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Addition of HCl to perfluorocarbene complexes of iridium occurs regiospecifically and stereospecifically.

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Abstract: Reductive activation of an \( \alpha \)-fluorine in the perfluoroalkyl complexes \( \text{Cp}^*\)(L)(I)Ir-CF\(_2\)RF using Mg/graphite leads to perfluorocarbene complexes \( \text{Cp}^*\)(L)Ir=CF\(_2\)RF (L= CO, PMe\(_3\); R\(_F\) = CF\(_3\), C\(_2\)F\(_5\), C\(_6\)F\(_5\)). New complexes E-Cp*(PMe\(_3\))Ir=CF\(_2\)F\(_5\) and E-Cp*(CO)Ir=CF\(_2\)F\(_5\) have been characterized by single crystal X-ray diffraction studies, and a comparison of metric parameters with previously reported analogues is reported. Experimental NMR and computational DFT (B3LYP/LACV3P**) studies agree that for Ir=CF\(_2\)F complexes (R\(_F\) = CF\(_3\), CF\(_2\)CF\(_3\)) the thermodynamic preference for the E or Z isomer depends on the steric requirements of ligand L; when
L=CO the Z-isomer (F cis to Cp*) is preferred and for L= PMe₃ the E-isomer is preferred. When reduction of the precursors is carried out in the dark the reaction is completely selective to produce E- or Z-isomers. Exposure of solutions of these compounds to ambient light results in slow conversion to a photostationary non-equilibrium mixture of E and Z isomers. In the dark, these E/Z mixtures convert thermally to their preferred E or Z equilibrium geometries in an even slower reaction. A study of the temperature dependent kinetics of this dark transformation allows $\Delta G^{\ddagger}_{298}$ for rotation about the Ir=CFCF₃ double bond to be experimentally determined as 27 kcal/mol; a DFT/B3LYP/LACV3P**++ calculation of this rotation barrier is in excellent agreement (29 kcal/mol) with the experimental value.

Reaction of HCl with toluene solutions of Cp*(L)Ir= CFR₃ (L = CO, PMe₃) or Cp*(CO)Ir=C(CF₃)₂ at low temperature resulted in regiospecific addition of HCl across the metal carbon double bond, ultimately yielding Cp*(L)Ir(CHFR₃)Cl and Cp*(CO)Ir[CH(CF₃)₂]Cl, which have been characterized crystallographically, spectroscopically, and computationally. Reaction of HCl with single E or Z diastereomers of Cp*(L)Ir=CFR₃ gives stereospecific cis-addition to give single diastereomers of Cp*Ir(L)(CHFR₃)Cl; addition of HCl to several different E/Z ratios of Cp*Ir=CFR₃ affords ratios of diastereomeric products Cp*(L)Ir(CHFR₃)Cl identical to the original ratio of starting material isomers. The addition of HCl is therefore demonstrated to be unambiguously regio- and stereo-specific. The observed product regiochemistry of addition of HCl to Ir=CF₂, Ir=CFR₃, and Ir=C(CF₃)₂ ligands is the same and is not dependent on the ground state energy preference (singlet or triplet) for the free perfluorocarbene. DFT calculations on model HCl addition reactions indicate that this regiochemistry is strongly preferred thermodynamically, but predict that in Hδ⁺-Clδ⁻ addition to Cp(PH₃)Ir=CF₂, Hδ⁺ attack at Ir has a lower energy transition state, while for Cp(PH₃)Ir=CFCF₃ and Cp(PH₃)Ir=C(CF₃)₂, Hδ⁺ attack at C is the kinetically preferred pathway. The carbene carbon atoms in Ir=CFCF₃ and Ir=C(CF₃)₂ complexes are unambiguously basic towards HCl, while in the Ir=CF₂ analogues the carbene carbon is less basic than its Ir partner, and the eventual regiochemistry of HCl addition arises from thermodynamic control.
Introduction

Complexes with transition-metal carbon double bonds are well known and are extremely useful for a number of synthetic and catalytic applications, most notably in the metathesis reactions of alkenes.\textsuperscript{1, 2} The bonding and chemical reactivity of these heteronuclear double bonds have been subjects of considerable discussion; metal carbene complexes have been characterized as nucleophilic (Schrock type) or electrophilic (Fischer type), based on their chemistry with electrophile/nucleophile combinations. Whether these compounds should be referred to as metal-carbene or metal-alkylidene compounds is also part of this bonding discussion, and is sometimes ambiguous. The compounds all formally contain a carbon-heteroatom(metal) double bond, which, depending on the metal, its oxidation state, ancillary ligands, and heteroatoms on the carbene carbon, can be represented by differently weighted combinations of the resonance forms shown in Scheme 1. Generally, electrophilic Fischer type carbene complexes contain at least one heteroatom (usually O or N) on the $\alpha$-carbon of the carbene ligand, leading to greater contributions from resonance forms C and D (Scheme 1) and a greater tendency to electrophilic reactivity at the carbene carbon atom. Schrock type compounds are thought to be best represented by resonance forms A and B, with resultant nucleophilic carbene reactivity. In general, Fischer carbene complexes are viewed as involving a donor/acceptor interaction between a singlet carbene and an empty metal orbital, with backbonding from a filled metal-d into the empty singlet carbene p-orbital, while Schrock carbene complexes are thought to be better represented as forming the double bond by interactions between a triplet carbene and orbitals containing two unpaired metal electrons. It has been suggested that free carbenes that are ground state singlets tend to form Fischer type complexes and those that are ground state triplets tend to form Schrock type systems.\textsuperscript{3} The metal-carbon bonding and rationalizations for the Schrock/Fischer designations have been extensively discussed and summarized.\textsuperscript{4-7} In this paper we will refer to all these kinds of compounds containing carbene ligands consistently as carbene-metal compounds.
The structure and reactivity of fluorinated ligands typically vary significantly from their hydrocarbon counterparts, but the effect of fluorine as a carbene substituent (X) in such complexes is not so easily predicted. As the most electronegative element, resonance form B would be inductively stabilized, but fluorine is also an excellent π-donor to carbon, leading to stabilization of resonance form D. In contrast, a perfluoroalkyl substituent (R_F) such as CF_3 is not a π-donor, but is a strong σ-electron withdrawing group and a π-acceptor via negative hyperconjugation into the C-F σ*-antibonding orbitals, both effects resulting in stabilization of resonance form B. Free difluorocarbene is a ground state singlet, with a triplet state almost 57 kcal/mol higher in energy, changing one fluorine for a CF_3 group to give fluoro(trifluoromethyl)carbene lowers the singlet-triplet energy gap to approximately 9 kcal/mol with the singlet still lower in energy, and replacing the second fluorine with CF_3 to give bis(trifluoromethyl)carbene results in a ground state triplet, calculated to be 18 kcal/mol more stable than its singlet excited state. So, at first blush, we might expect metal complexes of CF_2 and CF(CF_3) to favor Fischer type behavior, while those of C(CF_3)_2 should favor the Schrock type reactivity pattern. However these reactivity motifs also depend strongly on the metal, its oxidation state and ancillary ligands.

Reaction regiochemistry is crucial to such reaction characterization for addition of electrophile/nucleophile combinations; the location in the product of the electrophilic and nucleophilic components of the reactant are often used to define the electrophilic or nucleophilic nature of the carbene carbon. Such additions to half sandwich carbene compounds has been explored by several groups. For example, addition of HCl to compounds 1 (Scheme 2) (R = Me, Ph, ^3Pr), afforded addition products 2 consistent with the carbene carbon being nucleophilic.
However, the carbene carbon in rhenium compound 3 appears to be amphiphilic, reacting with nucleophilic phosphines to afford 4a, but with HCl or HBr to give regioselective formation of compounds 4b (Scheme 3).\textsuperscript{23, 24} Stereochemical information was obtained using the tethered carbene compound 5,\textsuperscript{25} which added HX (X = Cl, Br) to give 6 via a stereoselective cis-addition across the double bond. While the regiochemistry of the HX reactions suggests a nucleophilic carbene carbon, the authors caution that this reaction could also occur by initial protonation at the metal followed by H-migration to carbon.\textsuperscript{25} Such apparently amphiphilic behavior of a CF\textsubscript{2} ligand was reported by Roper, who demonstrated that Ru(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}(CF\textsubscript{2}) reacted with CH\textsubscript{3}NH\textsubscript{2} to afford Ru(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}(CH\textsubscript{3}CN) by apparent nucleophilic attack of the amine at an electrophilic CF\textsubscript{2} carbon, but reacted with HCl to give Ru(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}(CF\textsubscript{2}H)Cl, in which the CF\textsubscript{2} carbon implicitly behaves as a nucleophile.\textsuperscript{26} However, the kinetic site of protonation is unclear, as pointed out later by Roper;\textsuperscript{10} subsequent experiments illustrated that the migration of H from metals to CF\textsubscript{2} ligands are facile in the presence of a halide nucleophile.\textsuperscript{27, 28}
Pioneering work of Roper and his group in the synthesis and characterization of fluorocarbene (and other halocarbene) complexes has been extensively reviewed, but, before our initial forays into this field, only a single report of a perfluoroalkylcarbene complex had appeared. Reger and Dukes reported the preparation of \([\text{Cp}(\text{CO})_3\text{Mo} = \text{CF}_{2}\text{CF}_{2}\text{CF}_3]\)^{7}\text{SbF}_6\] (7) by addition of \text{SbF}_5 in liquid \text{SO}_2 to \text{Cp}(\text{CO})_3\text{Mo-CF}_{2}\text{CF}_{2}\text{CF}_3 \text{29}. This compound was never isolated or studied further and was characterized solely by NMR, although other cationic \text{CF}_2 complexes of Mo were isolated and characterized fully.\text{29, 30}

Study of the addition of \text{HX} to perfluorocarbene compounds was a particularly appealing topic for study in our group in view of previous observations for which perfluorocarbene intermediates were proposed. It was found that upon addition of acids \text{HX} to solutions of half sandwich compounds \text{Cp*}(\text{PMe}_3)\text{Ir}(\text{CF}_2\text{R}_F)(\text{R}) \text{8} (\text{R} = \text{H, Me, Ph}) in non-polar solvents, \text{a-C-F} bond activation occurred with migration of the \text{R} group to the \text{a}-carbon to ultimately yield exclusively a single diastereomer of \text{Cp*}(\text{PMe}_3)\text{Ir}(\text{CF}(\text{R}_F)(\text{R}))(\text{X}) \text{9} with the relative stereochemistries at \text{Ir} and \text{C} shown in Scheme 3.\text{31-34} In the proposed mechanism, initial \text{a-C-F} bond activation by the external acid yields the cationic carbene compound, \([\text{Cp*}(\text{PMe}_3)\text{Ir}(\text{R})(=\text{C}(\text{R}_F)(\text{F}))]^+ \text{X} \text{10} with loss of \text{HF} providing some thermodynamic compensation for breaking the \text{C-F} bond.\text{31, 35} Migration of \text{R} to the carbene carbon\text{36} yields cationic intermediate \([\text{Cp*}(\text{PMe}_3)\text{Ir}(\text{C}(\text{R}_F)(\text{F})(\text{R}))(\text{X})]^+ \text{X} \text{11}, which is then trapped by anion prior to configurational isomerism at the metal center to yield observed product \text{9} with the relative stereochemistries shown. These reactions were confirmed to occur under kinetic control\text{33} and the stereochemistry of the product therefore reflects the preferred stereochemistries of the individual reaction steps. If \text{10} is indeed an intermediate in this reaction then the kinetic product must arise from a net cis-addition to the \text{E}-isomer of the perfluoroalkylcarbene (\text{R}_F \text{cis} to \text{Cp*} as shown in \text{10}) (or a rather gymnastically spectacular trans-addition to the \text{Z} isomer). In addition, the stereochemistry of the \text{Ir} = \text{C} double bond in \text{10} must be retained, as must the configuration at \text{Ir} in \text{11} prior to anion trapping. In very polar solvents, such as nitromethane, we have shown that configurational inversion at the metal center of \text{9} (\text{R}=\text{H}) does occur via the ion-pair \text{11}.\text{33}
We have previously reported the synthesis of a novel class of perfluoroalkylcarbene-iridium compounds by reductive activation of iridium perfluoroalkyl iodide precursors.\textsuperscript{28, 37} Clearly addition of HX to these double bonds should afford identical compounds 9 (R = H), depending on the regiochemistry of addition. Recently our reductive approach to generation of fluorocarbene ligands from fluoroalkyl ligands has been extended to the formation of much more reactive Cp(L)Co=CFR (R = F, CF\textsubscript{3}) analogues.\textsuperscript{38, 39}

Here we report more complete studies of these iridium compounds, evaluation of their configurational stabilities under photochemical and thermal conditions, and experimental measurement of the rotation barrier about the Ir=C bond. We also provide an unambiguous demonstration that the addition of HCl to the Ir=C bond occurs in both a regio- and stereospecific manner, and that the regiospecificity does not depend on whether the free fluorocarbene has a singlet or triplet ground state.

**Results and Discussion**

**Preparation and characterization of perfluoroalkylcarbene complexes**

The perfluoroalkylcarbene compounds \( \text{Cp}^*\text{(L)}\text{Ir=CFR}_R \) (L=CO, PMe\textsubscript{3}; R = CF\textsubscript{3}, CF\textsubscript{2}CF\textsubscript{3}, C\textsubscript{6}F\textsubscript{5}) \textsuperscript{12-16}, can be formed in a facile manner by the action of a number of reducing agents on starting materials of the type, \( \text{Cp}^*\text{Ir(L)(CF}_2\text{R}_F)\text{(I) (L=CO, PMe}_3; \text{R}_F = \text{CF}_3, \text{CF}_2\text{CF}_3, \text{C}_6\text{F}_5) \). Compounds were
produced as variable mixtures of geometric isomers, with the higher priority $\alpha$-F group syn (Z) or anti (E) to the higher priority Cp* ligand; factors influencing this E/Z ratio are presented in more detail later.

The preparation and crystallographic characterization of E-Cp*(PMe$_3$)Ir=CFCF$_3$ 13a,28 and Z-Cp*(CO)Ir=CFCF$_2$CF$_3$ 14b$^{37}$ have been previously communicated as have the structures of the parent CF$_2$ analogues 17$^{37}$ and 18.$^{28}$ We note with apologies that in a previous communication$^{37}$ the relative stereochemistries of the E- and Z-isomers of Cp*(CO)Ir=CFCF$_3$ were incorrectly assigned.

In a typical procedure, Cp*($L$)Ir(CF$_2$R$_F$)(I) was added to a THF suspension of magnesium graphite at room temperature, and subsequent hexane extraction yielded spectroscopically pure carbene complexes 12-16. In general, the carbonyl compounds were found to be less air sensitive than the phosphine compounds and could even be purified on a neutral alumina column run in air at room temperature. The carbene compounds were characterized by X-ray crystallography as well as NMR and IR ($\nu_{CO}$) spectroscopy and microanalysis.

ORTEP diagrams of 12b (Figure 1), 15a (Figure 2) and 16a (Figure 3) are presented below. The X-ray crystal structures clearly confirm formation of the carbene ligands. Except for the perfluorobenzylidene complex 16a, the crystallographically characterized isomer was the major isomer formed in the synthesis. Selected bond lengths and angles are shown in Table 1, along with a comparison of the crystallographic structures with those determined by Density Functional Theory (DFT) using the B3LYP functional$^{40-44}$ with the Grimme D3 dispersion correction,$^{45, 46}$ and the LACV3P**++ basis set.$^{47-50}$ DFT
calculated structures for those isomers not characterized crystallographically are also included in Table 1. Structures of compounds 13a, 14b, 17 and 18 have been previously reported, but comparative data are included with those for 12b, 15a and 16a.

Figure 1. ORTEP diagram of the non-hydrogen atoms of isomer 12b, showing a partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. Two independent molecules crystallized in the asymmetric unit. Selected bond distances (Å) and angles (°):  
  - Ir-C12, 1.875(10), 1.852(10); C12-F1, 1.383(12), 1.385(11); C12-C13, 1.495(14), 1.529(14); Ir-C11, 1.843(11), 1.860(10); C11-O1, 1.159(12), 1.142(11); Ir-Ct, 1.880(9), 1.886(10); C11-Ir-C12, 95.0(4), 95.4(4); F1-Ir-C12, 121.1(7), 122.7(7); F1-C12-C13, 103.2(8), 102.1(8); C13-Ir-C12, 135.7(8), 135.2(8); Ct-Ir-C11, 131.24(4), 131.11(4); Ct-Ir-C12, 133.73(4), 133.50(4).
**Figure 2.** ORTEP diagram of the non-hydrogen atoms of the isomer 15a, showing a partial atom-labeling scheme. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (°): Ir-C11, 1.864(6); Ir-P, 2.2445(18); F1-C11, 1.441(7); C11-C12, 1.455(9); Ir-Ct 1.916(6); Ct-Ir-C11, 142.27(3); Ct-Ir-P, 132.02(19); F1-C11-Ir, 126.9(4); C11-Ir-P, 85.6(2).

**Figure 3.** ORTEP diagram of the non-hydrogen atoms of isomer 16a, showing a partial atom-labeling scheme. The molecule lies on a crystallographic mirror plane. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (°): Ir-C8, 1.858(4); Ir-C7, 1.850(5); Ir-Ct 1.903(4); F1-C8, 1.390(5); C8-C9, 1.503(6); C7-Ir-C8 90.3(2); F1-C8-Ir 124.3(3); C9-C8-Ir, 130.4(3); Ct-Ir-C7, 130.51(18); Ct-Ir-C8, 139.20(17).

**Table 1.** Comparison of selected bond lengths and angles in the crystal structures of perfluoroalkyl carbene complexes and DFT/B3LYP-D3/LACV3P**++ calculated structures (boldface). Two independent molecules of 12b crystallized in the unit cell, and data for both compounds are shown.

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The DFT calculated structures show excellent agreement with the metrics determined crystallographically, and for the most part are within the ESDs for the crystallographic values, boosting confidence in the calculated DFT metrics for the non-crystallographically characterized isomers. All the complexes show Ir=C distances of between 1.8-1.9 Å with no significant differences for CO or PMe₃ analogues. These are significantly less than a typical Ir-Rₖ distances of ~2.1 Å for the starting perfluoroalkyl compounds⁵¹ and are consistent with double bond character between the iridium and the α-carbon. In general the L-Ir-Cₐ angles are in the range of 85-95° while the two angles between the ligated atoms of the carbene or L and the Cp* centroids (Ct) are significantly larger, in the 130-140° range. For the Ir=CF₂ complexes 17 and 18 these inter-ligand angles are almost independent of whether the ancillary ligand is CO or PMe₃. Introduction of a CF₃ group on the carbene ligand in the isomers of compound 12 results in opening of the OC-Ir-C when CF₃ is cis to CO (12b) and corresponding contracting of the Ct-Ir-C angle, illustrating some steric interaction between CO and the cis-CF₃ group. Nevertheless the Z-isomer 12b is the major one observed experimentally in solution (see below), and is
predicted by DFT to have a free energy 3.0 kcal/mol lower than 12a. Replacement of CO by PMe$_3$ to give perfluoroethylidene compounds 13 reverses this order of stability and the E-isomer 13a is predicted to be 3.0 kcal/mol lower than 13b. The opening of the Me$_3$P-Ir-C angle and contraction of the Ct-Ir-C angle between isomers 13a and 13b are both more pronounced than for the CO analogues 12. Thus the isomer energetics appear to be determined predominantly by steric effects between the CF$_3$ group and the ancillary ligand at 90°. Likewise the perfluoropropylidene complexes show a preference for the Z-isomer when L=CO (14b is 1.6 kcal/mol more stable than 14a) and the E-isomer when L=PMe$_3$ (15a is 3.0 kcal/mol more stable than 15b). Similar angle variations are observed. For the perfluorobenzylidene complexes 16 the free energy difference is less pronounced, with the Z-isomer 16a being only 0.6 kcal/mol lower in energy than its E-analogue; notably in both isomers the pentafluorophenyl ring is essentially perpendicular to the L-Ir-C$_\alpha$ plane, with less two-dimensional steric demand than a three dimensional perfluoroalkyl group.

The NMR data are also characteristic for perfluoroalkylcarbene ligands. Typical features include very low field chemical shifts for the $\alpha$-carbon and fluorine$^7, 10, 29, 52$ and a large $^{1}J_{CF}$ ($\sim$300-350 Hz) coupling.$^{28, 29}$ The $\alpha$-fluorine also couples with the other fluorines in the ligand chain. In the phosphine compounds an additional three bond coupling is observed between the $\alpha$-fluorine and the phosphorus, which is larger in the isomers in which phosphorus and the $\alpha$-fluorine are cis, as observed previously for fluoroaryl complexes.$^{53}$ In the minor isomer of 16 a long range coupling is observed between the carbene fluorine and the $p$-fluorine of the phenyl ring ($^{6}J_{FF} = 5$ Hz); this coupling has previously been observed in several fluorinated styrene compounds$^{54}$ as well as in the previously reported perfluorobenzylidene compound, Cp*($\text{PMe}_3$)Ir=CFC$_6$F$_5$.$^{28}$

Finally, the formal reduction of the metal from iridium Ir$^{\text{III}}$ to Ir$^{\text{I}}$ is indicated by a decrease ($\sim$30 cm$^{-1}$) in the carbonyl stretching frequency. For example, in reducing Cp*($\text{CO}$)Ir(I)(CF$_2$CF$_2$CF$_3$) to 14 the value of $v_{\text{CO}}$ decreases from 2050 cm$^{-1}$ (hexanes)$^{51}$ to 2011 cm$^{-1}$ (hexanes).$^{37}$
Interconversion of E/Z Geometric Isomers.

Under ambient light conditions the carbene complexes are formed in this reductive procedure as variable mixtures of E/Z diastereomers. The geometries in solution were determined by $^{19}$F/$^1$H Heteronuclear Overhauser (HOESY) NMR experiments, analogous to those we have used previously to determine configurations and conformations in fluorinated organometallic compounds of this type.\(^{55}\) For example, in the carbonyl complexes 12, 14 and 16 the major Z-isomers showed a strong cross-peak between the α-fluorine and the Cp* proton resonance, indicating a <5 Å average distance between these two groups, while the minor isomer showed a cross-peak between Cp* and fluorines in the R group.<Bourgeois, 2006 #8420> As noted above it was incorrectly reported earlier that the major isomer of 12 adopted the E configuration.\(^{37}\) For the PMe$_3$ analogues 13 and 15 the major E-isomers showed a cross-peak between the α-fluorine and the PMe$_3$ and the minor isomers a cross-peak between Cp* and the α-fluorine. As discussed above, this can be rationalized on steric grounds bearing in mind the approximately 90° relationship between L and the carbene ligand. In every case except that of the perfluorobenzylidene complex 16 the major isomer was the one that crystallized from solution, allowing samples containing individual E- and Z-isomers to be obtained.

On stirring a solution of the pure Z-isomers of carbonyl complexes 12a and 14a under ambient light the E isomer slowly increased in concentration; similar treatment of the E-isomers of PMe$_3$ complexes 13b and 15b resulted in slow increase in concentration of the corresponding Z-isomers. Eventually in each case an apparent photostationary state\(^{56}\) was reached. In the dark, each mixture returned even more slowly to its equilibrium isomer ratio; this process was accelerated by heating. Figure 4 illustrates the isomerization of 14a and Scheme 4 shows the ratios of E- and Z-isomers in the photostationary state, and after thermal equilibration. This constitutes a rare example of photoisomerization of an carbene complex.\(^{57}\) No attempts were made to determine any frequency dependence or other quantitative aspects of this ambient light photoisomerization. It simply provided a convenient way in which non-equilibrium mixtures of diastereomers could be obtained, and their thermal return to equilibrium monitored kinetically.
Figure 4. Time course of the interconversion of the Z- and E-isomers of complex 14 on exposure to ambient light (C₆H₆ solution, 20°C), followed by removal of the light source.

Concentrations of isomers were measured by $^{19}$F NMR integration over time for the thermal return to equilibrium at four different temperatures (30, 40, 47, and 55°C). The difference between the initial concentration, $[A]_0$ and the concentration at time $t$ is $X$ and at equilibrium $X = X_c$. A plot of $\ln(X_c-X)$ versus $t$ gave a straight line with slope equal to $-(k_1+k_{-1})$. Knowledge of $K_{eq}$ allows $k_1$ and $k_{-1}$ to be determined.  

An Eyring plot of $\ln(k/T)$ versus $1/T$ gives the thermodynamic parameters for thermal isomerization by rotation about the Ir=C bond as $\Delta H^\ddagger = 19$ kcal/mol, $\Delta S^\ddagger = -25$ cal/mol, and $\Delta G_{298}^\ddagger = 25$ kcal/mol. The value for the free energy barrier for this rotation calculated by DFT (B3LYP/LACV3P**++) is 27 kcal/mol, in excellent agreement with experiment.

Recognition of the role of ambient light in the E/Z isomerization of these perfluorocarbene complexes, led to reductive synthesis in the dark which afforded formation of a single E-stereoisomer.
for PMe$_3$ compounds and Z-stereoisomer for CO compounds; only on workup did slow photoisomerization commence. Clearly the favored isomer in the synthesis is the thermodynamically favored one. This dark synthesis coupled with the slow approach to, and return from, the non-equilibrium photostationary state provided us with the capability of obtaining different ratios of the E/Z isomers that changed very slowly with time.

**Addition Reactions of Perfluoroalkylcarbene Complexes with HCl**

Addition of HCl in toluene to a toluene solution of the Z-perfluoroalkylcarbene complexes 12b, 14b or 16b at low temperature resulted in rapid addition of HCl across the double bond to yield single diastereomers of 19b, 21b and 23b respectively, which were configurationally stable in toluene solution, and each of which was characterized crystallographically. ORTEP diagrams are presented in Figures 5-7 and clearly define the regiochemistry and stereochemistry of addition. The protons on the $\alpha$-carbons were not located crystallographically, but their presence and the stereochemistry at the $\alpha$-carbon atoms are clear.
Figure 5. ORTEP diagram of the non-hydrogen atoms of 19b, showing a partial atom-labeling scheme. The hydrogen attached to C11 is shown. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (°): Ir-C11, 2.091(5); C11-F1, 1.397(6); Ir-Cl, 2.3979(13); Ir(1)-C(13), 1.882(5); C13-O, 1.121(6); C(13)-Ir(1)-Cl(1) 92.64(15); C(11)-Ir(1)-Cl(1), 83.89(14); C(13)-Ir(1)-C(11) 90.6(2); Ir-C11-C12, 118.6(3); F1-C11-C12, 105.4(4).

Figure 6. ORTEP diagram of the non-hydrogen atoms of 21b, showing a partial atom-labeling scheme. The hydrogen attached to C11 is shown. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (°): Ir-C14, 1.884(7); Ir-Cl, 2.3949(13); Ir-C11, 2.093(6); C11-C12, 1.486(8);
C11-F1, 1.4131(6); C14-Ir-C11, 89.2(3); C14-Ir-Cl, 93.07(18); Cl-Ir-C11, 82.87(18); Ir-C11-C12, 117.9(4); F1-C11-C12, 105.3(5).

**Figure 7.** ORTEP diagram of the non-hydrogen atoms of 23b, showing a partial atom-labeling scheme. The hydrogen attached to C12 is shown. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (°): Ir-C11, 2.038(10); Ir-Cl, 2.367(2); Ir-C12, 2.086(9); C12-C13, 1.512(10); C12-F1, 1.452(11); C11-Ir-C12, 88.7(4); C12-Ir-Cl, 91.2(3); F1-C12-C13, 107.5(6); F1-C12-Ir 109.3(6).

Each structure shows that addition of HCl occurred regiospecifically, with the electrophilic H$^{δ+}$ adding to C and Cl$^{δ−}$ to Ir. It is also clear that each structure resulted from an exclusive cis-addition of HCl to the original Z-isomer of the respective perfluorocarbene complex. As an extra check that the crystallographically determined structure was not that of a rogue crystal arising from a tiny amount of another diastereomer or regio-isomer present in small enough amounts so as to be invisible by NMR, each crystallographic determination was followed by dissolution of the specific crystal on which the diffraction experiment was performed, and determination of its NMR spectra. In all cases the spectra of the dissolved crystal matched those of the observed product, confirming the correlation between the crystallographic structure and the solution data. In structures 19b and 21b the fluoroalkyl ligand conformation is that in which the R$_F$ group situates itself in the region of space between Cp* and CO,
while the F sits between Cp* and Cl and the H occupies the smallest space, between CO and Cl (Figure 4).

The NMR spectra confirm addition of the hydrogen to the carbene carbons; the H resonates at low field, between $\delta$ 6.5 and 7 ppm, and shows large coupling with the geminal fluorine ($^{2}J_{HF} \sim 47$ Hz). This proton also couples with the fluorines on the $\beta$-carbon. The $\alpha$-fluorine, which resonates far downfield in the carbene compound (vide supra) moves upfield by almost 200 ppm in the alkyl product to around $\delta$ –190 ppm and show a large coupling to the geminal proton as well as the other fluorines in the molecule. The perfluorobenzyl product 23b again shows long range coupling ($^{6}J_{FF} = 2$ Hz).

Various isomeric ratio of perfluorocarbene precursors were obtained by varying their exposure to light. Addition of HCl to an X:1 ratio of 12b:12a (X = 2, 6, 11) gave X:1 ratios of diastereomeric products 19b:19a. Likewise X:1 ratios of 14b:14a (X = 3, 20) gave identical X:1 ratios of 21b:21a, and a 5:1 ratio of 16b:16a gave a 5:1 ratio of 23b:23a. In all cases the individual product ratios did not change on heating in toluene, indicative of configurational stability. Clearly, if pure 12b gives only pure 19b, then isomer 12a must give only 19a. The addition is both regio- and stereospecific in all three cases.

Identical regiochemical and stereochemical conclusions result from reactions of the PMe$_3$ analogues with HCl. Reaction of pure E isomer 13a yielded a single diastereomer of 20a while a 4:1 mixture of 15a:15b yielded a 4:1 ratio of 22a:22b. The major diastereomers 20a and 22a have been previously reported and fully characterized.$^{33}$
The previously reported\textsuperscript{59} bis(trifluoromethyl)carbene complex 24 also reacted with HCl to afford addition product 25 with identical regiochemistry.

The observed regiochemistry of HCl addition to the perfluorocarbene complexes 12a-16a and 24 parallels that observed previously in addition of HI to the corresponding Cp*(PMe\textsubscript{3})Ir=CF\textsubscript{2} complex 18 to give 26.\textsuperscript{28} In that study it was shown that addition of triflic acid to 18 at low temperatures resulted in cation 27, in which the added proton resided on Ir, while protonation of the CF(CF\textsubscript{3}) analogue 13 afforded 28 in which the proton was bound to C; whether or not triflate was bound to Ir could not be determined.

Taken together, these results illustrate that, regardless of whether the free perfluorocarbene ligand is a ground state singlet or a triplet, the experimentally observed products of HCl addition are invariably those formed by electrophilic H\textsuperscript{δ+} adding to C and Cl\textsuperscript{δ−} to Ir. However, the observation of 26
and observations from our group, \(^{31-34}\) and others, \(^{21, 22, 10, 25, 26}\) that H (and other groups) can migrate from their original locus on a metal to the perfluorocarbene carbon in the presence of a coordinating anion, in some cases with complete preservation of stereochemistry at C and at Ir, calls into question whether the HCl adducts formed here are those resulting from a kinetic controlled addition, or whether an initial protonation at Ir, followed by H-migration to C is a viable pathway.

**DFT Studies of the Addition of HCl.**

In the absence of further experimental approaches, these pathways have been examined using DFT, for HCl addition to the model compounds Cp(PH\(_3\))Ir=CF\(_2\), E-Cp(PH\(_3\))Ir=CFCF\(_3\), and Cp(PH\(_3\))Ir=C(CF\(_3\))\(_2\). Since all the observed chemistry occurs at low temperature in a non-polar and poor donor solvent (toluene) a solvent model was not included. For each pre-optimized carbene ligand system starting structures were generated by placing a pre-optimized HCl at several initial distances (d) and angles (\(\theta\)) from the Ir=C double bond, as shown for Cp(PH\(_3\))Ir=CF\(_2\) in Figure 8, thereby providing some reasonable constraints to the complex hypersurface. Saddle points having a single imaginary frequency and linking each of these starting structures and each appropriate regio-isomeric product were sought. For each regiochemistry the same transition states were found regardless of the starting angle (\(\theta\)) between the reactants. Free energy profiles for all three systems are shown in Figure 9, and calculated geometries for starting materials, transition states, and products are provided in Figure 10. Table 2 presents Natural Population Analysis (NPA) charges on selected atoms in starting materials and transition states. Full structural and calculation details are provided as Supplementary Information.
**Figure 8.** Starting structures for location of transition states for the two regiochemistries for HCl Cp(PH₃)Ir=CF₂; (d = 1-2Å in increments of 0.1Å) from Ir or C to the Hδ⁺ electrophile; θ = 90-180° in increments of 10°; with an Ir=C/H-Cl dihedral angle of 0°). Analogous constraints were applied to the two other carbene systems studied.

![Diagram showing relative free energy (kcal/mol) for addition of HCl to Cp(PH₃)Ir=CF₂, Cp(PH₃)Ir=CFCF₃, and Cp(PH₃)Ir=C(CF₃)₂ via transition states.](image)

**Figure 9.** DFT calculated (B3LYP-D3/LACV3P**++**) free energy profiles for the two regiochemical modes of addition of HCl to Cp(PH₃)Ir=CF₂, E-Cp(PH₃)Ir=CFCF₃, and Cp(PH₃)Ir=C(CF₃)₂ via the transition states shown in Figure 10. Pathways involving electrophilic addition of Hδ⁺ to C are linked by grey arrows; pathways involving electrophilic addition of Hδ⁺ to Ir are linked by red arrows.
Figure 10. DFT calculated (B3LYP-D3/LACV3P**++) structures for starting materials, transition states, and products for the two regiochemical modes of addition of HCl to Cp(PH₃)Ir=CF₂, E-Cp(PH₃)Ir=CFCF₃, and Cp(PH₃)Ir=C(CF₃)₂. Pathways involving electrophilic addition of Hδ⁺ to C are linked by grey arrows; pathways involving electrophilic addition of Hδ⁺ to Ir are linked by red arrows.
Table 3. Natural Population Analysis (NPA) charges in starting materials and transition states for HCl addition reactions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ir</th>
<th>C</th>
<th>H</th>
<th>Cl</th>
<th>P</th>
</tr>
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<tbody>
<tr>
<td>H-Cl</td>
<td>-</td>
<td>-</td>
<td>+0.25</td>
<td>-0.25</td>
<td>-</td>
</tr>
<tr>
<td>Cp(PH₃)Ir=CF₂</td>
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<td>+0.59</td>
<td>-</td>
<td>-</td>
<td>+0.38</td>
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<tr>
<td>C-H TS</td>
<td>+0.29</td>
<td>+0.41</td>
<td>+0.23</td>
<td>-0.70</td>
<td>+0.37</td>
</tr>
<tr>
<td>Ir-H TS</td>
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<td>+0.70</td>
<td>+0.14</td>
<td>-0.82</td>
<td>+0.47</td>
</tr>
<tr>
<td>Cp(PH₃)Ir=CFCF₃</td>
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<td>+0.14</td>
<td>-</td>
<td>-</td>
<td>+0.39</td>
</tr>
<tr>
<td>C-H TS</td>
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<td>-0.08</td>
<td>+0.25</td>
<td>-0.63</td>
<td>+0.37</td>
</tr>
<tr>
<td>Ir-H TS</td>
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<td>+0.36</td>
<td>+0.16</td>
<td>-0.63</td>
<td>+0.43</td>
</tr>
<tr>
<td>Cp(PH₃)Ir=C(CF₃)₂</td>
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<td>-0.41</td>
<td>-</td>
<td>-</td>
<td>+0.38</td>
</tr>
<tr>
<td>C-H TS</td>
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<td>-0.62</td>
<td>+0.27</td>
<td>-0.54</td>
<td>+0.37</td>
</tr>
<tr>
<td>Ir-H TS</td>
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<td>-0.15</td>
<td>+0.18</td>
<td>-0.54</td>
<td>+0.44</td>
</tr>
</tbody>
</table>

It is clear from the reaction energetics that in all three systems the product observed experimentally, arising from addition of H to C and Cl to Ir, is calculated to be strongly preferred thermodynamically over the other regioisomer. However there are significant differences in the kinetically preferred pathways. For the Ir=CF₂ system, the transition state leading to the Ir-H product lies well below that for the C-H transition state. Successive introduction of CF₃ groups on the carbene leads to progressive stabilization of the C-H transition state and destabilization of the Ir-H transition state, so that for the Ir=CFCF₃ and Ir=C(CF₃)₂ systems the C-H transition state is preferred. Clearly the observed regiochemistry for the CF₃ substituted carbenes is both kinetically and thermodynamically preferred. So why is a different pathway kinetically favorable in the Ir=CF₂ system?

Comparison of the NPA charges in the Ir=C functional group in the starting carbene complexes illustrates the dramatic diminution of positive charge at carbon on changing from CF₂ → CFCF₃. Introduction of a second CF₃ group results in a negative charge on carbon in the C(CF₃)₂ starting material. This is consistent with the idea that π-donor F-substituents help stabilize adjacent positive carbon while exclusively acceptor (σ and π) CF₃ substituents better stabilize adjacent negative charge,
and also with the resonance structure arguments presented in the introduction. In all three cases the calculated transition states for reaction of the carbon terminus of the Ir=\text{C} functional group with the electrophilic H\textsuperscript{δ+} of HCl involves an almost linear C--H--Cl angle, with progressively longer C--H and shorter H--Cl distances on going from CF\textsubscript{2} → CFCF\textsubscript{3} → C(CF\textsubscript{3})\textsubscript{2}. There is also considerable lengthening of the Ir-C bond and pyramidalization at C, consistent with the π-electrons of the Ir=\text{C} bond being used to bind to HCl. Compared to free HCl, the NPA charges on H in the C-H transition states remain essentially unchanged, while the charge on Cl becomes substantially more negative. In the Ir-H transition states the Ir--H--Cl angle is significantly more bent, the H is less positive than free HCl while the charges on Cl remain essentially identical to those in the CH transition states. In addition there is considerably less lengthening of the Ir-C bond and very little pyramidalization at C, consistent with interaction of HCl with a non-bonding Ir d-electron pair. In the C-H transition states there is an increase in negative charge (or decrease in positive charge) at C and an increase in positive charge at Ir; the positive charge at P remain constant. In contrast, the Ir-H transition state NPAs reveal increased positive (or decreased negative charge) at C. By simple charge arguments, substituents best able to stabilize build-up of negative charge in the CH transition states should favor that pathway, and substituents best able to stabilize positive charge at C should favor the Ir-H pathway. The Ir=CF\textsubscript{2} and C(CF\textsubscript{3})\textsubscript{2} systems provide an unambiguous prediction, while the Ir=CFCF\textsubscript{3} system, with one of each type of substituent, is ambiguous.

We have been unable to locate computationally any additional intermediates or transition states corresponding to separate formation of the Ir-Cl (or C-Cl) bonds. We conclude that either these reactions are examples of extremely asynchronous concerted additions or that the barrier for formation of the eventual bond to Cl from any intermediate is extremely small. This is consistent with the stereochemical results described above for the Ir=CFCF\textsubscript{3} systems, in which preservation of stereochemical relationships between the C and Ir centers is preserved in the kinetically controlled products. The Ir=CF\textsubscript{2} system still remains frustratingly ambiguous and we cannot distinguish, experimentally or computationally, between: 1) a rapid, reversible addition of HCl to give an
unobserved, kinetically controlled, regioisomer, with a subsequent addition of opposite regiochemistry under thermodynamic control; or 2) a polar two step pathway involving protonation at Ir, followed by migration of H from Ir to C with rapid incorporation of chloride at the metal center. Experimental evidence for the latter pathway has been discussed (vide supra) but involves entry via a different reaction manifold and the conclusions do not necessarily transfer to the system studied here.

Conclusions.

Our most important conclusion is that the relative nucleophilicity or basicity of carbene ligands cannot necessarily be deduced by examination of the electronic structures of the starting materials, and certainly cannot be deduced by examination of product structure and regiochemistry, unless it is known that the observed product and its regiochemistry are the result of kinetic control. Here we have shown that the perfluorocarbene ligands CF(CF₃) and C(CF₃)₂ in these iridium complexes are unequivocally basic (and probably nucleophilic) at carbon, but that the CF₂ ligand is less basic (or nucleophilic) than the iridium center to which it is bound and implicitly less basic than its perfluoroalkylcarbene relatives. We have not demonstrated electrophilic behavior for CF₂.

Experimental Section

All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen which had been deoxygenated over BASF catalyst and dried over molecular sieves or in a Braun drybox. Solvents were deoxygenated and dried over activated alumina under nitrogen. NMR spectra were recorded on a Varian Unity Plus 300 or 500 FT spectrometer at 21°C. ¹H NMR spectra were reference to the protio impurity in the solvent: C₆D₆ (7.16 ppm). ¹⁹F NMR spectra were referenced to external CFCl₃ (0.00 ppm). ³¹P NMR spectra were referenced to external 85% H₃PO₄. Coupling constants are reported in Hertz and are absolute values. IR spectra were recorded on a Perkin-Elmer FTIR 1600 Series spectrophotometer. Elemental analyses were performed by Schwartzkopf (Woodside, NY) and X-ray crystallographic analyses at the University of California, San
Diego. HCl/toluene was prepared by bubbling HCl into dry, deoxygenated toluene and determining the concentration by titration with standard NaOH. Potassium graphite and magnesium graphite were prepared using literature procedures.\(^{61, 62}\) Compounds \(\text{Cp}^*\text{(CO)}\text{Ir}(\text{CF}_2\text{CF}_3)\text{(I)}, \text{Cp}^*\text{(PMe}_3\text{)}\text{Ir}(\text{CF}_2\text{CF}_3)\text{(I)}, \text{Cp}^*\text{(CO)}\text{Ir}(\text{CF}_2\text{CF}_2\text{CF}_3)\text{(I)}, \text{Cp}^*\text{(PMe}_3\text{)}\text{Ir}(\text{CF}_2\text{CF}_2\text{CF}_3)\text{(I)}, \text{and} \text{Cp}^*\text{(CO)}\text{Ir}(\text{CF}_2\text{C}_6\text{F}_5)\text{(I)},\)\(^{51}\text{Cp}^*\text{(CO)}\text{Ir}=\text{CFCF}_3\) \(^{12, 37}\text{Cp}^*\text{(PMe}_3\text{)}\text{Ir}=\text{CFCF}_3\) \(^{13, 28}\text{Cp}^*\text{(CO)}\text{Ir}=\text{CFCF}_2\text{CF}_3\) \(^{14, 37}\text{and} \text{Cp}^*(\text{CO})\text{Ir}=\text{C(CF}_3\text{)}_2\) \(^{24, 59}\) were prepared as previously described. More detailed experimental procedures for 12-14 are included here.

**\text{Cp}^*\text{(CO)}\text{Ir}=\text{CFCF}_3\) \(^{12}\)**

A Schlenk flask was charged with potassium graphite (0.4485 g, 3.318 mmol) and magnesium chloride (0.1582 g, 1.66 mmol) and THF (3 mL) added. The mixture was refluxed for 30 min. \(\text{Cp}^*\text{(CO)}\text{Ir}(\text{CF}_2\text{CF}_3)\text{(I)}\) (0.100 g, 0.166 mmol) was added as a solution in THF (3 mL) at room temperature and the suspension allowed to stir at room temperature (1 hour). The solvent was removed, the product extracted into hexanes, and the solvent removed to give a yellow solid (55 mg, 73%), found to be a mixture of isomers: major-Z (12b):minor-E (12a): 10:1. Anal Calcd for C\(_{13}\)H\(_{15}\)F\(_4\)IrO (455.48): C, 34.37; H, 3.45. Found: C, 34.28; H, 3.32. IR (hexanes) \(\nu_{\text{CO}} = 2010\text{ cm}^{-1}\). \(^{12}\text{b}\): \(^1\text{H NMR (500 MHz, C}_6\text{D}_6, 21^\circ\text{C}) \delta 1.69 (s, C}_5\text{Me}_5\)). \(^{19}\text{F NMR (470 MHz, C}_6\text{D}_6, 21^\circ\text{C}) \delta -72.32 (d, \text{^3J}_\text{FF}= 12 \text{ Hz, 3F}, -0.1 (q, \text{^3J}_\text{FF}= 12 \text{ Hz, 1F}). \(^{13}\text{C NMR (125 Hz, C}_6\text{D}_6, 21^\circ\text{C}) \delta 9.4(s, 5\text{C, C}_5\text{Me}_5\)), 98.6(s, 5\text{C, C}_5\text{Me}_5\)), 129.1(qd, \text{^1J}_\text{CF}= 278 \text{ Hz, ^2J}_\text{CF}= 42 \text{ Hz, 1C, CF}_3\)), 177.7 (qd, \text{^4J}_\text{CF}= 3 \text{ Hz, ^3J}_\text{CF}= 2 \text{ Hz, 1C, CO}_2\)), 208.5(dq, \text{^1J}_\text{CF}= 354 \text{ Hz, ^2J}_\text{CF}= 38 \text{ Hz, 1C, CF}).\)**

**\text{Cp}^*\text{(PMe}_3\text{)}\text{Ir}=\text{CFCF}_3\) \(^{13}\)**

\(^{12}\text{a}: \(^1\text{H NMR (500 MHz, C}_6\text{D}_6, 21^\circ\text{C}) \delta 1.68 (s, C}_5\text{Me}_5\)). \(^{19}\text{F NMR (470 MHz, C}_6\text{D}_6, 21^\circ\text{C}) \delta 0.72 (d, \text{^3J}_\text{FF}= 10 \text{ Hz, 3F}, 9.58 (q, \text{^3J}_\text{FF}= 10 \text{ Hz, 1F}). When the reaction was carried out and worked up in the dark, only isomer 12b was produced.
A Schlenk flask was charged with potassium graphite (84.4 mg, 0.624 mmol) and THF (5 mL) was added. Cp*(PMe3)Ir(CF2CF3)(I) (40 g, 0.0628 mmol) was added as a solution in THF (3 mL) and the suspension was stirred at room temperature (1 hour). The solvent was removed, the product extracted into hexanes, filtered, and the solvent removed to give a yellow solid (23.6 mg, 75%), found to be a mixture of isomers: major-E (13a): minor-Z (13b): 11:1.

13a: 1H NMR (C6D6 500 MHz, 21°C) δ 1.85 (m, C5Me5), 1.33 (dd, 2JPH = 10 Hz, 3JFH = 1 Hz, PMe3). 19F NMR (C6D6, 470 MHz, 21°C) δ -69.9 (d, 3JFF = 13 Hz, 3F), -14.2 (dq, 3JPF = 73 Hz, 3JFF = 13 Hz, 1F). 31P{1H} NMR (C6D6 202 MHz, 22°C) δ 0.40 (dq, 3JFP = 73 Hz, 4JFP = 3 Hz, 1P, PMe3).

13b: 1H NMR (C6D6 500 MHz, 21°C) δ 1.88 (d, 4JPH = 1.5 Hz C5Me5), 1.40 (dq, 2JPH = 10 Hz, 6JFH = 1 Hz, PMe3). 19F NMR (C6D6, 470 MHz, 21°C) δ -67.2 (dd, 4JPF = 4 Hz, 3JFF = 14 Hz, 3F), -1.6 (q, 3JFF = 14 Hz, 1F). 31P{1H} NMR (C6D6 121.42 MHz, 21°C) δ -49.5 (q, 4JFP = 4 Hz, 1P, PMe3). When the reaction was carried out and worked up in the dark, only isomer 13a was produced.

Cp*(CO)Ir=CF=CF2CF3 14

A Schlenk flask was charged with potassium graphite (0.106 g, 0.784 mmol) and magnesium chloride (0.035 g, 0.368 mmol) and THF (5 mL) added. The mixture was refluxed for 30 min. Cp*(CO)Ir(CF2CF2CF3)(I) (0.036 g, 0.055 mmol) was added at room temperature and the suspension allowed to stir at room temperature (1 hr 45 min). The solvent was removed, the product extracted into hexanes, and the solvent removed to give an analytically pure yellow solid, 0.018 g (64%). The NMR spectra showed formation of the two isomers of the carbene: major Z 14b: minor E 14a in a ratio of 4:1.

Anal Calcd for C14H15F6IrO (505.46): C, 33.26; H, 2.99. Found: C, 33.23; H, 2.89. IR (hexanes) νCO = 2011 cm⁻¹. 14b: 1H NMR (C6D6, 500 MHz, 21°C) δ 1.70 (s, C5Me5).

19F NMR (C6D6, 470 MHz, 21°C)
δ 12.8 (tq, ³J_{FF} = 18 Hz, ⁴J_{FF} = 9 Hz, 1F, CFC₂F₃), -81.9 (dt, ⁴J_{FF} = 8 Hz, ³J_{FF} = 3 Hz, 3F, CF₃), -113.2 (dq, ³J_{FF} = 18 Hz, ³J_{FF} = 3 Hz, 2F, CF₂). **14a**: ¹H NMR (C₆D₆, 500 MHz, 21°C) δ 1.69 (s, C₅Me₅). ¹⁹F NMR (C₆D₆, 470 MHz, 21°C) δ 4.3 (tq, ³J_{FF} = 18 Hz, ⁴J_{FF} = 8 Hz, 1F, CFC₂F₃), -82.0 (dt, ⁴J_{FF} = 8 Hz, ³J_{FF} = 3 Hz, 3F, CF₃) -113.7 (d, ³J_{FF} = 19 Hz, 2F, CF₂). When the reaction was carried out and worked up in the dark, only isomer **14b** was produced.

**Cp*(PMe₃)Ir=CFCF₂CF₃ 15**

A Schlenk flask was charged with potassium graphite (0.090 g, 0.666 mmol) and THF (5 mL) added. To this suspension was added Cp*(PMe₃)Ir(CF₂CF₂CF₃)(I) (0.0442 g, 0.0632 mmol) as a solid. The mixture was stirred at room temperature (4 h). The solvent was removed and the product extracted into hexanes, filtered and the solution evaporated. The product was recrystallized from hexanes at -78 °C to yield a yellow solid 0.024 g (69%), found to be a mixture of isomers with a ratio: major E (**15a**):minor Z (**15b**): 3:1. Anal Calcd for C₁₆H₂₄F₆IrP (455.48): C, 34.72; H, 4.37. Found: C, 32.67; H, 4.06. **15ª** =:

**1H NMR (C₆D₆, 500 MHz, 21°C):** 1.85 (s, 15H, Cp*), 1.31 (d, ²J_{PH} = 10 Hz, 9H, PMe₃).

**19F NMR (C₆D₆, 470 MHz, 21°C):** δ 011.6 (dtq, ³J_{PF} = 79 Hz, ³J_{FF} = 20 Hz, ⁴J_{FF} = 11 Hz, 1F, CF), -81.6 (dt, ⁴J_{FF} = 11 Hz, ³J_{FF} = 4 Hz, 3F, CF₃), -109.2 (d, ³J_{FF} = 20 Hz, 2F, CF₂). **³¹P NMR (C₆D₆, 121 MHz, 21°C):** δ -40.2 (d, ³J_{PF} = 79 Hz, PMe₃). **¹³C NMR (C₆D₆, 125 Hz, 21°C) δ 11.0 (dt, J_{CF} = 2 Hz, J_{CP} = 1 Hz, 5C, C₅Me₅), 21.4 (dd, ¹J_{CP} = 38 Hz, ⁴J_{CF} = 2 Hz, 3C, PMe₃), 94.3 (dd, ²J_{CP} = 3 Hz, ³J_{CF} = 1 Hz, 5C, C₅Me₅), 117.2 (qtdq, ¹J_{CF} = 289 Hz, ²J_{CF} = 40 Hz, ³J_{CF} = 5 Hz, ⁴J_{CP} = 1 Hz 1C, CF₃), 117.7 (tdqd, ¹J_{CF} = 251 Hz, ²J_{CF} = 55 Hz, ²J_{CF} = 36 Hz, ³J_{CP} = 1 Hz 1C, CF₂), 191.9 (dt, ¹J_{CF} = 310 Hz, ²J_{CF} = 37 Hz, ²J_{CP} = 21 Hz, 1C, CF). **15b**: ¹H NMR (C₆D₆, 500 MHz, 21°C): 1.87 (s, 15H, Cp*), 1.35 (d, J = 11 Hz, 9H, PMe₃). ¹⁹F NMR (C₆D₆, 470 MHz, 21°C): δ -0.07 (dtq, ³J_{PF} = 79, ³J_{FF} = 20, ⁴J_{FF} = 11 Hz, 1F, CF), -80.4 (dt, ⁴J_{FF} = 13, ³J_{FF} = 4 Hz, 3F, CF₃), -106.4 (d mult, ³J_{FF} = 20 Hz, 2F, CF₂). When the reaction was carried out and worked up in the dark, only isomer **15a** was produced.
Cp*(CO)Ir=CFC≡CFC6F5 16

A Schlenk flask was charged with potassium graphite (0.100 g, 0.740 mmol) and THF (8 mL) was added. Solid Cp*(CO)Ir(CF2C6F5)(I) (0.0483 g, 0.0691 mmol) was added and the suspension allowed to stir at room temperature (1.5 hrs). The solvent was removed, the product extracted into hexanes and the solvent removed to yield a bright yellow film. Recrystallization from hexanes at -78°C yielded the product in an isomer ratio of 2.5:1. Yield 0.030 g, 78%. Anal. Calcd for C18H15F6IrO (553.5): C, 39.06; H, 2.73. Found: C, 39.21; H, 2.91. IR (hexanes) νCO = 1993 cm⁻¹. Major (Z isomer) ¹H NMR (C6D6, 500 MHz, 21°C): δ 1.87 (s, Cp*). ¹⁹F NMR (C6D6, 470 MHz, 21°C): δ 44.5 (t, 4JFF = 11 Hz, 1F, CF), -142.5 (ddd, 3JFF = 24, 4JFF = 11, 5JFF = 8 Hz, 2F, o-CF2), -155.3 (t, 3JFF = 21 Hz, 1F, p-CF), -163.2 (ddd, 5J = 24, 3JFF = 21, 3J = 8 Hz, 2F, m-CF2). Minor (E isomer) ¹H NMR (C6D6, 500 MHz, 21°C): δ 1.48 (s, Cp*). ¹⁹F NMR (C6D6, 470 MHz, 21°C): δ 56.5 (s, 1F, CF), -143.6 (dd, 3JFF = 25, 5JFF = 8 Hz, 2F, o-CF2), -155.7 (td, 3JFF = 22, 6JFF = 6 Hz, 1F, p-CF), -163.1 (ddd, 3JFF = 25, 3JFF = 22, 5JFF = 8 Hz, 2F, m-CF2).

Reaction of 12 with HCl.

Cp*(CO)Ir=CFC≡CFC6F5 (80 mg, 0.17 mmol, isomer ratio 11:1, Z:E) was dissolved in toluene (4 mL) and an HCl-toluene solution (0.18 M, 1 mL, 0.18 mmol) was added at -78°C. The dark yellow solution became lighter. NMR spectra of the crude solution showed formation of two diastereomers of the product, Cp*(CO)Ir(CHFC≡CFC6)(Cl) 19, in an 11:1 ratio. The solvent was evaporated under vacuum to give yellow solid (81 mg, 91%). The same procedure was repeated for starting material Z:E ratios of 6:1, 5:1, and 2:1 and the product showed 6:1, 5:1 and 2:1 diastereomer ratios respectively. Anal. Calcd for C13H16ClF4IrO (491.93): C, 31.74; H, 3.28. Found: C, 31.96; H, 3.64. IR: νCO = 2039 cm⁻¹ (CH2Cl2). Major diastereomer: ¹H NMR (CD2Cl2, 500 MHz, 21°C) δ 1.37 (s, C5Me5), 7.42 (dq, 2JHF = 47 Hz, 3JHF = 11 Hz, 1H, CHF). ¹⁹F NMR (CD2Cl2, 470 MHz, 21°C) δ -73.6 (dd, 3JFF = 15 Hz, 3JH,F = 11 Hz, 3F, CF3), -194.7 (dq, 2JHF = 47 Hz, 3JFF = 15 Hz, 1F, CHF). Minor diastereomer: ¹H NMR (CD2Cl2, 500 MHz, 21°C) δ1.24 (s, C5Me5), 6.23 (dq, 2JHF = 47 Hz, 3JHF = 10 Hz, 1H, CHF). ¹⁹F NMR (CD2Cl2, 470 MHz, 21°C) δ
-72.41 (dd, \(^3\)J\(^{\text{FF}}\) = 15 Hz, \(^3\)J\(^{\text{HF}}\) = 10 Hz, 3F, CF\(_3\)), -186.25(dq, \(^2\)J\(^{\text{HF}}\) = 47 Hz, \(^3\)J\(^{\text{FF}}\) = 15 Hz, 1F, CHF).

Crystals of the major diastereomer were sent for X-ray diffraction. The specific crystal used for the diffraction experiment was returned and its NMR spectra confirmed to be of the major isomer, allowing identification of the relative stereochemistries of Ir and C in the major diastereomer to be confirmed.

**Reaction of 13 with HCl.**

The stereochemically pure carbene complex Cp*(PMe\(_3\))Ir=CF\(_3\) (0.023 g, 0.05 mmol, E isomer) was dissolved in toluene (5 mL) and cooled to -78°C. HCl-toluene (0.18 M, 0.3 mL, 0.05 mmol) was added at -78°C and the mixture was stirred (10 min). The solvent was evaporated under vacuum to give yellow solid product (0.021 g, 80%), shown to be a single diastereomer of Cp*(PMe\(_3\))Ir(CHFCF\(_3\))(Cl) 20, the stereochemistry of which has been characterized previously.\(^{33}\) Reaction of a 4:1 (E:Z) mixture of starting material gave a 4:1 mixture of product diastereomers.

**Reaction of 24 with HCl.**

Cp*(CO)Ir=C(CF\(_3\))\(_2\) (37 mg, 0.073 mmol) was dissolved in toluene (10 mL). An HCl (1.25mL, 0.087 mmol, 0.07 M toluene solution) was added at -78°C. The \(^{19}\)F NMR spectrum showed all of the starting material was converted to Cp*(CO)Ir(Cl)[CH(CF\(_3\))\(_2\)] 25. The solvent was removed to give a yellow solid product (39 mg, 99%). Calcd for C\(_{14}\)H\(_{16}\)ClF\(_6\)IrO (541.94): C, 31.03; H, 2.98. Found: C, 30.92; H, 2.96. IR (hexane): ν(CO) = 2048 cm\(^{-1}\). \(^1\)H NMR (C\(_6\)D\(_6\), 500 MHz, 21°C) δ 1.27 (s, 15H, C\(_5\)Me\(_5\)), 4.43 (septet, \(^3\)J\(^{\text{FH}}\) = 12 Hz, 1H, IrCH). \(^{19}\)F NMR (C\(_6\)D\(_6\), 470 MHz, 21°C) δ -53.3 (dq, \(^3\)J\(^{\text{FH}}\) =12 Hz, \(^4\)J\(^{\text{FF}}\) = 10 Hz, 3F, CF\(_3\)), -56.0 (dq, \(^3\)J\(^{\text{FH}}\) =12 Hz, \(^4\)J\(^{\text{FF}}\) = 10 Hz, 3F, CF\(_3\)).

**Reaction of 14 with HCl.**

Cp*(CO)Ir=CFC\(_2\)F\(_5\) (0.026 g, 0.0514 mmol, 3:1 ratio of Z:E isomers) was dissolved in toluene (8 mL) to give a bright yellow solution. This was cooled to -78°C, HCl in toluene (0.23M, 0.45 mL, 0.104
mmol) was added and the solution was stirred at -78°C (2 hours) before warming to room temperature. NMR spectra showed formation of product Cp*(CO)Ir(CFHCF₂CF₃)(Cl) 21, as a 3:1 ratio of diastereomers. The solvent was removed to give an analytically pure yellow solid. Anal. Calcd for C₁₄H₁₆ClF₆IrO (541.92): C, 31.03; H, 2.98. Found: C, 31.37; H, 3.07. IR: ν₀₀ = 2042 cm⁻¹ (hexanes).

Major diastereomer: ¹H NMR (C₆D₆, 500 MHz, 21°C) δ 7.68 (ddd, 2J₉₁₁ = 47, 3J₈₁₁ = 30, 3J₈₁₁ = 8 Hz, 1H, CFH), 1.40 (s, 15H, Cp*). ¹⁹F NMR (C₆D₆, 470 MHz, 21°C) δ -81.88 (d, 4J₁₁₁ = 13 Hz, 3F, CF₃), -114.8 (ddd, 2J₁₁₁ = 275, 3J₁₁₁ = 30, 3J₁₁₁ = 17 Hz, 1F, CF₂), -115.6 (ddd, 2J₁₁₁ = 275, 3J₁₁₁ = 22, 3J₁₁₁ = 8 Hz, 1F, CF₂), -196.3 (dddq, 2J₁₁₁ = 47, 3J₁₁₁ = 22, 3J₁₁₁ = 17, 4J₁₁₁ = 13 Hz, 1F, CFH). Minor diastereomer: ¹H NMR (C₆D₆, 500 MHz, 21°C) 7.46 (ddd, 2J₉₁₁ = 47, 3J₈₁₁ = 25, 3J₈₁₁ = 10 Hz, 1H, CFH), 1.26 (s, 15H, Cp*). ¹⁹F NMR (C₆D₆, 470 MHz, 21°C) δ -81.84 (d, 4J₁₁₁ = 13 Hz, 3F, CF₃), -116.0 (ddd, 2J₁₁₁ = 273, 3J₁₁₁ = 21, 3J₁₁₁ = 10 Hz, 1F, CF₂), -116.7 (ddd, 2J₁₁₁ = 273, 3J₁₁₁ = 25, 3J₁₁₁ = 17 Hz, 1F, CF₂), -188.2 (dddq, 2J₁₁₁ = 47, 3J₁₁₁ = 21, 3J₁₁₁ = 17, 4J₁₁₁ = 13 Hz, 1F, CFH). Crystals of the major diastereomer were sent for X-ray diffraction. The specific crystal used for the diffraction experiment was returned and its NMR spectra confirmed to be of the major isomer, allowing identification of the relative stereochemistries of Ir and C in the major diasteromer to be confirmed.

**Reaction of 15 with HCl.**

Cp*(PMe₃)Ir=CFCF₂CF₃ (0.024 g, 0.043 mmol; 3:1 E:Z ratio) was dissolved in toluene (5 mL) and cooled to -78°C to give a bright yellow solution. HCl/toluene (0.07M, 0.6 mL, 0.042 mmol) was added and the color became paler. NMR analysis showed the product to consist of a 3:1 mixture of diastereomers of Cp*(PMe₃)Ir(CFHCF₂CF₃)(Cl) 22, the stereochemistries of which have been characterized previously.³³ Reaction of a 4:1 (E:Z) mixture of starting material gave a 4:1 mixture of product diastereomers.

**Reaction of 16 with HCl.**
Cp*(CO)Ir=CF_CFC (0.086 g, 0.155 mmol; 5:1, Z:E ratio) was dissolved in toluene (5 mL) to give a bright yellow solution and cooled to -78ºC. HCl in toluene (0.07 M, 2.3 mL, 0.161 mmol) was added and the solution allowed to stir at -78ºC (30 min). NMR analysis showed the formation of the product Cp*(CO)Ir(CFHC_F_6)(Cl) 23, as a 5:1 mixture of diastereomers. Recrystallized from methylene chloride/hexanes yielded an analytically pure sample 0.055g (60%). Anal. Calcd for C_{18}H_{16}ClF_6IrO (589.958): C, 36.64; H, 2.73. Found: C, 36.75; H, 2.61. IR: ν_CO (CH_2Cl_2) = 2032 cm\(^{-1}\). Major diastereomer: \(^1\)H NMR (C_6D_6, 500 MHz, 21°C): δ 7.07 (d, \(^2\)J_{HF} = 49 Hz, 1H, CHF), 1.32 (s, 15H, Cp*). \(^19\)F NMR (C_6D_6, 470 MHz, 21°C): δ -141.0 (td, \(^4\)J_{FF} = 12, \(^3\)J_{FF} = 8, 2F, o-F), -158.5 (td, \(^3\)J_{FF} = 21, \(^6\)J_{FF} = 2 Hz, 1F, p-F), -164.1 (dtd, \(^2\)J_{HF} = 49, \(^4\)J_{FF} = 12, \(^6\)J_{FF} = 2 Hz, 1F, CHF), -164.9 (dt, \(^3\)J_{FF} = 21, \(^3\)J_{FF} = 8 Hz, 2F, m-F). Minor diastereomer: \(^1\)H NMR (C_6D_6, 500 MHz, 21°C): δ 7.69 (\(^2\)J_{HF} = 49 Hz, 1H, CHF), 1.20 (s, 15H, Cp*). \(^19\)F NMR (C_6D_6, 470 MHz, 21°C): δ -141.2 (br s, 2F, o-F), -158.7 (td, \(^3\)J_{FF} = 21, \(^6\)J_{FF} = 2 Hz, 1F, p-F), -164.2 (dt, \(^3\)J_{FF} = 21, \(^3\)J_{FF} = 8 Hz, 2F, m-F), -170.5 (dt, \(^2\)J_{HF} = 49, \(^4\)J_{FF} = 11 Hz, 1F, CHF). Crystals of the major diastereomer were sent for X-ray diffraction. The specific crystal used for the diffraction experiment was returned and its NMR spectra confirmed to be of the major isomer, allowing identification of the relative stereochemistry of Ir and C in the major diastereomer to be confirmed.

**General procedure for determination of isomerization kinetics**

A known amount of Cp*(CO)Ir=CF_R (5-10 mg) and an external standard, C_6F_6, was dissolved in a known amount of C_6D_6 (0.6-0.8 mL) and allowed to reach its photostationary composition under ambient light conditions. \(^1\)H and \(^19\)F NMR spectra recorded. The NMR tubes were covered with aluminum foil and placed in an oil bath at a set temperature (30, 40, 47, 61°C). NMR spectra were taken periodically until thermal equilibrium was reached. From the integration and the known concentration of the alkylidene in solution, the concentration of each isomer was determined at each time point. The difference between the initial concentration, [A]_0, and the concentration at time t was found and termed X. The difference between X at equilibrium, X_e, and X at time t was then calculated. A plot of the
natural log of \((X_c-X)\) versus time (seconds) resulted in a line with slope equal to \(- (k_1 + k_{-1})\). From this information and the known equilibrium constant, \(k_1\) and \(k_{-1}\) were calculated. Plotting the ln of \(k/T\) versus \(1/T\) (Eyring plot) for the rate constants determined at each temperature resulted in a line with slope equal to \(-\Delta H^\ddagger/R\). The entropy of activation, \(\Delta S^\ddagger\), was determined from the y-intercept using the equation, \(y = \ln(k_B/h) + \Delta S^\ddagger/R\). Errors were found by determining the equations of the lines representing the two extremes of the error bars and calculating the respective \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\) values.

**X-ray Crystal Structure Determinations.**

Diffraction intensity data were collected with Bruker Smart Apex CCD diffractometers. The structures were solved using the Patterson function, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on \(F^2\). SADABS absorption corrections were applied to all structures. In all structures, all non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of scattering factors are contained in the SHELXTL (5.10) program package (G. Sheldrick, Bruker XRD, Madison, WI).

**DFT calculations.**

Calculations were carried out using the hybrid B3LYP functional\(^{41-44}\) with the zero-damping, two-body only D3 correction of Grimme et al.,\(^{45, 46}\) and the LACV3P**++ basis, which uses a pseudopotential for iridium,\(^{47-50}\) and the 6-311++G** basis\(^{63-66}\) for other atoms, as implemented in the Jaguar\(^{67}\) suite of programs. Computed structures were confirmed as energy minima or transition states by calculating the vibrational frequencies using second derivative analytic methods, and confirming the absence of imaginary frequencies for minima and single imaginary frequency for transition states. Thermodynamic quantities were calculated assuming an ideal gas, and are zero point energy corrected.

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Electronic Supplementary Information Available

Details of all DFT calculated structures described herein. CCDC 1406693-1406699. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

References