Carbon−Fluorine Bond Activation Coupled with Alkynyl Migration to Give Fluorinated Allenyl Complexes of Iridium

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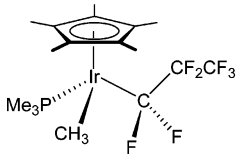
The propynyl(perfluoropropyl) iridium complex $Cp^*Ir(PMe_3)(CF_2CF_2CF_3)(C{\equiv}CCH_3)$ has been prepared and crystallographically characterized. It reacts with lutidinium iodide to afford α-CF bond activation and propynyl migration to carbon, to give the allenyl complex $Cp^*Ir(PMe_3)(I)[(CH_3)C{=}C{=}CF(CF_2\text{-}CF_3)]$ as a single diastereomer, for which the relative configurations at Ir and at the helical allenyl ligand were shown to be (S_{Ir},*M*)(R_{Ir},*P*) by X-ray crystallography. On standing in solution the (S_{Ir},*M*)(R_{Ir},*P*) diastereomer rearranges slowly to the thermodynamically more stable (R_{Ir},*M*)(S_{Ir},*P*) diastereomer, also characterized crystallographically, illustrating that the initial diastereomer is formed under conditions of kinetic control. A detailed mechanism is presented to rationalize these observations, and comparisons to previous CF activation/CC coupling reactions are made.

Introduction

Despite the undisputed importance of organofluorine compounds, the generation of fluorinated carbon stereocenters by C−F bond-forming reactions remains rare and particularly challenging.[1,2] The introduction of fluorine atom(s) strongly modifies the physical, chemical, and biological properties in a molecule.[3,4] In fluorobioorganic chemistry the replacement of strategic C−H or C−OH bonds by C−F could lead to important information regarding the structure and mechanism of action of enzymatic systems. Therefore, it is important to control the regio- and stereoselectivity of any step involved in formation of a fluorinated stereocenter. Recent success in enantioselective incorporation of fluorine has been achieved by using a chiral fluorinating reagent or a combination of a fluorinating agent and a chiral auxiliary, and several reports of enantioselective fluorination of organic molecules catalyzed by transition metal complexes have appeared.[5−13]

Recently we reported examples of a new and potentially complementary approach involving selective defluorination of a CF_2 group by exogenous protonation.[14−17] Our studies of this selective defluorination were stimulated by the long known observations that aliphatic C−F bonds are susceptible to protonation or reactions with external Lewis acids when they are α to certain transition metal centers and that C−F bond activation by various exogenous protic acids[18−21] and Lewis acids[22−26] can be achieved quite easily. For example, formation of a new fluorinated stereocenter was accomplished with complete diastereoselectivity in the transformation of **1** to **2** by external acid, in the form of lutidinium chloride (LutHCl). It is also quite remarkable that these protonation reactions occur selectively at the α-C−F bond in the presence of the Ir−CH_3 bond, with no evolution of methane. The relative configurations at the α-carbon and at Ir were shown unambiguously to be (R_C,R_{Ir}) or (S_C,S_{Ir}) by X-ray crystallography.[16]



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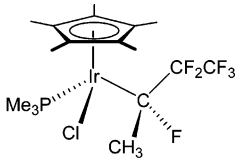

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For the transformation of **1** to **2**, this relative stereochemistry is depicted as occurring with retention of configuration at

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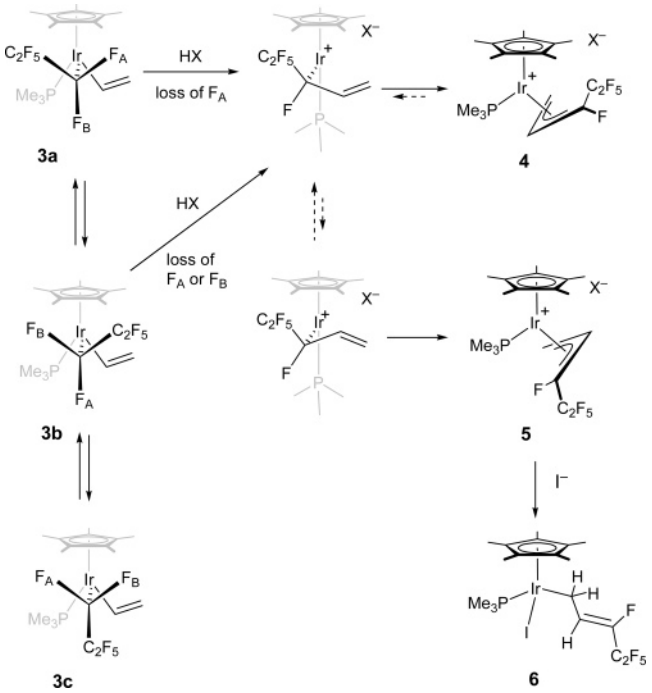
Scheme 1 [a]



[a] X = $B(ArF)_4$.

iridium. In one of our more recent contributions we addressed the question whether pathways that involve inversion at the metal may be operational.[17] As shown in Scheme 1 the vinyl group in complex **3** acts as an intramolecular trap at the metal, in the absence of halide, to give an η^3-allylic ligand immediately after, or concomitant with,[27] formation of the new C−C bond and new carbon stereocenter. Making the migrating group the trapping agent effectively guarantees that the kinetically formed allyl species is formed with retention at the metal, thereby also revealing the relative configuration at carbon. The low-temperature observation of the true kinetic products of this reaction, complexes **4** (major) and **5** (minor; also the thermodynamic product), allowed us to reduce the number of possible pathways of C−F bond activation to those shown in Scheme 1. The ground state conformation of the starting material was established to be **3a** (identical with that in the solid state) using $^{19}F\{^1H\}$ HOESY experiments.[17,28] The crucial conclusion is that the immediate precursor to kinetic product **4** must have the C_2F_5 group oriented toward the Cp* ring, so that trapping by the vinyl group at iridium affords the C_2F_5 group in the *anti* position of the resultant η^3-allyl ligand. Thus, the C−F activation occurs either from the ground state conformation **3a** by loss of F_A or from conformation **3b** by loss of either F_A or F_B, while **3c** is an unreactive conformation. Whether the reaction occurs in a concerted fashion, as shown in Scheme 1, or via initial loss of fluoride to give an intermediate cationic iridium−perfluoroalkylidene species,[29] followed by vinyl migration to the carbene

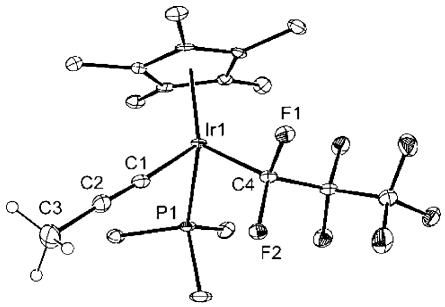


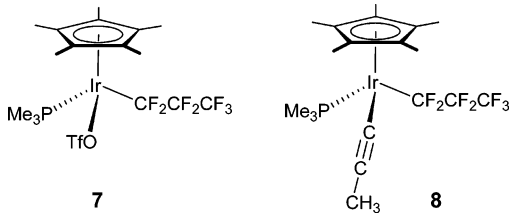
Figure 1. ORTEP diagram for **8** with ellipsoids drawn at the 30% probability level. Hydrogen atoms are excluded except for those on methyl group C3. Selected bond lengths (Å) and angles (deg): Ir(1)−C(1), 2.016(6); Ir(1)−C(4), 2.059(6); Ir(1)−P(1), 2.2791(14); Ir(1)−Cp*(cent), 1.904(6); C(1)−C(2), 1.171(9); C(2)−C(3), 1.500(9); C(1)−Ir(1)−C(4), 86.8(2); C(1)−Ir(1)−P(1), 83.93(16); Cp*(cent)−Ir(1)−P(1), 128.42(16).

carbon, remains to be determined. Treatment of **5** with iodide, or initial reaction of **3** with LutHI, afforded the η^1-allyl complex **6**.

To examine whether other unsaturated groups could participate in this kind of migratory chemistry, we set out to make a propargyl analogue of **3** with the hope that when treated with acid it would afford a propargyl fluorinated stereocenter at the α-carbon. The C≡C triple bond is endlessly versatile in organic synthesis, especially in transition metal-mediated reactions,[30] and this strategy has been envisaged and exploited before in the synthesis of propargylic fluorides from enantioenriched propargylic alcohols.[8]

Results and Discussion

The iridium propynyl complex **8** was readily prepared as a yellow crystalline material in good yield by the reaction of the triflate precursor **7**[16] with propynyllithium in ether. Compound **8** was characterized by ^1H, ^{19}F, and ^{31}P NMR spectroscopy as well as by a single-crystal X-ray crystallographic study; an ORTEP diagram of the structure is shown in Figure 1. Details of the crystallographic determination are presented in Table 1. The structure is consistent with many analogous perfluoropropyl iridium compounds[16,17,31] in that the perfluoroalkyl ligand adopts a conformation in which the C_2F_5 group is located between the Cp* and PMe_3 ligands. $^{19}F\{^1H\}$ HOESY experiments demonstrate that compound **8** adopts the same ground state conformation in solution as well.



Reaction of **8** with 1 equiv of 2,6-lutidinium iodide (LutHI) in CH_2Cl_2 solution at room temperature did not afford the anticipated propargyl complex **9**, but instead gave the allenyl compound **10** as the major *kinetic* product. This slowly

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

	8	**10**	**11**
formula	$C_{19}H_{27}F_7IrP$	$C_{19}H_{27}F_6IIrP$	$C_{19}H_{27}F_6IIrP$
fw	611.58	719.48	719.48
space group	*P*2(1)/*n*	*P*2(1)/*c*	*P*2(1)/*n*
a, Å	8.5245(16)	18.0611(7)	8.5951(3)
b, Å	15.212(3)	9.0056(4)	28.9571(11)
c, Å	16.639(3)	15.2247(6)	9.5666(4)
α, deg	90	90	90
β, deg	95.051(3)	113.3650(10)	91.6000(10)
γ, deg	90	90	90
V, Å^3	2149.3(7)	2273.25(16)	2380.09(16)
Z	4	4	4
cryst color, habit	colorless, block	orange, block	orange, block
D(calcd), g/cm^3	1.890	2.102	2.008
abs coeff, mm^{-1}	6.347	7.352	7.022
no. of indep reflns	4888 [R_{int} = 0.0277]	5139 [R_{int} = 0.0175]	5564 [R_{int} = 0.0245]
$R(F)$ [$I > 2\sigma(I)$], %[a]	4.19	2.11	3.66
$R(wF^2)$ [$I > 2\sigma(I)$], %[a]	11.18	5.09	8.69
temp, K	100(2)	100(2)	213(2)
diffractometer		Bruker Smart Apex	
radiation		Mo Kα (λ = 0.71073 Å)	

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R(wF^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

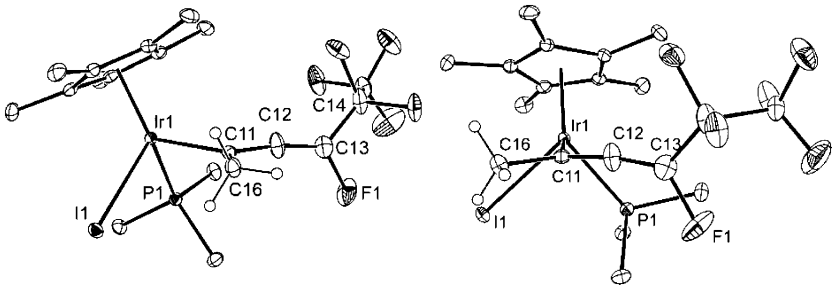
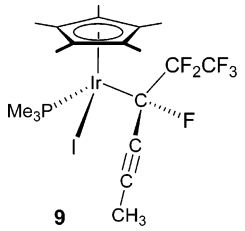


Figure 2. ORTEP diagrams for **10** from two different perspectives with ellipsoids drawn at the 30% probability level. Hydrogen atoms except for those on the allenic CH_3 group (C16) are excluded. The enantiomer depicted has the (S_{Ir},*M*) relative configurations. Selected bond lengths (Å) and angles (deg): Ir(1)−C(11), 2.073(3); C(11)−C(12), 1.298(5); C(12)−C(13), 1.316(6); C(13)−F(1), 1.377(5); F(1)−C(13)−C(14), 104.2(4); Ir(1)−C(11)−C(16), 119.9(2); C(11)−C(12)−C(13), 171.3(5).

rearranged in CH_2Cl_2 solution at room temperature over several days to an equilibrium mixture with its diastereomer **11**; the ratio of **10**:**11** is 1:3. Since the rate of the original CF activation/migration reaction is significantly higher than the rate of the rearrangement, initial formation of **10** must be kinetically controlled. The rate of the migration can be speeded up by increasing the LutHI concentration. For example, when 3 equiv of LutHI is used, by the time starting material **8** is essentially fully converted into products, the ratio **10**:**11** is about 10:1.



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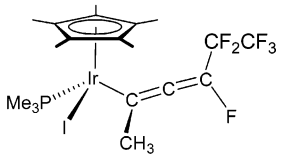
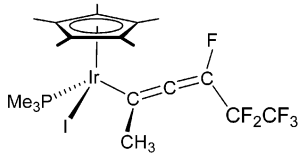


10



11

The identities and relative configurations of **10** and **11** were unambiguously established by X-ray diffraction studies. Due to the slow rate of interconversion, samples of both isomers can be obtained as crystals suitable for crystallographic analysis. ORTEP diagrams for **10** and **11** are shown in Figures 2 and 3, respectively, along with selected bond lengths and angles; details of the crystallographic determinations are compiled in Table 1. The two stereocenters at the asymmetric iridium and at the helical allene[32] generate four possible stereoisomers in the form of two racemates. The crystallographic determinations unambiguously define the relative *configurations* of the iridium and the allenic stereocenters in the kinetic diastereomer **10** as (S_{Ir},*M*)-(R_{Ir},*P*), respectively, and those in the thermodynamically more stable diastereomer **11** as (R_{Ir},*M*)(S_{Ir},*P*).

In Figures 2 and 3 it can be seen that the *conformations* of the fluorinated allenic ligand in each case are those in which the methyl group of the η^1-allenyl ligand oriented toward iodide appears to be more favorable, probably for steric reasons. In **10** the C_2F_5 substituent is oriented toward Cp*, while in **11** it is located closer to the PMe_3 ligand. It appears that steric strain between these two groups may cause the allenic ligand in **11** to cant relative to that in **10**, as shown in the figures. The relative configurations and the conformations of both of these compounds in solution were deduced by $^{19}F\{^1H\}$ HOESY spectroscopy,[28,33] which showed them to be the same as those observed in the solid state.

With the relative stereochemistry of the kinetic product **10** firmly established, a mechanism for formation of **10** can be envisaged, based on an understanding of the analogous chem-

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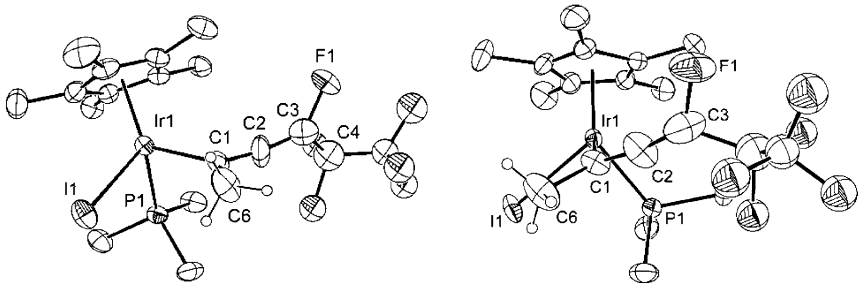
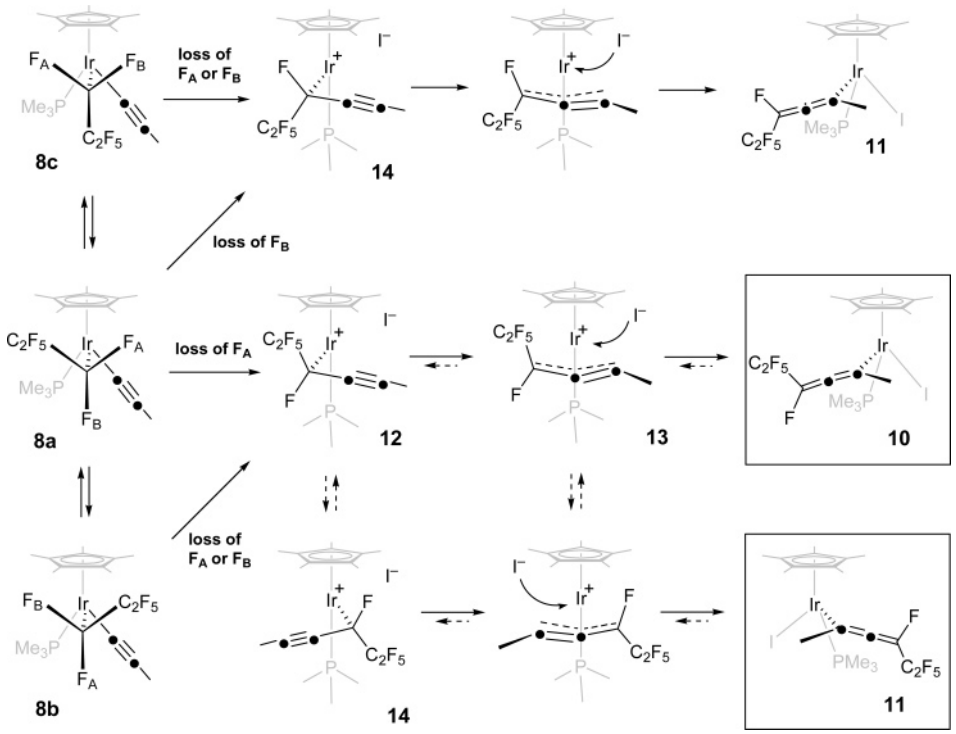


Figure 3. ORTEP diagrams for **11** from two different perspectives with ellipsoids drawn at the 30% probability level. Hydrogen atoms except for those on the allenic CH_3 group (C6) are excluded. The enantiomer depicted has the (S_{Ir},*P*) relative configurations. Selected bond lengths (Å) and angles (deg): Ir(1)−C(1), 2.059(6); C(1)−C(2), 1.266(11); C(2)−C(3), 1.315(14); C(3)−F(1), 1.390(11); F(1)−C(3)−C(4), 100.1(10); Ir(1)−C(1)−C(6), 123.0(6); C(1)−C(2)−C(3), 169.7(12).

Scheme 2



istry using the vinyl migrating group shown in Scheme 1. Scheme 2 illustrates the three staggered conformations of starting material **8**; we know **8a** to be the populated ground state in solution (vide supra). Exogenous acid promoted loss of F_A from **8a**, and migration of the propynyl group affords intermediate **12**, which, in a fashion analogous to its vinyl migration analogue shown in Scheme 1, can undergo intramolecular trapping to afford the η^3-propargyl species **13** with the C_2F_5 substituent oriented toward the Cp* ring. Analogous η^3-propargyl−transition metal complexes are well precedented.[34−37] Attack at the metal by iodide with ligand slippage to the η^1-allenyl form, as shown, affords kinetic product **10** with the observed relative stereochemistry. Indeed, kinetic product **10** can be formed only from an η^3-propargyl intermediate **13** having the stereochemistry shown, and in turn any η^1-propargyl precursor must have the stereochemistry shown for **12**. Thus, loss of F_B from **8a** with propynyl migration must afford **14**, which in turn must evolve to afford **11**, which is the observed thermodynamic product. Likewise, loss of either F_A or F_B from conformation **8c** can lead only to **11**. Since only small amounts of **11** are observed, and since **10** rearranges to **11** very slowly, these pathways can be excluded. However, loss of either F_A or F_B from conformation **8b** leads to the observed kinetic product **10**, so we are left with the same three stereochemically indistinguishable options for propynyl migration that were previously deduced for vinyl migration.[17] The two systems are mechanistically self-consistent in this regard.

In an attempt to observe an η^3-propargyl intermediate such as **13**, **8** was treated with the 2,6-lutidinium salt of the weakly coordinating tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.[38] Unlike the corresponding vinyl migration system[17] however, this afforded very disappointing results in the form of a complex mixture of products that could not be identified.

Finally, the slow rearrangement of **10** to **11** is presumed to occur via one of the two or both pathways shown in the lower part of Scheme 2. We have made no efforts to examine the

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details of this rearrangement further, but have simply taken advantage of its relatively slow rate to define the kinetic pathway for the overall reaction of interest.

Conclusions

These results reported here are completely consistent with conclusions reached in our previous report[17] that the sequence of C−F bond activation and C−C bond formation occurs with complete diastereoselectivity by one of three indistinguishable pathways. This provides an interesting route to new iridium complexes of fluorinated allenyl ligands in which true kinetic control of stereochemistry can be achieved.

Experimental Section

Air-sensitive reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen that has been deoxygenated over BASF catalyst and dried over Aquasorb, or in a Braun drybox. Methylene chloride, hexane, and diethyl ether were dried over an alumina column under nitrogen. 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 (7.15 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 in hertz. Elemental analyses were performed by Schwartzkopf (Woodside, NY). Lutidinium iodide[14] and Cp*Ir(PMe_3)($CF_2CF_2CF_3$)OTf (**7**)[16] were prepared according to the literature procedures.

Cp*Ir(PMe_3)($CF_2CF_2CF_3$)(C≡CCH_3) (8). Cp*Ir(PMe_3)(CF_2-CF_2CF_3)OTf (52 mg, 0.072 mmol), LiC≡CCH_3 (6.7 mg, 0.146 mmol), and dry ether (15 mL) were combined, and the resultant mixture was stirred for 3 h at room temperature. By that time the color of the mixture changed from yellow to brown. Then ether was removed in vacuo, and solids were extracted with hexane to give, after filtration and evaporation, the product (39 mg; 88%). Pure, pale yellow crystals suitable for X-ray diffraction were obtained by recrystallization from ether/hexane. Anal. Calc for $C_{19}F_7H_{27}IrP$: C, 37.31; H, 4.45. Found: C, 37.40; H, 4.38. ^{1}H NMR (C_6D_6 300 MHz, 21 °C): δ 1.26 (d, $^2J_{HP}$ = 10.8 Hz, 9H, PMe_3), 1.60 (d, $^4J_{HP}$ = 2.1 Hz, 15H, C_5Me_5), 2.22 (d, $^5J_{HP}$ = 2.1 Hz, 3H, CH_3). ^{19}F NMR (C_6D_6, 282 MHz, 21 °C): δ −68.98 (br d, $^2J_{F(AB)}$ = 286 Hz, 1F, α-CF_2), −74.40 (br d, $^2J_{F(AB)}$ = 286 Hz, 1F, α-CF_2), −78.90 (apparent triplet, $^3J_{FF}$ = 12.4 Hz, 3F, CF_3), −114.36 (d, $^2J_{F(AB)}$ = 280 Hz, 1F, β-CF_2), −116.22 (d, $^2J_{F(AB)}$ = 280 Hz, 1F, β-CF_2). ^{31}P{^{1}H} NMR (C_6D_6 121 MHz, 21 °C): δ −36.08 (dd, $^3J_{FP}$ = 19.4 Hz, $^3J_{FP}$ = 11.0 Hz, PMe_3).

***(S*$_{Ir}$*,M)(R*$_{Ir}$*,P)*-Cp*Ir(PMe_3)(C(CH_3)=C=CFC_2F_5)I (10).** Cp*Ir-(PMe_3)(*n*-C_3F_7)(C≡CCH_3) (30.0 mg, 0.049 mmol) and lutidinium iodide (34.7 mg, 0.147 mmol) were dissolved in CD_2Cl_2 (0.75 mL), and the resultant solution was allowed to stand for 13 h at room temperature. Then the solvent was removed under vacuum and the solids were extracted with hexane (10 mL) to afford an orange, oily material, which crystallizes within minutes after redissolving in hexane (0.5 mL). Orange crystalline material was obtained (31 mg) contaminated with **11** (10% according to ^{1}H NMR integration). The yield of **10** was 28 mg (79%). X-ray quality crystals were obtained by recrystallization from ether/hexane. Anal. Calc for $C_{19}H_{27}F_6IIrP$: C, 31.72; H, 3.78. Found: C, 31.87; H, 3.84. ^{1}H NMR (CD_2Cl_2 500 MHz, 21 °C): δ 1.695 (d, $^2J_{PH}$ = 10.5 Hz, 9H, PMe_3), 1.81 (d, $^4J_{PH}$ = 2.0 Hz, 15H, Cp*), 2.57 (dd, $^5J_{FH}$ = 8.9 Hz, $^4J_{PH}$ = 1.0 Hz, 3H, CH_3). ^{19}F NMR (CD_2Cl_2, 470.3 MHz, 21 °C): δ −83.90 (ddd, $^4J_{FF}$ = 8.8 Hz, $^3J_{FF}$ = 3.4 Hz, $^3J_{FF}$ = 3.4 Hz, 3F, CF_3), −115.7 (ddq, $^2J_{F(AB)}$ = 272 Hz, $^3J_{FF}$ = 30.6 Hz, $^3J_{FF}$ = 3.4 Hz, 1F, CF_2), −115.84 (ddq, $^2J_{F(AB)}$ = 272 Hz, $^3J_{FF}$ = 30.6 Hz, $^3J_{FF}$ = 3.4 Hz, 1F, CF_2), −170.27 (ddqqd, $^3J_{FF}$ = 30.6 Hz, $^3J_{FF}$ = 30.6 Hz, $^5J_{FH}$ = 8.9 Hz, $^4J_{FF}$ = 8.8 Hz, $^5J_{FP}$ = 6.1 Hz, 1F, CF). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.3 MHz, 21 °C): δ −39.70 (d, $^5J_{FP}$ = 6.1 Hz, 1P, PMe_3).

***(R*$_{Ir}$*,M)(S*$_{Ir}$*,P)*-Cp*Ir(PMe_3)(C(CH_3)=C=CFC_2F_5)I (11).** The mixture of **10** (90%) and **11** (10%) from above was dissolved in CD_2Cl_2 (0.75 mL), and the resultant solution was allowed to stand for 10 days at room temperature. Then the solvent was removed to vacuum and the solids were extracted with hexane, affording an orange, oily material (31 mg) containing mostly **11** contaminated with **10** (30% according to ^{1}H NMR integration). The yield of **11** was 22 mg (70%). Crystals suitable for X-ray diffraction were obtained by recrystallization from ether/hexane. ^{1}H NMR (CD_2Cl_2 500 MHz, 21 °C): δ 1.67 (d, $^2J_{PH}$ = 11 Hz, 9H, PMe_3), 1.83 (d, $^4J_{PH}$ = 2.0 Hz, 15H, Cp*), 2.56 (dd, $^5J_{FH}$ = 9.0 Hz, $^4J_{PH}$ = 1.5 Hz, 3H, CH_3). ^{19}F NMR (CD_2Cl_2, 470.3 MHz, 21 °C): δ −84.105 (ddd, $^4J_{FF}$ = 8.5 Hz, $^3J_{FF}$ = 3.3 Hz, $^3J_{FF}$ = 3.3 Hz, 3F, CF_3), −115.60 (ddq, $^2J_{F(AB)}$ = 272 Hz, $^3J_{FF}$ = 30.1 Hz, $^3J_{FF}$ = 3.3 Hz, 1F, CF_2), −116.22 (ddq, $^2J_{F(AB)}$ = 272 Hz, $^3J_{FF}$ = 30.1 Hz, $^3J_{FF}$ = 3.3 Hz, 1F, CF_2), −166.63 (bm, 1F, CF). ^{31}P{^{1}H} NMR (CD_2Cl_2, 202.3 MHz, 21 °C): δ −39.49 (d, $^5J_{FP}$ = 7.9 Hz, 1P, PMe_3).

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Supporting Information Available: CIF files for compounds **8**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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