_5Me_5). ^{19}F NMR ($CDCl_3$, 470 MHz, 21 °C): δ −59.36 (dm, $^2J_{F(AB)}$ = 274 Hz, 1F, α-CF$_A$), −71.29 (dm, $^2J_{F(AB)}$ = 274 Hz, 1F, α-CF$_B$), −81.35 (tt, $^4J_{FF}$ = 10 Hz, $^5J_{FF}$ = 4 Hz, 3F, CF$_3$), −109.96 (dm, $^2J_{F(AB)}$ = 287 Hz, 1F, β-CF$_A$), −113.94 (dm, $^2J_{F(AB)}$ = 287 Hz, 1F, β-CF$_B$), −124.89 (dm, $^2J_{F(AB)}$ = 290 Hz, 1F, γ-CF$_A$), −126.12 (dm, $^2J_{F(AB)}$ = 290 Hz, 1F, γ-CF$_B$).

Cp*Ir(CO)(*n*-C$_6$F$_{13}$)I (3e). To a yellow solution of Cp*Ir(CO)$_2$ (50 mg, 0.130 mmol) in dry CH_2Cl_2 (10 mL) was added *n*-C$_6$F$_{13}$I (60 mg, 30 μL, 0.135 mmol) dropwise. The resultant mixture was stirred for 15 min under an atmosphere of nitrogen. The solvent was removed, and the solids were washed with hexane (3 mL) to afford an analytically pure product as a yellow crystalline material in quantitative yield (104 mg, 100% yield). Anal. Calcd for $C_{17}H_{15}F_{13}IIrO$: C, 25.48; H, 1.89. Found: C, 25.64; H, 2.03. ^{1}H NMR (C_6D_6, 500 MHz, 21 °C): δ 1.49 (s, 15H, C_5Me_5). ^{19}F NMR (C_6D_6, 470 MHz, 21 °C): δ −59.53 (dm, $^2J_{F(AB)}$ = 275 Hz, 1F, α-CF$_A$), −70.55 (dm, $^2J_{F(AB)}$ = 275 Hz, 1F, α-CF$_B$), −81.39 (tm, J_{FF} = 10 Hz, 3F, CF$_3$), −108.23 (dm, $^2J_{F(AB)}$ = 286 Hz, 1F, β-CF$_A$), −112.90 (dm, $^2J_{F(AB)}$ = 286 Hz, 1F, β-CF$_B$), −120.75 (dm, $^2J_{F(AB)}$ = 296 Hz, 1F, CF$_2$), −121.67 (dm, $^2J_{F(AB)}$ = 296 Hz, 1F, CF$_2$), −122.56 (dm, $^2J_{F(AB)}$ = 300 Hz, 1F, CF$_2$), −123.04 (dm, $^2J_{F(AB)}$ = 300 Hz, 1F, CF$_2$), −126.17 (dm, $^2J_{F(AB)}$ = 293 Hz, 1F, CF$_2$), −126.66 (dm, $^2J_{F(AB)}$ = 293 Hz, 1F, CF$_2$).

Cp*Ir(CO)(*n*-C$_8$F$_{17}$)I (3f). *n*-C$_8$F$_{17}$I (136.3 mg, 0.25 mmol) was added to a solution of Cp*Ir(CO)$_2$ (95.9 mg, 0.25 mmol) in CH_2Cl_2 (20 mL) to give a yellow solution. The solution was stirred vigorously at room temperature (4 h). The solvent was removed in vacuo to give a yellow solid, which was then recrystallized from CH_2Cl_2/hexanes to give a yellow solid (191 mg, 85%). Anal. Calcd for $C_{19}H_{15}F_{17}IIrO$: C, 25.31; H, 1.68. Found: C, 25.50; H, 1.66. ^{1}H NMR (CD_2Cl_2, 300 MHz, 21 °C): δ 2.11 (s, 15H, C_5Me_5). ^{19}F NMR (CD_2Cl_2, 282 MHz, 21 °C): δ −59.95 (dm, $^2J_{F(AB)}$ = 277 Hz, 1F, α-CF$_A$), −71.31 (dm, $^2J_{F(AB)}$ = 277 Hz, 1F, α-CF$_B$), −81.54 (s, 3F, CF$_3$), −108.91 (dm, $^2J_{F(AB)}$ = 277 Hz, 1F, β-CF$_A$), −113.49 (dm, $^2J_{F(AB)}$ = 289 Hz, 1F, β-CF$_B$), −121.49 (dm, $^2J_{F(AB)}$ = 301 Hz, 1F, CF$_2$), −121.79 (dm, $^2J_{F(AB)}$ = 301 Hz, 1F, CF$_2$), −122.26 (s, 2F, CF$_2$), −122.51 (s, 1F, CF$_2$), −123.32 (s, 1F, CF$_2$), −126.74 (s, 2F, CF$_2$).

Cp*Ir(CO)(*n*-C$_{10}$F$_{21}$)I (3g). Cp*Ir(CO)$_2$ (47.9 mg, 0.125 mmol) and *n*-C$_{10}$F$_{21}$I (80.8 mg, 0.125 mmol) were dissolved in CH_2Cl_2 (20 mL). The solution was stirred vigorously at room temperature (4 h). The solvent was removed in vacuo to give a brown solid, which was recrystallized from CH_2Cl_2/hexane to give a yellow solid (102 mg, 82%). Anal. Calcd for $C_{21}H_{15}F_{21}IIrO$: C, 25.18; H, 1.51. Found: C, 25.43; H, 1.43. ^{1}H NMR (CD_2Cl_2, 300 MHz, 21 °C): δ 2.11 (15H, s, C_5Me_5). ^{19}F NMR (CD_2Cl_2, 282 MHz, 21 °C): δ −59.99 (dm, $^2J_{F(AB)}$ = 277 Hz, 1F, α-CF$_A$), −71.38 (dm, $^2J_{F(AB)}$ = 241 Hz, 1F, α-CF$_B$), −81.50 (s, 3F, CF$_3$) −108.89 (dm, $^2J_{F(AB)}$ = 289 Hz, 1F, β-CF$_A$), −113.46 (dm, $^2J_{F(AB)}$ = 289 Hz, 1F, β-CF$_B$), −121.45 (dm, $^2J_{F(AB)}$ = 301 Hz, 1F, CF$_2$), −121.83 (dm, $^2J_{F(AB)}$ = 301 Hz, 2F, CF$_2$), −122.30 (s, 8F, 4CF$_2$), −123.28 (s, 2F, CF$_2$), −126.74 (s, 2F, CF$_2$).

Cp*Ir(CO) (*n*-C$_{12}$F$_{25}$)I (3h). Cp*Ir(CO)$_2$ (47.9 mg, 0.125 mmol) and *n*-C$_{12}$F$_{25}$I (93.3 mg, 0.125 mmol) were dissolved in CH_2Cl_2 (20 mL). The solution was stirred vigorously at room temperature (4 h). The solvent was removed in vacuo to give a brown solid, which was recrystallized from CH_2Cl_2/hexane to give a yellow solid (117 mg, 85%). Anal. Calcd for $C_{23}H_{15}F_{25}IIrO$: C, 25.08; H, 1.37. Found: C, 25.90; H, 1.43. ^{1}H NMR (CD_2Cl_2, 300 MHz, 21 °C): δ 2.08 (15H, s, C_5Me_5). ^{19}F NMR (CD_2Cl_2, 282 MHz, 21 °C): δ −59.93 (d, $^2J_{F(AB)}$ = 289 Hz, 1F, α-CF$_A$), −71.35 (d, $^2J_{F(AB)}$ = 277 Hz, 1F, α-CF$_B$), −81.54 (s, 3F, CF$_3$), −109.95 (d, $^2J_{F(AB)}$ = 289 Hz, 1F, β-CF$_A$), −113.52 (d, $^2J_{F(AB)}$ = 277 Hz, 1F, β-CF$_B$), −120.91 (d, $^2J_{F(AB)}$ = 301 Hz, 1F, γ-CF$_A$), −113.52 (d, $^2J_{F(AB)}$ = 273 Hz, 1F, γ-CF$_B$), −122.30 (s, 12F, 6CF$_2$), −123.32 (s, 2F, CF$_2$), −126.79 (s, 2F, CF$_2$).

Cp*Ir(PMe$_3$)(*n*-C$_4$F$_9$)I (4d). To a yellow solution of Cp*Ir(CO)(*n*-C$_4$F$_9$)I (180 mg, 0.258 mmol) in dry toluene (20 mL) was added PMe$_3$ (22 mg, 30 μL, 0.289 mmol). A white suspension formed in the yellow solution. The mixture was refluxed under an atmosphere of N_2 for 12 h, then allowed to stand at room temperature for 10

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h. A small quantity of colorless crystals of [Cp*Ir(PMe_3)$_2$(*n*-C_4F_9)]I (**5d**) formed at the bottom of the flask. The yellow solution was filtered and the solvent was removed, affording the product as an orange oil (176 mg, 92%). Crystals of X-ray quality were prepared by slow evaporation of toluene at −30 °C. Anal. Calcd for $C_{17}H_{24}F_9$IIrP: C, 27.24; H, 3.23. Found: C, 27.62; H 3.20. ^{1}H NMR ($CDCl_3$, 500 MHz, 21 °C): δ 1.73 (d, $^2J_{PH}$ = 10.5 Hz, 9H, PMe_3), 1.89 (d, $^4J_{PH}$ = 2.0 Hz, 15H, C_5Me_5). ^{19}F NMR ($CDCl_3$, 470 MHz, 21 °C): δ −65.53 (dm, $^2J_{F(AB)}$ = 288 Hz, 1F, α-CF_A), −66.00 (dm, $^2J_{F(AB)}$ = 288 Hz, 1F, α-CF_B), −81.21 (tt, $^4J_{FF}$ = 9 Hz, $^5J_{FF}$ = 5 Hz, 3F, CF_3), −110.93 (dm, $^2J_{F(AB)}$ = 284 Hz, 1F, β-CF_A), −112.58 (dm, $^2J_{F(AB)}$ = 284 Hz, 1F, β-CF_B), −124.77 (dddt, $^2J_{F(AB)}$ = 289 Hz, $^4J_{FF}$ = 18 Hz, $^4J_{FF}$ = 13 Hz, $^3J_{FF}$ = 4 Hz, 1F, γ-CF_A), −125.46 (dddt, $^2J_{F(AB)}$ = 289 Hz, $^4J_{FF}$ = 18 Hz, $^4J_{FF}$ = 14 Hz, $^3J_{FF}$ = 4 Hz, 1F, γ-CF_B). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 21 °C): δ −39.9 (dd, $^3J_{PF}$ = 14 Hz, $^3J_{PF}$ = 8 Hz, 1P).

Cp*Ir(PMe_3)(*n*-C_6F_{13})I (4e). To a yellow solution of Cp*Ir(CO)(*n*-C_6F_{13})I (105 mg, 0.130 mmol) in dry toluene (20 mL) was added PMe_3 (11 mg, 15 μL, 0.145 mmol). The resultant mixture was stirred under reflux for 12 h under an atmosphere of nitrogen. After cooling the reaction mixture, the yellow solution of Cp*Ir(PMe_3)(*n*-C_6F_{13})I in toluene was filtered off. Removal of the solvent afforded an analytically pure product as an orange crystalline material in quantitative yield. Anal. Calcd for $C_{19}H_{24}F_{13}$IIrP: C, 26.86; H, 2.85. Found: C, 27.23; H, 3.03. ^{1}H NMR (C_6D_6, 500 MHz, 21 °C): δ 1.34 (d, $^2J_{PH}$ = 10.5 Hz, 9H, PMe_3), 1.50 (d, $^4J_{PH}$ = 2.0 Hz, 15H, C_5Me_5). ^{19}F NMR (C_6D_6, 470 MHz, 21 °C): δ −65.22 (dm, $^2J_{F(AB)}$ = 290 Hz, 1F, α-CF_A), −65.54 (dm, $^2J_{F(AB)}$ = 290 Hz, 1F, α-CF_B), −81.37 (tm, J_{FF} = 10 Hz, 3F, CF_3), −109.56 (dm, $^2J_{F(AB)}$ = 284 Hz, 1F, β-CF_A), −111.50 (dm, $^2J_{F(AB)}$ = 284 Hz, 1F, β-CF_B), −120.61 (dm, $^2J_{F(AB)}$ = 301 Hz, 1F, CF_2), −121.24 (dm, $^2J_{F(AB)}$ = 301 Hz, 2F, CF_2), −122.46 (dm, $^2J_{F(AB)}$ = 298 Hz, 1F, CF_2), −122.89 (dm, $^2J_{F(AB)}$ = 298 Hz, 1F, CF_2), −126.19 (dm, $^2J_{F(AB)}$ = 292 Hz, 1F, CF_2), −126.47 (dm, $^2J_{F(AB)}$ = 292 Hz, 1F, CF_2). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz, 21 °C): δ −40.75 (ddd, $^3J_{PF}$ = 13 Hz, $^3J_{PF}$ = 7, $^4J_{PF}$ = 4 Hz, P).

Cp*Ir(PMe_3)(*n*-C_8F_{17})I (4f). Cp*Ir(CO)I(*n*-C_8F_{17}) (380 mg, 0.42 mmol) was dissolved in toluene (20 mL), and PMe_3 (48 μL, 0.46 mmol) was added into the solution by syringe. The mixture was refluxed overnight and cooled, and the solvent was removed by rotary evaporator to give a brown-yellow solid, which was recrystallized in hexane at −70 °C to give a yellow solid (339.0 mg, 85%). Anal. Calcd for $C_{21}H_{24}F_{17}$IIrP: C, 26.56; H, 2.41. Found: C, 26.84; H, 2.46. ^{1}H NMR (CD_2Cl_2, 300 MHz, 21 °C): δ 1.87 (d, $^4J_{HP}$ = 1.8 Hz, 15H, C_5Me_5), 1.71 (d, $^2J_{HP}$ = 10.8 Hz, 9H, PMe_3). ^{19}F NMR (CD_2Cl_2, 282 MHz, 21 °C): δ −65.74 (s, 2F, α-CF_2), −81.54 (s, 3F, CF_3), −109.85 (d, $^2J_{F(AB)}$ = 289 Hz, 1F, β-CF_A), −111.85 (d, $^2J_{F(AB)}$ = 289, 1F, β-CF_B), −121.36 (m, 2F, CF_2), −122.21 (s, 2F, CF_2), −122.51 (s, 2F, CF_2), −123.32 (s, 2F, CF_2), −126.74 (s, 2F, CF_2). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz, 21 °C): δ −40.09 (ddd, $^3J_{FP}$ = 14 Hz, $^3J_{FP}$ = 5, $^4J_{FP}$ = 3, P).

Cp*Ir(PMe_3)(*n*-$C_{10}F_{21}$)I (4g). Cp*Ir(CO)I(*n*-$C_{10}F_{21}$) (90 mg, 0.09 mmol) was dissolved in toluene (20 mL), and PMe_3 (9.35 μL, 0.09 mmol) was added by syringe. The mixture was refluxed overnight and cooled, and the solvent was removed in vacuo to give a brown-yellow, oily solid, which was recrystallized from hexane at −70 °C to give a yellow solid (77 mg, 82%). Anal. Calcd for $C_{23}H_{24}F_{21}$IIrP: C, 26.32; H, 2.31. Found: C, 26.59; H, 2.34. ^{1}H NMR (CD_2Cl_2, 300 MHz, 21 °C): δ 1.87 (d, $^4J_{HP}$ = 2.10 Hz, 15H, C_5Me_5), 1.71 (d, $^2J_{HP}$ = 10.5 Hz, 9H, PMe_3). ^{19}F NMR (CD_2Cl_2, 282 MHz, 21 °C): δ −65.78 (s, 2F, α-CF_2), −81.50 (s, 3F, CF_3), −109.80 (d, $^2J_{F(AB)}$ = 277 Hz, 1F, β-CF_A), −111.85 (d, $^2J_{F(AB)}$ = 277 Hz, 1F, β-C F_B), −121.40 (s, 2F, CF_2), −122.34 (s, 8F, 4CF_2) −123.32 (s, 2F, CF_2), −126.74 (s, 2F, CF_2). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz, 21 °C): δ −40.08 (ddd, $^3J_{FP}$ = 15 Hz, $^3J_{FP}$ = 5, $^4J_{FP}$ = 3, P).

Cp*Ir(PMe_3)(*n*-$C_{12}F_{25}$)I (4h). Cp*Ir(CO)I(*n*-$C_{12}F_{25}$) (88.1 mg, 0.08 mmol) was dissolved in toluene (10 mL), and PMe_3 (16.6 μL, 0.16 mmol) was added by syringe. The mixture was refluxed overnight to give a light yellow solution and cooled, and the solvent was removed to give a brown-yellow solid, which was recrystallized from hexane at −70 °C to give a yellow solid (74 mg, 80%). Anal. Calcd for $C_{25}H_{24}F_{25}$IIrP: C, 26.12; H, 2.19. Found: C, 26.36; H, 2.20. ^{1}H NMR (CD_2Cl_2, 300 MHz, 21 °C): δ 1.86 (d, $^4J_{HP}$ = 2.1 Hz, 15H, C_5Me_5), 1.70 (d, $^2J_{HP}$ = 10.5 Hz, 9H, PMe_3). ^{19}F NMR (CD_2Cl_2, 282 MHz, 21 °C): δ −65.74 (2F, s, α-CF_2), δ −81.50 (3F, s, CF_3), −109.80 (d, $^2J_{F(AB)}$ = 277 Hz, 1F, β-CF_A), −111.85 (d, $^2J_{F(AB)}$ = 277 Hz, 1F, β-CF_B), −121.40 (s, 2F, CF_2), −122.30 (s, 12F, 6CF_2) −123.28 (s, 2F, CF_2), −126.74 (s, 2F, CF_2). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz, 21 °C): δ −40.14 (ddd, $^3J_{FP}$ = 15 Hz, $^3J_{FP}$ = 5, $^4J_{FP}$ = 3, P).

[Cp*Ir(CF_3)(PMe_3)$_2$]$^+$I$^-$ (5a). To a solution of Cp*Ir(CF_3)(CO)I (862 mg, 1.56 mmol) in toluene (40 mL) was added PMe_3 (0.19 mL, 1.84 mmol) and the mixture heated under reflux for 3 h. The resultant suspension was cooled to room temperature and filtered, and the pale yellow solid washed with toluene. The solid was suspended in fresh toluene (20 mL), heated under reflux for 1 h, cooled to room temperature, and filtered. The solid was suspended in fresh toluene (15 mL), and PMe_3 (0.10 mL, 0.966 mmol) was added. The mixture was heated under reflux for 1 h and the resulting suspension cooled to room temperature and filtered. The yellow solid was suspended in fresh toluene (15 mL) and heated under reflux for 1 h. The resultant suspension was cooled to room temperature, filtered, and washed with toluene and hexanes. The yellow solid was recrystallized from CH_2Cl_2/toluene. Anal. Calcd for $C_{17}H_{33}F_3$IIrP$_2$: C, 30.23; H, 4.92. Found: C, 29.97; H, 4.96. ^{1}H NMR (CD_2Cl_2, 300 MHz, 23 °C): δ 1.78 (d, $^{2,4}J_{HP}$ = 10.8 Hz, 18H, PMe_3), 1.92 (t, $^4J_{HP}$ = 2.1 Hz, 15H, C_5Me_5). ^{19}F NMR (CD_2Cl_2, 282 MHz, 23 °C): δ −5.1 (t, $^3J_{FP}$ = 6 Hz, CF_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz, 23 °C): δ −38.9 (q, $^3J_{PF}$ = 6 Hz, 2P, PMe_3).

[Cp*Ir(PMe_3)$_2$(*n*-C_2F_5)]$^+$I$^-$ (5b). [Cp*Ir(PMe_3)(CO)(C_2F_5)]I (130 mg, 0.192 mmol) was suspended in dry toluene, the mixture was degassed, and PMe_3 (15 mg, 20 μL, 0.195 mmol) was added. The resultant mixture was refluxed for 12 h and cooled, the yellow toluene solution was filtered, and a white residue was obtained, containing a mixture of [Cp*Ir(PMe_3)(CO)(C_2F_5)]I and [Cp*Ir(PMe_3)$_2$(C_2F_5)]I. Fresh toluene was added along with more PMe_3 (15 mg, 20 μL, 0.195 mmol), and the refluxing overnight was repeated. After the workup the white residue still contained some starting material. Again toluene was added and the suspension was refluxed overnight. Filtration of the solvent afforded the white solid, which was now analytically pure [Cp*Ir(PMe_3)$_2$(C_2F_5)]I (70 mg (50%). Anal. Calcd for $C_{18}H_{33}F_5$IIrP$_2$: C, 29.80; H, 4.58. Found: C, 29.72; H, 4.43. ^{1}H NMR (CD_2Cl_2, 500 MHz, 21 °C): δ 1.77 (m, $^2J_{PH}$ = 10.4 Hz, 18H, PMe_3), 1.88 (t, $^4J_{PH}$ = 2.15 Hz, 15H, C_5Me_5). ^{19}F NMR (CD_2Cl_2, 470 MHz, 21 °C): δ −71.21 (br t, $^3J_{FP}$ = 15 Hz, 2F, α-CF_2), −82.06 (s, 3F, CF_3); (CD_2Cl_2, 470 MHz, −88 °C) δ −71.36 (br d, $^2J_{F(AB)}$ = 266 Hz, 1F, α-CF_A), −73.75 (br d, $^2J_{F(AB)}$ = 266 Hz, 1F, α-CF_B), −82.49 (s, 3F, CF_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202 MHz, 21 °C): δ −42.23 (tq, $^3J_{PF}$ = 15 Hz, $^4J_{PF}$ = 2 Hz, 2P, PMe_3).

[Cp*Ir(PMe_3)$_2$(*n*-C_3F_7)]$^+$I$^-$ (5c). The product was obtained as a side product of the reaction of Cp*Ir(CO)(*n*-C_3F_7)I with PMe_3 in dry toluene under reflux for 12 h. PMe_3 was added in slight excess (1.2 equiv) to give the major product Cp*Ir(PMe_3)(*n*-C_3F_7)I, soluble in toluene, and 5−10% of [Cp*Ir(PMe_3)$_2$(*n*-C_3F_7)]I as a white solid, insoluble in toluene. The orange solution of Cp*Ir(PMe_3)(*n*-C_3F_7)I was filtered off to afford the desired product as an off-white solid. Anal. Calcd for $C_{19}H_{33}F_7$IIrP$_2$: C, 29.43; H, 4.29. Found: C, 29.67; H, 4.23. ^{1}H NMR (CD_2Cl_2, 500 MHz, 21 °C): δ 1.78 (m, $^2J_{PH}$ =

10.3 Hz, 18H, PMe_3), 1.88 (t, $^4J_{PH}$ = 2.1 Hz, 15H, C_5Me_5). ^{19}F NMR (CD_2Cl_2, 470.3 MHz, 21 °C): δ −67.95 (br s, 2F, α-CF_2), −79.44 (t, $^4J_{FF}$ = 13 Hz, 3F, CF_3), −115.17 (br s, 2F, β-CF_2); (CD_2Cl_2, 470.3 MHz, −80 °C) δ −65.84 (br d, $^2J_{F(AB)}$ = 284 Hz, 1F, α-CF_A), −72.22 (br d, $^2J_{F(AB)}$ = 284 Hz, 1F, α-CF_B), −79.25 (t, $^4J_{FF}$ = 11 Hz, 3F, CF_3), −112.86 (br d, $^2J_{F(AB)}$ = 281 Hz, 1F, β-CF_A), −118.78 (br d, $^2J_{F(AB)}$ = 281 Hz, 1F, β-CF_B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 21 °C): δ −42.49 (tt, $^3J_{PF}$ = 15 Hz, $^4J_{PF}$ = 5 Hz, P).

[Cp*Ir(PMe$_3$)$_2$(*n*-C$_4$F$_9$)]$^+$I$^-$ (5d). To a yellow solution of Cp*Ir(CO)(*n*-C_4F_9)I (180 mg, 0.258 mmol) in dry toluene (20 mL) was added PMe_3 (22 mg, 30 μL, 0.289 mmol) at room temperature. A white suspension formed in the yellow solution. The mixture was refluxed under N_2 for 12 h, cooled, and allowed to stand at room temperature for 10 h. Colorless crystals of [Cp*Ir(PMe_3)$_2$(*n*-C_4F_9)]I formed at the bottom of the flask. The yellow solution containing Cp*Ir(PMe_3)(*n*-C_4F_9)I was filtered off to give **5d** (17 mg; 8%). Anal. Calcd for $C_{20}H_{33}F_9IIrP_2$: C, 29.10; H, 4.03. Found: C, 29.35; H, 4.27. ^1H NMR (CD_2Cl_2, 500 MHz, 21 °C): δ 1.78 (m, $^2J_{PH}$ = 10.4 Hz, 18H, PMe_3), 1.88 (t, $^4J_{PH}$ = 2.1 Hz, 15H, C_5Me_5). ^{19}F NMR (CD_2Cl_2, 470 MHz, 21 °C): δ −67.53 (br m, 2F, α-CF_2), −81.59 (tt, $^4J_{FF}$ = 10 Hz, $^5J_{FF}$ = 4 Hz, 3F, CF_3), −111.96 (br s, 2F, β-CF_2), −125.29 (br t, $^4J_{FF}$ = 17 Hz, 2F, γ-CF_2); (CD_2Cl_2, 470 MHz, −80 °C) δ −64.57 (br dm, $^2J_{F(AB)}$ = 284 Hz, 1F, α-CF_A), −72.53 (br dm, $^2J_{F(AB)}$ = 284 Hz, 1F, α-CF_B), −81.43 (br m, 3F, CF_3), −108.56 (br dm, $^2J_{F(AB)}$ = 286 Hz, 1F, β-CF_A), −116.61 (br dm, $^2J_{F(AB)}$ = 286 Hz, 1F, β-CF_B), −123.55 (br dm, $^2J_{F(AB)}$ = 289 Hz, 1F, γ-CF_A), −128.37 (br dm, $^2J_{F(AB)}$ = 289 Hz, 1F, γ-CF_B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 21 °C): δ −42.49 (tt, $^3J_{PF}$ = 16 Hz, $^4J_{PF}$ = 5 Hz, 2P).

[Cp*Ir(PMe$_3$)$_2$(*n*-C$_6$F$_{13}$)]$^+$I$^-$ (5e). To a yellow solution of Cp*Ir(PMe_3)(*n*-C_6F_{13})I (180 mg, 0.258 mmol) in dry toluene (20 mL) was added PMe_3 (6 mg, 8 μL, 0.075 mmol). The mixture was refluxed under N_2 for 12 h, cooled, and allowed to stand at room temperature for 10 h. The yellow solution of Cp*Ir(PMe_3)(*n*-C_4F_9)I in toluene was filtered off to give colorless crystals of [Cp*Ir(PMe_3)$_2$(*n*-C_4F_9)]I, which were washed with toluene. The product was analytically pure (15 mg; 8%). Anal. Calcd for $C_{22}H_{33}F_{13}IIrP_2$: C, 28.55; H, 3.59. Found: C, 28.40; H, 3.70. ^1H NMR (CD_2Cl_2, 500 MHz, 21 °C): δ 1.78 (m, $^2J_{PH}$ = 10.5 Hz, 18H, PMe_3), 1.88 (t, $^4J_{PH}$ = 2.0 Hz, 15H, C_5Me_5). ^{19}F NMR (CD_2Cl_2, 470 MHz, 21 °C): δ −67.32 (br s, 2F, α-CF_2), −81.54 (br s, 3F, CF_3), −111.02 (br s, 2F, β-CF_2), −121.44 (br s, 2F, γ-CF_2), −123.15 (br s, 2F, δ-CF_2), −126.66 (br s, 2F, ϵ-CF_2); (CD_2Cl_2, 470 MHz, −80 °C) δ −63.84 (br dm, $^2J_{F(AB)}$ = 282 Hz, 1F, α-CF_A), −72.83 (br dm, $^2J_{F(AB)}$ = 282 Hz, 1F, α-CF_B), −81.27 (br m, 3F, CF_3), −106.49 (br dm, $^2J_{F(AB)}$ = 287 Hz, 1F, β-CF_A), −117.11 (br dm, $^2J_{F(AB)}$ = 287 Hz, 1F, β-CF_B), −121.04 (dm, $^2J_{F(AB)}$ = 300 Hz, 1F, CF_2), −123.21 (dm, $^2J_{F(AB)}$ = 300 Hz, 1F, CF_2), −122.67 (dm, $^2J_{F(AB)}$ = 295 Hz, 1F, CF_2), −124.77 (dm, $^2J_{F(AB)}$ = 295 Hz, 1F, CF_2), −125.45 (dm, $^2J_{F(AB)}$ = 295 Hz, 1F, CF_2), −129.09 (dm, $^2J_{F(AB)}$ = 295 Hz, 1F, CF_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.3 MHz, 21 °C): δ −42.49 (tt, $^3J_{PF}$ = 15 Hz, $^4J_{PF}$ = 5 Hz, P).

[Cp*Ir(PMe$_3$)$_2$(*n*-C$_{10}$F$_{21}$)]$^+$I$^-$ (5g). Cp*Ir(CO)(I)(*n*-$C_{10}F_{21}$) (31 mg, 0.03 mmol) was dissolved in toluene (15 mL), PMe_3 (4 μL, 0.04 mmol) was added, and the solution was refluxed overnight. The solvent was removed to give a yellow solid, which was washed with ether to give a pale yellow powder. Recrystallization from CH_2Cl_2/ether gave a pale yellow solid (7 mg; 20%). Anal. Calcd for $C_{26}H_{33}F_{21}IIrP_2$: C, 27.74; H, 2.96. Found: C, 27.76; H, 3.24. ^1H NMR (CD_2Cl_2, 300 MHz, 21 °C): δ 1.86 (d, $^4J_{PH}$ = 2.1 Hz, 15H, C_5Me_5), 1.75 (d, $^2J_{PH}$ = 10.5 Hz, 18H, PMe_3). ^{19}F NMR (CD_2Cl_2, 470 MHz, 21 °C): δ −65.74 (s, 2F, CF_2), −81.50 (s, 3F, CF_3), −110.79 (s, 2F, CF_2), −121.36 (s, 2F, CF_2), −122.30 (s, 8F, 4CF_2), −123.28 (s, 2F, CF_2), −126.74 (s, 2F, CF_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz, 21 °C): δ −40.02 (tt, $^3J_{PF}$ = 16 Hz, $^4J_{PF}$ = 5 Hz, P).

[Cp*Ir(PMe$_3$)$_2$(C$_2$F$_5$)]$^+$OTf$^-$ (6b). Cp*Ir(PMe_3)(C_2F_5)I (50 mg, 0.077 mmol) was dissolved in dry CH_2Cl_2, and the resultant solution was added to the suspension of AgOTf (21 mg, 0.082 mmol) in CH_2Cl_2 dropwise over 5 min. Then neat PMe_3 (7.5 mg, 10 μL, 0.097 mmol) was added to the suspension followed by stirring for 5 min. The solution was filtered, the solvent was removed, and the residue was washed with toluene to afford an off-white solid (45 mg, 85%). Anal. Calcd for $C_{19}H_{33}F_8IrO_3P_2S$: C, 30.52; H, 4.45. Found: C, 30.44; H, 4.35. ^1H NMR (CD_2Cl_2, 500 MHz, 21 °C): δ 1.74 (m, $^2J_{PH}$ = 10.4 Hz, 18H, PMe_3), 1.87 (t, $^4J_{PH}$ = 2.2 Hz, 15H, C_5Me_5). ^{19}F NMR (CD_2Cl_2, 470 MHz, 21 °C): δ −71.19 (br t, $^3J_{FP}$ = 15 Hz, 2F, α-CF_2), −79.30 (s, 3F, OTf), −82.07 (s, 3F, CF_3); (CD_2Cl_2, 470 MHz, −88 °C) δ −71.36 (br d, $^2J_{F(AB)}$ = 266 Hz, 1F, α-CF_A), −73.75 (br d, $^2J_{F(AB)}$ = 266 Hz, 1F, α-CF_B), −79.69 (s, 3F, OTf), −82.49 (s, 3F, CF_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz, 21 °C): δ −42.36 (tq, $^3J_{PF}$ = 15 Hz, $^4J_{PF}$ = 2 Hz, 2P).

[Cp*Ir(PMe$_3$)$_2$(*n*-C$_8$F$_{17}$)]$^+$OTf$^-$ (6f). A solution of Cp*Ir(PMe_3)I(*n*-C_8F_{17}) (47 mg, 0.05 mmol) in CH_2Cl_2 (5 mL) was added slowly to a suspension of AgOTf (14.7 mg, 0.06 mmol) in CH_2Cl_2 (2 mL) over 10 min. After a further 15 min the mixture was filtered, and PMe_3 (5.2 μL, 0.05 mol) was added to the yellow filtrate, which quickly became almost colorless. It was allowed to react overnight. The solvent was removed to give a yellow solid, which was recrystallized from CH_2Cl_2/ether to give a pale yellow solid (47 mg, 90%). Anal. Calcd for $C_{25}H_{33}F_{20}IrO_3P_2S$: C, 28.66; H, 3.17. Found: C, 28.88; H, 3.09. ^1H NMR (CD_2Cl_2, 300 MHz, 21 °C): δ 1.87 (d, $^4J_{PH}$ = 2 Hz, 15H, C_5Me_5), 1.75 (d, $^2J_{PH}$ = 6 Hz, 18H, PMe_3). ^{19}F NMR (CD_2Cl_2, 282 MHz, 21 °C): δ −67.27 (s, 2F, CF_2), −79.32 (s, 3F, OTf), −81.50 (t, $^4J_{FF}$ = 8 Hz, 3F, CF_3), −111.02 (s, 2F, CF_2), −121.23 (s, 2F, CF_2), −122.17 (s, 2F, CF_2), −122.47 (s, 2F, CF_2), −123.32 (s, 2F, CF_2), −126.74 (s, 2F, CF_2); (CD_2Cl_2, 470 MHz, −75 °C) δ −63.78 (br dm, $^2J_{F(AB)}$ = 284 Hz, 1F, α-CF_A), −72.26 (br dm, $^2J_{F(AB)}$ = 284 Hz, 1F, α-CF_B), −79.68 (S, 3F, OTf), −81.19 (t, $^4J_{FF}$ = 8 Hz, 3F, CF_3), −106.62 (br d, $^2J_{F(AB)}$ = 290 Hz, 1F, β-CF_A), −116.87 (br d, $^2J_{F(AB)}$ = 290 Hz, 1F, β-CF_B), the remaining fluorine resonances consisted of a complex series of peaks between −120 and −130 ppm, which were not assigned. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz, 21 °C): δ −42.54 (tt, $^3J_{PF}$ = 15 Hz, $^4J_{PF}$ = 5 Hz, P).

[Cp*Ir(PMe$_3$)$_2$(*n*-C$_{10}$F$_{21}$)]$^+$OTf$^-$ (6g). A solution of Cp*Ir(PMe_3)I(*n*-$C_{10}F_{21}$) (36 mg, 0.034 mmol) in CH_2Cl_2 (5 mL) was transferred slowly to a suspension of AgOTf (10.6 mg, 0.041 mmol) in CH_2Cl_2 (10 mL) over 10 min. It was allowed to react (15 min) and then filtered to give a pale yellow solution. PMe_3 (10.0 μL, 0.10 mol) was added, and the color of the solution changed to almost colorless quickly. It was allowed to react for 1 h. The solvent was removed to give a yellow solid, which was recrystallized from CH_2Cl_2/ether to give a pale yellow solid (35 mg, 78%). Anal. Calcd for $C_{27}H_{33}F_{24}IrO_3P_2S$: C, 28.25; H, 2.90. Found: C, 28.64; H, 2.63. ^1H NMR (CD_2Cl_2, 300 MHz, 21 °C): δ 1.87 (15H, d, $^4J_{HP}$ = 1.8 Hz, C_5Me_5), 1.75 (d, 18H, $^4J_{PH}$ = 10.2 Hz, PMe_3). ^{19}F NMR (CD_2Cl_2, 282 MHz, 21 °C): δ −67.19 (s, 2F, CF_2), −79.32 (s, 3F, OTf), −81.45 (t, $^4J_{FF}$ = 10 Hz, 3F, CF_3), −110.98 (s, 2F, CF_2), −121.19 (s, 2F, CF_2), −122.26 (s, 8F, 4CF_2), −123.28 (s, 2F, CF_2), −126.70 (s, 2F, CF_2). (CD_2Cl_2, 470 MHz, −75 °C) δ −63.92 (br dm, $^2J_{F(AB)}$ = 285 Hz, 1F, α-CF_A), −72.83 (br dm, $^2J_{F(AB)}$ = 286 Hz, 1F, α-CF_B), −79.82 (br m, 3F, OTf), −81.63 (s, 3F, CF_3), −106.80 (br dm, $^2J_{F(AB)}$ = 283 Hz, 1F, β-CF_A), −116.94 (br dm, $^2J_{F(AB)}$ = 283 Hz, 1F, β-CF_B), the remaining fluorine resonances consisted of a complex series of peaks between −120 and −130 ppm, which were not assigned. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz, 21 °C): δ −42.63 (tt, $^3J_{PF}$ = 17 Hz, $^4J_{PF}$ = 5 Hz, P).

[Cp*Ir(PMe$_3$)$_2$(*n*-C$_{12}$F$_{25}$)]$^+$OTf$^-$ (6h). A solution of Cp*Ir(PMe_3)I(*n*-$C_{12}F_{25}$) (106 mg, 0.11 mmol) in CH_2Cl_2 (5 mL) was transferred slowly to a suspension of AgOTf (31.5 mg, 0.12 mmol) in CH_2Cl_2 (10 mL) over 10 min. It was allowed to react (15 min) and filtered to give a pale yellow solution. PMe_3 (12.5 μL, 0.12

mol) was added to the solution, which became colorless quickly. It was allowed to react overnight. The solvent was removed to give a yellow solid, which was recrystallized from CH_2Cl_2/ether to give a pale yellow solid (123 mg, 90%). Anal. Calcd for $C_{29}H_{33}F_{28}IrO_3P_2S$: C, 27.91; H, 2.67. Found: C, 28.19; H, 2.89. ^{1}H NMR (CD_2Cl_2, 300 MHz, 21 °C): δ 1.87 (s, 15H, C_5Me_5), 1.74 (d, 18H, $^2J_{PH}$ = 8.7 Hz, PMe_3). ^{19}F NMR (CD_2Cl_2, 282 MHz, 21 °C): δ −67.32 (s, 2F, CF_2), −79.32 (s, 3F, OTf), −81.59 (t, $^4J_{FF}$ = 9 Hz, 3F, CF_3), −111.02 (2, 2F, CF_2), −121.27 (s, 2F, CF_2), −122.34 (s, 12F, 6CF_2), −123.37 (s, 2F, CF_2), −126.83 (s, 2F, CF_2); (CD_2Cl_2, 470 MHz, −75 °C) δ −63.86 (br dm, $^2J_{F(AB)}$ = 282 Hz, 1F, α-CF_A), −72.77 (br dm, $^2J_{F(AB)}$ = 303 Hz, 1F, α-CF_B), −79.86 (br m, 3F, CF_3), −81.26 (br m, 3F, OTf), −106.73 (br dm, $^2J_{F(AB)}$ = 289 Hz, 1F, β-CF_A), −116.98 (br dm, $^2J_{F(AB)}$ = 282 Hz, 1F, β-CF_B), the remaining fluorine resonances consisted of a complex series of peaks between −120 and −130 ppm, which were not assigned. ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz, 21 °C): δ −24.58 (tt, $^3J_{PF}$ = 15 Hz, $^4J_{PF}$ = 5 Hz, P).

Cp*Ir(acac)(*n*-C_2F_5) (7b). Cp*Ir(CO)I(*n*-C_2F_5) (60 mg, 0.1 mmol) was dissolved in toluene (5 mL) and added to a toluene (10 mL) suspension of Tl(acac) (37 mg, 0.12mmol). The mixture was refluxed overnight, cooled, and filtered, and the solvent was removed in vacuo to give a brown solid. Recrystallization from hexane at −70 °C gave yellow crystals (38 mg, 70%). Anal. Calcd for $C_{17}H_{22}F_5IrO_2$: C, 37.42; H, 4.06. Found: C, 37.32; H, 4.14. ^{1}H NMR ($CDCl_3$, 300 MHz, 21 °C): δ 1.57 (s, 15H, C_5Me_5), 1.90 (s, 6H, CH_3-acac), 5.3 (s, 1H, H-acac). ^{19}F NMR ($CDCl_3$, 282.2 MHz, 21 °C): δ −82.74 (s, 3F, CF_3), −97.39 (s, 2F, CF_2).

Cp*Ir(acac)(*n*-C_3F_7) (7c). Cp*Ir(CO)I(*n*-C_3F_7) (65 mg, 0.1 mmol) was dissolved in toluene (5 mL) and added to a toluene (10 mL) suspension of Tl(acac) (33 mg, 0.11 mmol). The mixture was refluxed overnight, cooled, and filtered, and the solvent was removed in vacuo to give a brown solid. Recrystallization from hexane at −70 °C gave yellow crystals (42 mg, 75%). Anal. Calcd for $C_{18}H_{22}F_7IrO_2$: C, 36.30; H, 3.72. Found: C, 36.67; H, 3.98. ^{1}H NMR ($CDCl_3$, 500 MHz, 21 °C): δ 1.53 (s, 15H, C_5Me_5), 1.87 (s, 6H, CH_3-acac), 5.23 (s, H, H-acac). ^{19}F NMR ($CDCl_3$, 470.3 MHz, 21 °C): δ −79.98 (t, $^3J_{FF}$ = 12 Hz, 3F, CF_3), −97.95 (s, 2F, CF_2), −120.52 (s, 2F, CF_2).

[CpIr(PMe$_3$)$_2$(*n*-C_3F_7)]$^+$OTf$^-$ (8). CpIr(PMe_3)(*n*-C_3F_7)(I) (0.060 g, 0.095 mmol) was dissolved in methylene chloride (8 mL), and this yellow solution was added dropwise to a suspension of silver triflate (0.032 g, 0.125 mmol) in methylene chloride (5 mL). This was allowed to stir at room temperature away from direct light (20 h). The cloudy off-white suspension was then filtered to give a clear pale yellow solution. To this solution was added PMe_3 (11 μL, 0.106 mmol) and the solution allowed to stir at room temperature (1 h 45 min). The clear, colorless solution was concentrated under vacuum and ether added to precipitate a white solid. This was filtered and washed with ether and hexanes and dried under vacuum to yield the product as a white solid (43 mg, 62%). Anal. Calcd for $C_{15}H_{23}F_{10}IrO_3P_2S$: C, 24.76; H, 3.19. Found: C, 24.64; H, 2.85. ^{1}H NMR (CD_2Cl_2, 300 MHz, 21 °C): δ 5.79 (s, 5H, C_5H_5), 1.86 (d, $^2J_{PH}$ = 11 Hz, 18H, PMe_3). ^{19}F NMR (CD_2Cl_2, 282.2 MHz, 21 °C): δ −61.76 (2F, s, CF_2), −78.74 (s, 3F, CF_3), −78.84 (t, $^4J_{FF}$ = 12 Hz, 3F, OTf), −113.88 (2F, s, CF_2). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.3 MHz, 21 °C): δ −38.35 (tt, $^3J_{PF}$ = 14 Hz, $^4J_{PF}$ = 4 Hz, PMe_3).

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Supporting Information Available: CIF files for compounds **4g**, **5g**, and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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