ORGANOMETALLICS

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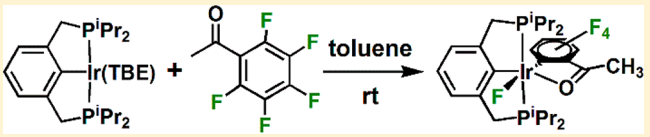
C(sp^2)−F Oxidative Addition of Fluorinated Aryl Ketones by ^{iPr}PCPIr

Miles Wilklow-Marnell, William W. Brennessel, and William D. Jones*

Department of Chemistry, University of Rochester, Rochester, New York 14627, United States

Supporting Information

ABSTRACT: The reaction of ^{iPr}PCPIrH$_4$ (^{iPr}PCP = κ^3-2,6-C$_6$H$_3$(CH$_2$P(^{i}Pr)$_2$)$_2$) with ≥2 equiv of 2,3,4,5,6-pentafluoroacetophenone (AP-F5) in aromatic solvents at room temperature leads to the hydrogenation of AP-F5 and formation of the corresponding 5-coordinate alkoxy hydride species (**I**) within several minutes. Heating at ≥120 °C quickly provides the cyclometalated trans C-H product ^{iPr}PCPIr(κ-O,C-OC$_8$H$_3$F$_4$)H (**III**), which slowly isomerizes to the cis C-H product ^{iPr}PCPIr(κ-C,O-OC$_8$H$_3$F$_4$)H (**V**). The fate of the fluoride during formation of **III** and **V** is not entirely clear, though the production of HF is implicated by significant glass etching and several crystal structures. When ^{iPr}PCPIrH$_4$ is allowed to react overnight with ≥2 equiv of AP-F5 at room temperature, formation of C−F oxidative addition product ^{iPr}PCPIr(κ-O,C-OC$_8$H$_3$F$_4$)F (**II**) is observed by ^{31}P and ^{19}F NMR spectroscopy. When ^{iPr}PCPIrH$_4$ activated with *tert*-butylethylene is employed, formation of **II** occurs within 10 min. Analogous reactivity is observed with several other fluorinated aryl ketones, and the crystal structure of the C−F oxidative addition product of 2,6-difluoroacetophenone (**II**$_{AF2}$) has been determined. This represents the first well-defined examples of stable iridium fluorides formed by C(sp^2)−F oxidative addition.



INTRODUCTION

Organofluorides have become pervasive in everyday life and chemical industry/research due to their use in common materials such as Gore-Tex fabrics and "non-stick" Teflon cookware coatings, a range of pharmaceuticals such as fluconazole and fluoxetine, as well as ligands and counterions for organometallic/coordination compounds such as triflate or BARF anions.[1,2] However, the selective fluorination of organic molecules remains challenging, and it is often easier to highly or completely fluorinate a given substrate, especially by methods amenable to large scale production.[3−5] The challenges of organofluorine chemistry arise from the unique properties fluorine imparts on C−F bonds, which are highly polarized and among the strongest of all chemical bonds. For example, simple changes in reagents or conditions can dictate whether electro/nucleophilic, radical, or other reaction mechanisms proceed, in part due to strong electrostatic interactions between fluorine and other atoms (e.g., hydrogen bonding).[3,6] Given these considerations, C−F bond formation and activation by transition metal complexes has been studied widely in recent decades as a means toward selective fluorination of organic molecules, or selective defluorination of highly fluorinated substrates to form useful synthetic intermediates or compounds useful in their own right.

Quite an extensive body of research on C−F activation by organometallic species and the reactivity of organometallic fluoride complexes now exists,[7−10] with iridium being no exception. However, while a number of systems have shown well-defined examples of C(sp^2)−F oxidative addition to metal centers, mainly group 6 and 10 metal species,[7,11−13] there are few with iridium. C−F activation by complexes of iridium has rarely been reported to proceed through oxidative addition, and when direct C−F oxidative addition is invoked, it is often proposed ex post facto based on reaction products which no longer contain one, or both, of the corresponding C−Ir−F bonds. Perhaps the earliest example of potential C−F oxidative addition to iridium was demonstrated by Doyle in 1982.[14] The reaction of Ir(CO)(PR$_3$)$_2$Cl (R = Ph, Me) in benzene with formyl fluoride at room temperature was found to provide IrH(F)(CO)(PR$_3$)$_2$Cl in good yields with concomitant release of CO (Figure 1). Initial C−F oxidative addition to form the iridium formyl fluoride, followed by decarbonylation to the iridiumfluorohydridocarbonyl with subsequent release of CO, was proposed due to initial C−H activation being deemed "unlikely" under ambient conditions. Unfortunately, characterization of the metal-fluoride products was limited to elemental analysis and IR spectroscopy. No mechanistic study was attempted, and the veracity of C−F oxidative addition in this case remains somewhat dubious, though certainly possible. Roughly a decade later, an example reported by Milstein and co-workers[15] involved the, then unknown, activation of C−F bonds by a phosphine assisted pathway. The complex MeIr(PEt$_3$)$_3$ was found to form Ir(PEt$_3$)$_2$(PEt$_2$F)(C$_6$F$_5$) upon thermolysis at 60 °C in C$_6$F$_6$ (Figure 1) with loss of methane and ethylene. At the time, a mechanism was proposed involving cyclometalation of a phosphine ethyl group via C−H activation, followed by electron transfer to C$_6$F$_6$, elimination of methane and ethylene to provide [Ir(PEt$_3$)$_2$(PEt$_2$)]$^{\bullet+}$[C$_6$F$_6$]$^{\bullet-}$, and oxidative addition of [C$_6$F$_6$]$^{\bullet-}$ to give the iridium(III) aryl-fluoride (unobserved), followed by reductive elimination, to yield the final product. Calculations conducted much later[16] indicate that 1,2 addition of the C−F bond across the Ir−P bond to form a metallophosphorane intermediate is more

Received: June 19, 2017

DOI: 10.1021/acs.organomet.7b00466
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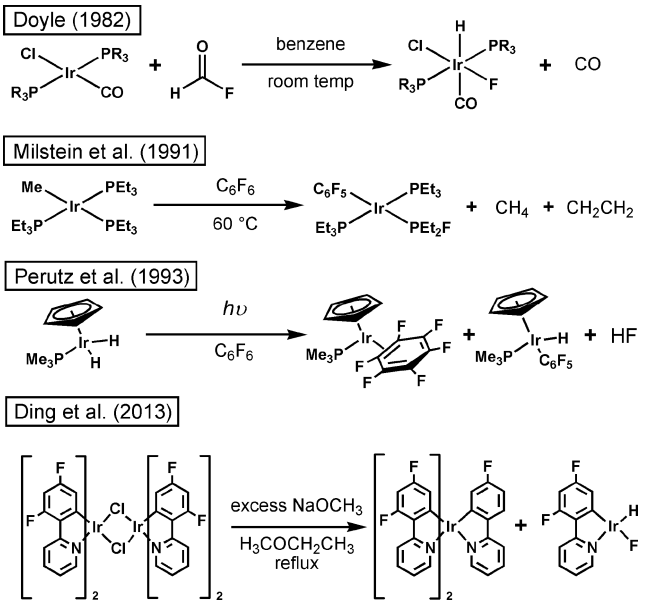

Figure 1. Notable examples of proposed C(sp^2)−F oxidative addition by iridium complexes.

likely. Nevertheless, this discovery has led to the successful incorporation of phosphine assisted C−F activation into reactions such as the iridium catalyzed synthesis of thioethers by C−S cross-coupling of aryl fluorides and disulfides in the presence of stoichiometric phosphine additives.[17]

Shortly after Milstein's report of phosphine assisted C−F activation, Perutz and co-workers demonstrated apparent C−F oxidative addition by CpIr(PMe_3)H_2 via photolysis in neat C_6F_6.[18] Both CpIr(PMe_3)(η^2-C_6F_6) and CpIr(PMe_3)(C_6F_5)H were formed concomitantly in a 6:5 ratio, with the C−F activation product forming presumably by loss of HF after C−F addition to Ir (Figure 1). It was proposed that these products form by independent mechanisms, in contrast to the rhodium analogue which was determined to participate in C−F oxidative addition subsequent to η^2-coordination. Again, however, a discrete C−F activation product was not observed or isolated. Experiments with deuterium labeling showed that the hydride of the pentafluorophenyl adduct comes from the starting complex making H_2 dissociation unlikely, and ring-slip or H-shift mechanisms were proposed to account for the open coordination sites necessary for C−F addition.

In a remarkable example related to the present work, Goldman and co-workers discovered the unprecedented activation of C(sp^3)−F bonds by ^{tBu}PCPIr, with several examples of isolated Ir−F complexes.[19] Although outwardly proceeding by C−F oxidative addition, combined experimental and computational studies revealed that C−H addition occurs first, followed by α-fluorine migration or β-fluoride elimination depending on substrate.

Somewhat more recently, Ding and co-workers proposed C(sp^2)−F oxidative addition during the reaction of (dfppy)$_2$Ir-(μ-Cl)$_2$Ir-(dfppy)$_2$ with sodium methoxide to form a heteroleptic mononuclear complex (dfppy = 2-(4,6-difluorophenyl)pyridyl) (Figure 1).[20] The intermediacy of iridium fluorides formed via oxidative addition in this process was proposed based on the observation of "characteristic" peaks in the ^{19}F NMR spectrum of a band obtained through TLC analysis of the reaction mixture without any reference to prior works establishing this characteristic nature. Furthermore, the provided spectrum contains more resonances than expected, the peak intensities are inconsistent with the proposed products, and one of the proposed products is an iridium hydrido-fluoride that would almost certainly display H−F coupling which could be indicative of this formulation, but is not mentioned in any way. As well, a large excess of sodium methoxide is used. Many bases are known to react with aryl-fluorides on their own,[9,11,21] and in particular, sodium methoxide has been demonstrated to efficiently undergo S_NAr substitution with 4-fluorobromobenzene to form 4-bromoanisole in methanol at 102 °C with added polar aprotic solvent.[22] These conditions are quite similar to those used by Ding, and it is surely possible that C(aryl)−O activation by iridium subsequent to defluoromethoxylation with sodium methoxide could lead to the observed products, among other possible mechanisms.

It seems there is a clear lack of well-defined examples of C(sp^2)−F oxidative addition by organometallic complexes of iridium. Here, we report the oxidative addition of *ortho* C−F bonds in fluorinated aryl ketones by ^{iPr}PCPIr (^{iPr}PCP = κ^3-2,6-$C_6H_3(CH_2P(^iPr)_2)_2$) to ultimately form cyclometalated iridium hydride species. The initial C−F activation products are surprisingly stable, in contrast to previous reports of C(sp^2)−F oxidative addition to iridium, and clear coupling between the PCP ligand phosphines and iridium bound fluoride is observed. None of the earlier reactions described above provide examples where simple C−F oxidative addition has occurred to give an Ir(C)(F) product. Here, the first crystal structure of an iridium fluoride resulting from C(sp^2)−F oxidative addition is reported, and variations in reactivity between ^{iPr}PCPIrH_4 and direct ^{iPr}PCPIr precursors, as well as the origin of the hydride ligand, are explored.

RESULTS AND DISCUSSION

While investigating molecular hydrogen acceptors for dehydrogenations catalyzed by ^{iPr}PCPIr, we considered fluorinated aryl ketones in the hope that the strong C−F bonds *ortho* to the ketone moiety would prevent the formation of stable cyclometalated species as we have previously observed with related non-fluorinated substrates.[23] In this effort, an excess (3 equiv) of the substrates 2,3,4,5,6-pentafluoroacetophenone (AP-F_5), 2,6-difluoroacetophenone (AP-F_2), and perfluorobenzophenone (BP-F_{10}) was reacted with ^{iPr}PCPIrH_4 in toluene at room temperature. Indeed, the disappearance of the hydride and phosphine signals of the starting complex was observed by NMR spectroscopy with AP-F_5 within 5−10 min, whereas AP-F_2 took somewhat longer (ca. 45 min). Dehydrogenation of ^{iPr}PCPIrH_4 was markedly slower with BP-F_{10}, requiring greater than 24 h for full disappearance of signals associated with the tetrahydride. In all instances, a number of resonances were seen by ^{31}P NMR spectroscopy, and a single product was not obtained over the course of 24−48 h at room temperature. The species observed were found to vary with reaction time, temperature, and substrate as described in more detail below.

In the case of AP-F_5 reacting at room temperature, the initial major product presented a singlet at δ 56.6 in the ^{31}P NMR spectrum. This peak correlates with a ^{1}H NMR resonance manifesting as a triplet at δ −32.1 (J_{PH} = 13 Hz). The chemical shift of the observed hydride is consistent with a 5-coordinate RO−H activation product.[23,24] The reaction of ^{iPr}PCPIr (generated from ^{iPr}PCPIrH_4 activated with *tert*-butylethylene [TBE]) and 2,3,4,5,6-pentafluorophenylethanol gave rise to the

DOI: 10.1021/acs.organomet.7b00466
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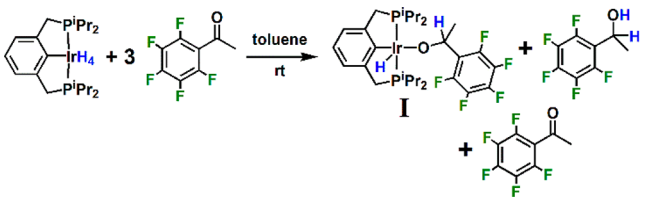
same major product, confirming the designation of this species as ^{iPr}PCPIr(κ-O-OC$_8$H$_4$F$_5$)H (**I**). Thus, in the presence of excess AP-F$_5$, ^{iPr}PCPIrH$_4$ will reduce 2 equiv of the ketone, with the second remaining attached as an alkoxy-hydride species (**I**), and any additional equivalents remaining unaffected (Scheme 1).

Scheme 1. Reaction of ^{iPr}PCPIrH$_4$ with 2,3,4,5,6-Pentafluoroacetophenone (AP-F$_5$) To Form I



In contrast, no clear evidence of a similar iridium O-H adduct was found with AP-F$_2$. When an excess (3 equiv) of AP-F$_2$ is reacted with ^{iPr}PCPIrH$_4$ at room temperature in toluene, a major product represented by a singlet at δ 59.2 in the ^{31}P NMR spectrum is observed, similarly to AP-F$_5$. However, no associated hydride signal is seen, which may indicate a fluxional species, either by reversible C−H or by O−H activation. The related complex ^{tBu}PCPIr has been reported to undergo rapid intermolecular arene exchange via reversible C−H activation faster than the NMR time-scale,[25] and accordingly, no hydride resonance is observed for ^{tBu}PCPIr(Ph)H and related arene C-H adducts at room temperature, though a defined singlet is found in the ^{31}P NMR spectrum.

When BP-F$_{10}$ was employed, ≥95% ^{iPr}PCPIrH$_4$ was consumed after 24 h at room temperature, and among other peaks, a very broad resonance (ca. 431 Hz) was observed in the ^{31}P NMR spectrum centered at δ 56.8, which may possibly be attributed to a highly fluxional O-H adduct. Again, at this point, the ^{1}H NMR spectrum did not display a hydride resonance which could clearly be assigned as an O−H activation product. These room temperature product mixtures were then heated to 150 °C to force additional reaction.

After heating at 150 °C for 24 h, none of the three substrates tested provided a single product, and they were deemed as poor candidates for hydrogen acceptors in dehydrogenation reactions. We likely would have moved on at this point and ceased investigating the reactivity of ^{iPr}PCPIrH$_4$ with fluorinated ketones were it not for the successful crystallization of an iridium complex from the reaction of ^{iPr}PCPIrH$_4$ and AP-F$_5$ (pentane, −17 °C). The molecular structure was determined by single crystal X-ray diffraction, which showed that, contrary to our expectations, cyclometalation via C−F activation *ortho* to the ketone moiety had indeed occurred but that, curiously, the anticipated fluoride was replaced by a hydride ligand to give complex **V** (Figure 2). Characterization of this species by NMR spectroscopy showed it to be the major product observed after 24 h at 150 °C, displaying a singlet at δ 46.2 in the ^{31}P{^{1}H} NMR spectrum (toluene). The hydride, found at δ −25.4, exhibits the usual phosphorus coupling as well as coupling to a single fluorine atom, most likely that *ortho* to the C−Ir bond (F1 in Figure 2), as evidenced by the resolution of this peak as a triplet of doublets (J_{PH} = 15.4 Hz, J_{FH} = 8.8 Hz in C$_6$D$_6$). The expected four resonances are clearly defined in the ^{19}F NMR spectrum between δ −104 and −166. Notably, the weakest coupling observed in an apparent overlapping doublet of

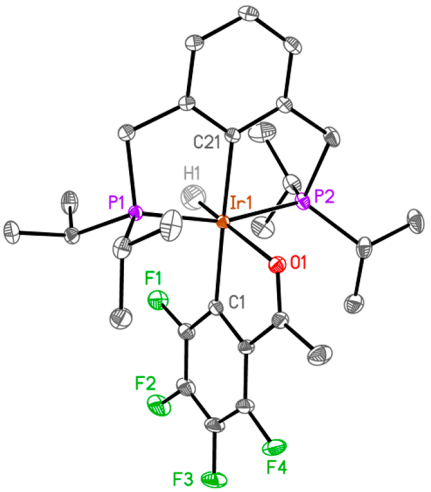


Figure 2. Molecular structure of ^{iPr}PCPIr(κ-C,O-OC$_8$H$_3$F$_4$)H (**V**) determined by X-ray crystallography.

doublets of doublets at δ −105.2 has a value of 8.7 Hz, in good accord with the observed hydride.

Intrigued, we set out to determine the origins of this species and whether more traditional oxidative addition of the C(sp^2)−F bond, followed by some exchange process, led to **V** or if one of the more unique pathways common to fluorocarbons, but otherwise rare, had been followed. First, an excess (3 equiv) of AP-F$_5$ was added to ^{iPr}PCPIrH$_4$ at room temperature in toluene, and then heated at 150 °C while monitoring by ^{31}P, ^{1}H, and ^{19}F NMR spectroscopy. Reaction times, product concentrations, and the number/proportions of "side" products were found to vary somewhat depending on the particular batch of solvent or metal complex used, as well as the newness of the NMR tube, and, though qualitatively informative, comparisons of reaction rates or "cleanliness" must be taken with some caution. Nonetheless, shortly after combining and mixing reagents, ^{31}P NMR spectroscopy showed that, besides **I**, and other species, a small signal attributed to **V** was already present in solution (∼2.5% of total products) as well as a somewhat unusual doublet at δ 38.4 (∼5.8%; most ^{31}P{^{1}H} NMR spectra of the ^{iPr}PCPIr complexes appear as singlets. A doublet could indicate a P−F coupling due to the presence of an Ir-F moiety). After heating at 150 °C for 1 h, though the concentration of **V** had increased (∼19%), by far the main product (∼66%) was represented by a singlet at δ 45.3, which slowly converted to **V** over the course of approximately 6 days at 150 °C (**V** ca. 97% of the combined concentration of **III** and **V**). This species (**III**) displays a broad hydride resonance at δ −11.5, as well as 4 peaks in the ^{19}F NMR spectrum which are very similar to those of **V**, though the peak attributed to the fluorine *ortho* to the C−Ir bond appears as more of a somewhat overlapped doublet of quartets, and is shifted upfield to δ −114.3. The chemical shift of this hydride, and slow conversion of **III** to **V**, is consistent with the assignment of **III** as the *trans* C−H isomer of **V** (Scheme 2). As shown in previous work,[23,26] C−H oxidative addition of aryl C−H bonds to ^{R}PCPIr is not directing group assisted, and instead a cyclometalated *trans* C−H species is formed first, followed by slow isomerization to the *cis* C−H complex.

Analogous reactivity is followed using AP-F$_2$ or BP-F$_{10}$ to form products **V$_{AF2}$** and **V$_{BF10}$**, respectively. However, while BP-F$_{10}$ required roughly the same reaction time as AP-F$_5$ at 150 °C, near complete conversion to **V$_{AF2}$** occurred within only ca. 24

DOI: 10.1021/acs.organomet.7b00466
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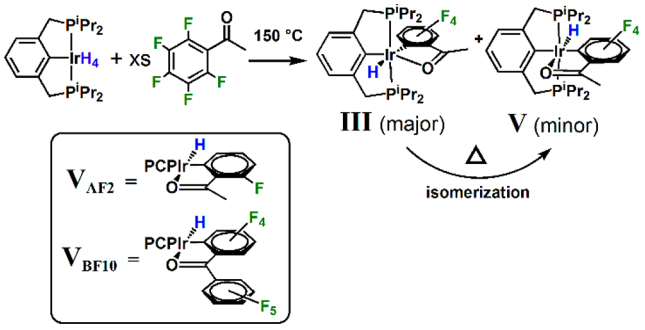
Scheme 2. Isomerization of *trans* C−H Adduct III to *cis* C−H Isomer V, and Related Products Formed with 2,6-Difluoroacetophenone (V_{AF2}) and Perfluorobenzophenone (V_{BF10})



h. The hydride resonances of all three *cis* C−H final products are shown in Figure 3. A simple triplet is seen for the hydride resonance of V_{AF2}, presumably due to the lack of a fluorine atom *ortho* to the PCPIr−C bond.

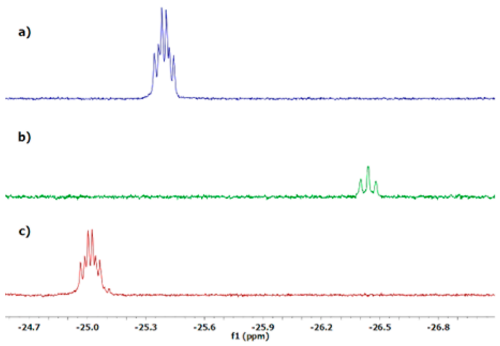


Figure 3. ^{1}H NMR spectra showing hydride resonances of **V** (a), V_{AF2} (b), and V_{BF10} (c) in toluene.

In light of the fact that a species readily identifiable as an iridium-fluoride was not observed during the formation of products **V**, V_{AF2}, and V_{BF10} at 150 °C, we considered the possibility that C−F cleavage by iridium was not involved in this process, or that the iridium fluoride formed was too short-lived to be detected by NMR spectroscopy. However, the feasibility of C−F addition to iridium was readily confirmed at lower temperature. When a toluene solution of ^{iPr}PCPIrH$_4$ and 3 equiv of AP-F$_5$ was instead allowed to mix at room temperature overnight, the small doublet observed shortly after mixing (vide supra) had grown to approximately 45% of total products (^{31}P NMR spectroscopy), representing the major species in solution. Analysis of the ^{19}F NMR spectrum showed 4 resonances of equal area in the normal aryl-fluoride region. The chemical shifts of these peaks are consistent with a tetrafluorobenzene bound *cis* to the PCP ligand Ir−C bond, and the carbonyl oxygen coordinated *trans*, as compared to **III**. A fifth resonance, a triplet, was also observed at δ −347.1 (vide infra) which seemed to indicate an iridium-bound fluoride coupled to two equivalent phosphorus atoms, and this species was deemed to be ^{iPr}PCPIr(κ-O,C-OC$_8$H$_3$F$_4$)F (**II**). In support of this assignment, the measured coupling constants of the doublet (^{31}P NMR) and triplet (^{19}F NMR) are both 25 Hz, and the far upfield ^{19}F NMR chemical shift of the fluoro ligand is similar to a number of reported organometallic iridium fluorides.[27−30] This species was found to be remarkably stable for an iridium-fluoride. The concentration of **II** only decreased to 44% of total products after 21 days at room temperature in toluene.

Using AP-F$_2$ under otherwise identical conditions, ^{31}P NMR spectroscopy revealed a doublet at δ 37.7 (J_{FP} = 26.2 Hz) as the major product (46%), and an associated virtual triplet was found at δ −358.5 in the ^{19}F NMR spectrum. Interestingly, over 4 days of mixing at room temperature, BP-F$_{10}$ did not lead to any identifiable iridium fluoride complexes under these conditions. Instead, as ^{iPr}PCPIrH$_4$ was slowly consumed, a signal at δ 50.3 in the ^{31}P NMR spectrum, attributable to V_{BF10}, was seen to grow in as the major species, among others. This result, and the observation of small amounts of **V** immediately after mixing ^{iPr}PCPIrH$_4$ and 3 equiv of AP-F$_5$ (vide supra), suggests that a path independent of **III** leads to **V** and its analogues at room temperature which is supplanted by another mechanism leading quickly to **III** at high temperatures, followed by slow isomerization to **V**.

Multiple attempts were made to crystallize complexes **II** and **III** from reaction mixtures in which they were the main product. Though neither was isolated, several crystals were obtained of complexes which demonstrated that HF was likely being generated during these reactions, and that fluoride loss from **II** does not necessarily lead directly to **III** or **V**. One of the structures determined is an analogue of **II** and **III** wherein an aquo ligand is located in place of the fluoride or hydride, respectively, denoted as $\mathbf{II}_{H2O}$ (Figure 4a). While this result points to the potential lability/reactivity of the iridium bound fluoride and possible role of water in this process, the likely formation of HF is also evident. Water being a neutral ligand, $\mathbf{II}_{H2O}$ requires a counterion to satisfy the positive charge of the Ir(III) center which, unexpectedly, was found to be BF_4^-, almost certainly resulting from the action of HF on the borosilicate glass of the NMR tube.[31] Although this material was completely insoluble in C$_6$D$_6$, it readily dissolved in THF-d_8, displaying a singlet at δ 36.1 in the ^{31}P NMR spectrum and the anticipated 4 aryl-F signals in the ^{19}F NMR spectrum as well as a large broad resonance at δ −151 for BF_4^-. Also obtained were several crystals of the minor product [^{iPr}PCPIr-(H$_2$O)$_2$H]F (**VI**), ostensibly the product of the reaction between ^{iPr}PCPIr, HF, and adventitious water (Figure 4b). The free fluoride counterion is stabilized by hydrogen bonding to four different aquo ligands in the extended lattice (Figure 4c), similarly to reported copper(II) fluoride complexes [Cu-(en)$_2$(H$_2$O)$_2$]F$_2$·4H$_2$O (en = ethylenediamine) and [Cu-(cyclam)$_2$(H$_2$O)$_2$]F$_2$·4H$_2$O (cyclam = 1,4,8,11-tetra-azacyclotetradecane).[32] The elucidation of these structures called into question the extent to which water facilitates the dissociation of fluoride from **II**. Bergman has reported that, in the presence of L-type ligands (including water), complexes of the family Cp′Ir(PMe$_3$)(aryl)F (Cp′ = C$_5$Me$_5$ or C$_5$Me$_4$Et) exist in an equilibrium with [Cp′Ir(PMe$_3$)(aryl)L]F which strongly favors Cp′Ir(PMe$_3$)(aryl)F in "dry" solvents.[33] Addition of water shifts this equilibrium with hydrogen bonding stabilizing the fluoride counterion, favoring [Cp′Ir(PMe$_3$)(aryl)L]F·(H$_2$O)$_n$ at water concentrations > 1.8M, illustrating the contribution of water in fluoride dissociation from this group of iridium complexes.

When Cp′Ir(PMe$_3$)(C$_6$H$_5$)F was monitored by NMR spectroscopy in THF-d_8 with 54.2 equiv of added water, equilibrium with [Cp′Ir(PMe$_3$)(C$_6$H$_5$)OH$_2$]F·(H$_2$O)$_n$ was established within <2 h at −31 °C. In contrast, when a mesitylene solution (~5 ppm of H$_2$O by Karl Fischer titration)

DOI: 10.1021/acs.organomet.7b00466
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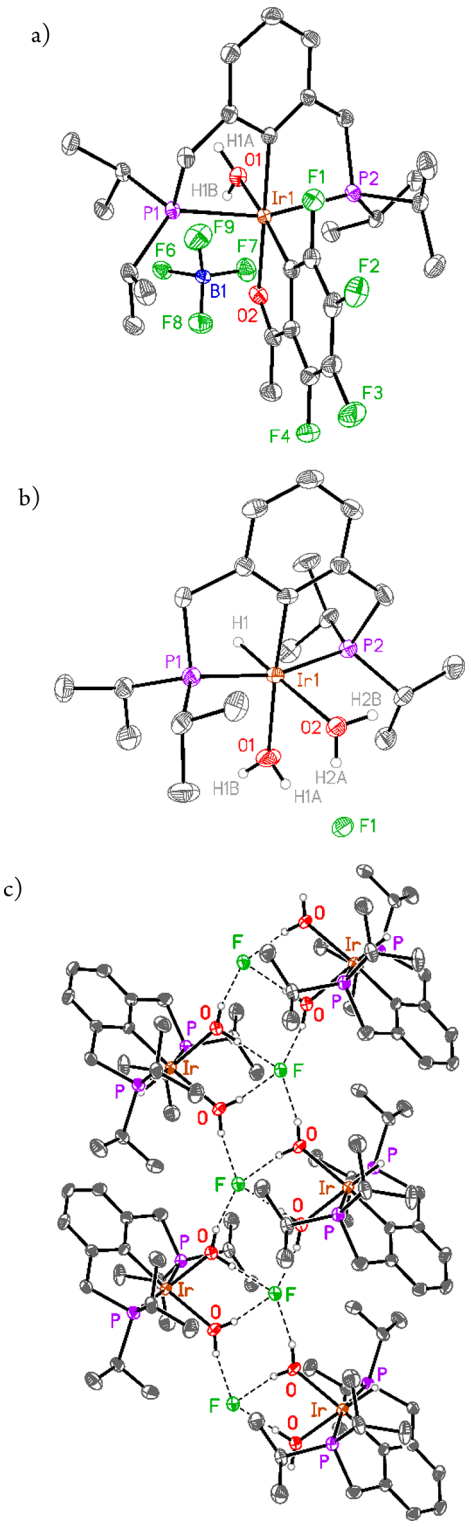

Figure 4. Molecular structures determined by X-ray crystallography of (a) [^{iPr}PCPIr(κ-O,C-$OC_8H_3F_4$)H_2O]BF_4 ($\mathbf{II}_{H2O}$), (b) [^{iPr}PCPIr-(H_2O)$_2$H]F (**VI**), and (c) extended lattice of **VI** showing hydrogen bonding of free fluoride anions to iridium aquo ligands.

of ^{iPr}PCPIrH_4 and 3 equiv of AP-F_5 which had progressed to 34% **II** was treated with 593 equiv of degassed deionized water, no effect on the concentration of **II** was observed by ^{31}P NMR spectroscopy after 24 h at room temperature. Admittedly, though used in greater excess, the effective concentration of water in this experiment is likely much lower than that used by Bergman due to the extremely poor solubility of water in mesitylene. However, during this period, repeated sonication was conducted to form a water−mesitylene emulsion and the sample was mixed by spinning in between sonications to facilitate contact of the reagents with water. Given the >50 °C higher temperature and 10-fold greater excess of water, it would seem that **II** is much less susceptible to water assisted fluoride dissociation than the complexes studied by Bergman. That said, when heated at 150 °C, peaks at δ 49.3 and 47.6 in the ^{31}P NMR spectrum, seen earlier as minor impurities, quickly (20 min) became the major species in solution. These new products each displayed hydride signals as triplets at δ −26.7 and −27.2 in the ^{1}H NMR spectrum, indicating possible O−H addition products with water. Formation of **III** was apparently inhibited under these conditions. After 5.5 h at 150 °C, **III** only represented about 19% of total products, and **II** was still readily detectable, whereas **II** was absent after only 1 h at 150 °C in "dry" toluene, though that sample was not held for a prolonged period at room temperature before heating. Full conversion to **V** (**III** not detectable) required approximately 9 days as the water generated products at δ 49.3 and 47.6 were slowly consumed as monitored by ^{31}P NMR spectroscopy.

When ^{iPr}PCPIrH_4 is reacted with AP-F_5 in C_6H_6 saturated with H_2O at room temperature, no evidence of **II** is observed by ^{31}P and ^{19}F NMR spectroscopy, even after 10 days. Instead, the same products seen after H_2O addition in the mesitylene experiments above at δ 49.3 and 47.7 are observed by ^{31}P NMR spectroscopy, representing ca. 70% of total species. Heating at 120 °C effects formation of **III** and subsequently **V**, albeit slower than at 150 °C in mesitylene with excess water (**V** ca. 43% of combined concentration **III** and **V** after 7 days for H_2O saturated C_6H_6).

When C_6H_6 saturated with D_2O was used, the formation of **III** and **V** was even slower. After 9 days, **V** represented only 45% of the combined concentration of **III** and **V**. This positive isotope effect indicates that water is activated by O−H/D cleavage when present in excess, and that conversion of these species to **III** is rate determining under the specific conditions. The hydride signal of **V** was readily found in the reaction conducted in D_2O saturated C_6H_6, though somewhat poorly resolved, demonstrating that this hydride does not necessarily originate from traces of water, but also does not rule out that water may act as a hydride source when present. It is worth noting that, when excess water is used, extensive etching of the NMR tube is observed, suggesting increased formation/activity of HF. Jensen and co-worker have reported the formation of ^{tBu}PCPIrH(OH) by addition of water to ^{tBu}PCPIrH_4 activated with excess TBE.[34] Replicating this procedure with ^{iPr}PCPIrH_4 generated an apparently highly fluxional species with a broad resonance in the ^{31}P NMR spectrum (ca. 324 Hz) at δ 49.1, and an associated broad hydride signal at δ −28.4 by ^{1}H NMR spectroscopy. Though not as well-defined as ^{tBu}PCPIrH(OH), this seemed consistent with formation of ^{iPr}PCPIrH(OH). Addition of AP-F_5 (1.5 equiv) to this species in toluene gave rise to the same products at δ 49.3 and 47.7 (SI section 1.1) seen in the ^{31}P NMR spectra of the benzene and mesitylene experiments above. The only other species present was a singlet at δ 46.6 (~20%).

We next employed ^{iPr}PCPIr(TBE)[35] as a precursor to ^{iPr}PCPIr in reactions with fluorinated aryl ketones, which presumably avoids the formation of free alcohols and iridium O−H addition products. We hypothesized that, under these conditions, exclusive formation of **II** might occur via direct C−

DOI: 10.1021/acs.organomet.7b00466
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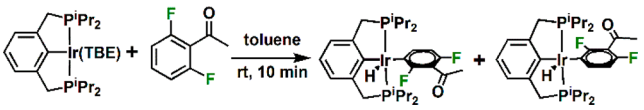
F oxidative addition to the 14 electron ^{iPr}PCPIr fragment. Though quantitative formation was not realized, within 10 min after combining ^{iPr}PCPIr(TBE) and AP-F_5 in toluene, **II** represented 54% of products as determined by ^{31}P NMR spectroscopy (^{iPr}PCPIrH_4 + AP-F_5 gave only 45% **II** after ≥14 h). After 3 h mixing at room temperature, the relative concentration of **II** had increased to 63%. Similarly, under analogous conditions using BP-F_{10}, a doublet was observed at δ 40.4 (~46%) in the ^{31}P NMR spectrum, with an associated ^{19}F NMR resonance, resolved as a triplet, at δ −359.6. Both peaks had coupling constants of 29.7 Hz, and this species was designated as $\mathbf{II}_{BF10}$.

The reactivity of AP-F_2 with ^{iPr}PCPIr(TBE) was somewhat divergent. After mixing reagents, the main product (>76%) seen by ^{31}P NMR spectroscopy was a singlet at δ 59.2, the same as that observed after addition of AP-F_2 to ^{iPr}PCPIrH_4, though a small doublet at δ 37.7 (~5%) was noted. Again, no hydride resonance was detected by NMR spectroscopy which appeared to account for this product, nor was an Ir−F resonance observed. However, low temperature ^{1}H NMR experiments (flame-sealed NMR tube, 500 MHz, other experiments 400 MHz) revealed that a partially resolved quartet observed at δ −12.3 at room temperature devolved into an undefined broad signal at 0 °C. At −20 °C, this signal decoalesced into two separate resonances at δ −12.1 and −12.7, which sharpened upon further cooling to −40 °C, though no distinct multiplicity was found. This behavior is consistent with the formation of a C−H activation product *ortho* to the C−F bond of AP-F_2 which resolves as two rotamers at low temperature (Scheme 3, Figure S-15), and may present as a quartet due to coincidentally equal ^{31}P and long-range ^{19}F coupling constants. Warming to room temperature gave an identical spectrum to that before cooling. Thermodynamic selectivity for oxidative addition of C−H bonds *ortho* to C−F bonds in fluoroarenes with cyclopentadienyl Rh complexes has been known for quite some time,[36] and has been found to be generally applicable to a range of transition metal-ligand systems.[12,37−39]

Scheme 3. Proposed Formation of C−H Activation Rotamers by the Reaction of ^{iPr}PCPIr(TBE) and AP-F_2 in Toluene



After mixing the reaction of ^{iPr}PCPIr(TBE) and AP-F_2 for 18 h at room temperature, the ^{31}P NMR doublet at δ 37.7 had grown to 58% of total products and the singlet at δ 59.2 was nearly undetectable. Inspection of the ^{19}F NMR spectrum revealed a virtual triplet at δ −358.5, consistent with products **II** and $\mathbf{II}_{BF10}$ as well as the results from the overnight room temperature reaction of ^{iPr}PCPIrH_4 and AP-F_2. Thus, this species was assigned as iridium fluoride $\mathbf{II}_{AF2}$. The characteristic ^{31}P and ^{19}F NMR resonances of products **II**, $\mathbf{II}_{AF2}$, and $\mathbf{II}_{BF10}$ are shown in Figure 5.

With more concentrated solutions of C−F oxidative addition products in hand, we again attempted crystallization. Though **II** and $\mathbf{II}_{BF10}$ did not provide material suitable for X-ray diffraction, a small amount of crystals were obtained from the reaction solution of ^{iPr}PCPIr(TBE) and AP-F_2 by removing volatiles in vacuo, extracting the residue with pentane, filtering, and

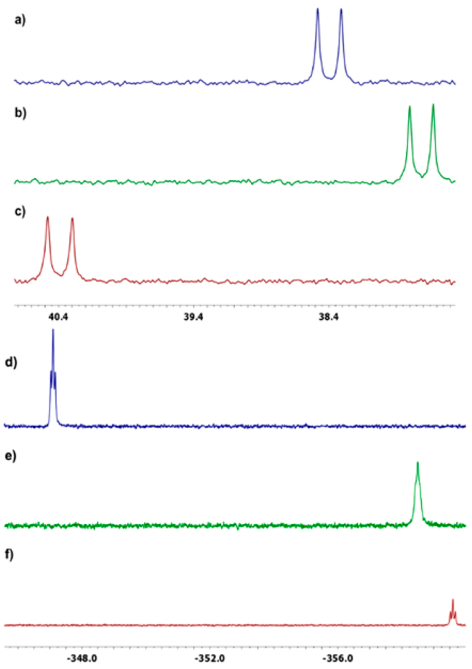


Figure 5. ^{31}P NMR resonances of iridium fluoride products (a) **II**, (b) $\mathbf{II}_{AF2}$, and (c) $\mathbf{II}_{BF10}$ as well as associated ^{19}F NMR Ir−F resonances (d−f).

allowing this solution to slowly evaporate at −10 °C. X-ray diffraction revealed that the expected product of C−F addition ($\mathbf{II}_{AF2}$) was in fact formed (Figure 6), substantiating the

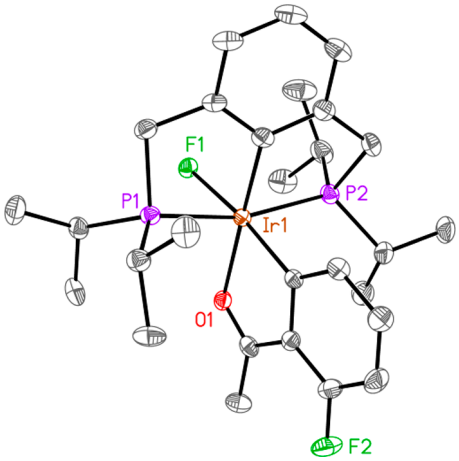


Figure 6. Molecular structure of C−F oxidative addition product ^{iPr}PCPIr(κ-O,C-OC_8H_6F)F ($\mathbf{II}_{AF2}$) determined by X-ray crystallography. The fluoro ligand (F1) is disordered by ~22% chloride substitution.

assignment of products **II** and $\mathbf{II}_{BF10}$ as well. An unusual amount of electron density was found around the fluoro ligand of $\mathbf{II}_{AF2}$ which modeled well as 22% substitution by chloride.

Redissolution of these crystals in toluene revealed the same doublet at δ 37.7 in the ^{31}P NMR spectrum as seen in the reaction solution, as well as a smaller singlet at δ 29.9 in the same ratio as determined between F and Cl in the crystal structure of $\mathbf{II}_{AF2}$. Treatment of a toluene solution concentrated in $\mathbf{II}_{AF2}$ with excess LiCl and stirring overnight led to the complete disappearance of $\mathbf{II}_{AF2}$ with an accompanying increase of the singlet at δ 29.9 ($\mathbf{II}_{AF2Cl}$), strongly supporting the X-ray

DOI: 10.1021/acs.organomet.7b00466
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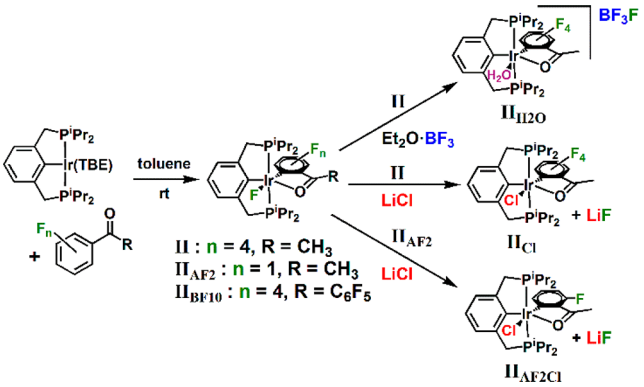
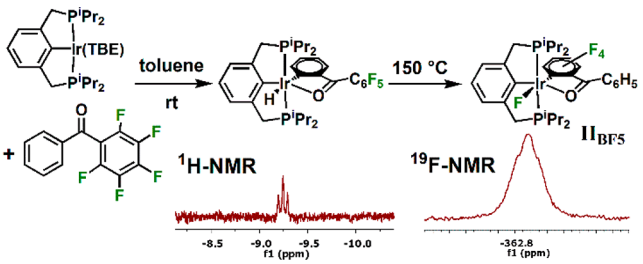
diffraction results. In conjunction, when a toluene solution of >50% **II** was treated in the same manner, consumption of **II** was observed with concomitant increase of a singlet at δ 30.2 ($\mathbf{II}_{Cl}$) in the ^{31}P NMR spectrum, which had been seen as an impurity in nearly all other reactions with AP-F_5. The source of chloride in these reactions likely stems from the use of $LiEt_3BH$ in the preparation of ^{iPr}PCPIrH$_4$ from ^{iPr}PCPIrHCl,[40] which could be expected to leave behind some amount of LiCl. In further support of the assignment of these iridium fluorides, when 11.5 mg of ^{iPr}PCPIr(TBE) was reacted with 1 equiv of AP-F_5 in toluene, generating **II** and subsequently treated with 1 equiv of $Et_2O{\cdot}BF_3$, complete disappearance of **II** and formation of a product at δ 41.8 (s) in the ^{31}P NMR spectrum occurred in 70% yield after 10 min, which increased to 77% after overnight mixing at room temperature. Filtration of this solution to remove a small amount of colorless solid and then storing at room temperature overnight in a sealed vial *not* dried by flame or oven led to the formation of ≤2.5 mg of pale orange crystals. These crystals were found to be spectroscopically (in THF-d_8) and crystallographically identical to $\mathbf{II}_{H2O}$. On the basis of these results, it is apparent that the first definitively observed, and in one case isolated, examples of C(sp^2)−F oxidative addition products of iridium have been demonstrated (Scheme 4).

Scheme 4. Formation of C−F Oxidative Addition Products II, $\mathbf{II}_{AF2}$, and $\mathbf{II}_{BF10}$ from the Reaction of ^{iPr}PCPIr(TBE)[37] and the Corresponding Fluorinated Aryl Ketones. Subsequent Reactivity of II and $\mathbf{II}_{AF2}$ with Fluoride Abstraction Reagents $Et_2O{\cdot}BF_3$ and LiCl Also Shown



Given the results with AP-F_2, we were also interested to determine the kinetic/thermodynamic preference for C−H versus C−F oxidative addition to ^{iPr}PCPIr. In this effort, an intramolecular competition experiment was conducted by the reaction of ^{iPr}PCPIr(TBE) with 3 equiv of 2,3,4,5,6-pentafluorobenzophenone (BP-F_5) in toluene. Within 10−20 min after combining reactants, ^{31}P NMR spectroscopy showed the major product to be a singlet at δ 46.4 (>50%), and the ^{1}H NMR spectrum exhibited a hydride triplet at δ −9.25. These chemical shifts are very similar to our previous results with benzophenone,[23] suggesting the product is the *trans* C−H activation product ^{iPr}PCPIr(κ-O,C-OC(C_6H_4)(C_6F_5))H (Scheme 5). In further corroboration, 3 new signals were observed by ^{19}F NMR spectroscopy consistent with an unaffected C_6F_5 moiety, though the *para*-F was largely obscured by excess BP-F_5. A small doublet (~12% total products) was observed as well at δ 39.2 in the ^{31}P NMR spectrum. Mixing for 24 h at room temperature resulted in only a slight difference in product ratios, with the ^{31}P NMR doublet only increasing to

Scheme 5. Intramolecular C−H vs C−F Oxidative Addition Experiment between ^{iPr}PCPIr(TBE) and BP-F_5 Showing Kinetically Preferred C−H Activation at Room Temperature with a Thermodynamic Preference for C−F Activation When Heated at 150 °C To Form $\mathbf{II}_{BF5}$



~16% of total products. Prolonged mixing at room temperature (5 days) did not affect product ratios further. However, if the sample was instead heated at 150 °C for 15 min, ^{31}P NMR spectroscopy showed the doublet at δ 39.2 to be the major species (~48%) and an associated virtual triplet was located in the ^{19}F NMR spectrum at δ −363 as well as 4 equal peaks with chemical shifts very similar to **II**. Thus, these resonances were attributed to the C−F activation product ^{iPr}PCPIr(κ-O,C-OC(C_6H_5)(C_6F_4))F ($\mathbf{II}_{BF5}$, Scheme 5, SI Table S-1). These findings are in line with calculations[41,42] that indicate C−H addition to Ir(I) is kinetically preferred over C−F addition, though the products of C−F addition are significantly more downhill thermodynamically, mainly due to repulsive interactions in the transition state for C−F addition and directionality of the fluorine orbitals involved in bond formation in comparison to the simple spherical s-type orbitals of hydrogen. Prolonged heating at 150 °C led to an iridium hydride species analogous to the other substrates employed ($\mathbf{V}_{BF5}$, SI section 1.1).

While some difference in initial reactivity is noted between substrates, all seem to progress to a *trans* C−F oxidative addition product when reacted with ^{iPr}PCPIr(TBE), ultimately forming *cis* C−H iridium hydrides given sufficient thermal impetus. The origin of the hydride in these products is the subject of much curiosity. As shown above, although water may play some role in this process, it is certainly not the exclusive source of hydrogen atoms as evidenced by the formation of **III** and **V** in D_2O saturated benzene. The hydride does not exclusively originate from the substrate either, as evidenced by the formation of $\mathbf{V}_{BF10}$. Attempts to remove potential sources of hydrogen atoms and prevent the formation of **III** or **V** were all unsuccessful. For example, using an oven-dried Teflon NMR tube liner only prolonged the overall reaction time slightly, and did not prevent formation of **III** or **V** during the reaction of ^{iPr}PCPIrH$_4$ and AP-F_5 in toluene at 150 °C. HF was not observed in the downfield region of the ^{1}H NMR spectrum. Likewise, conducting this reaction in C_6D_6, or employing ^{iPr}PCPIrD$_4$,[43] also did not prevent formation of **III** or **V**. When ^{iPr}PCPIr(TBE), or ^{iPr}PCPIr(CH_2CH_2),[44] is used as a precursor to ^{iPr}PCPIr, the overall reaction time is lengthened (by 1−3 days depending on conditions) and, importantly, the ^{31}P NMR resonance of **II** is observed to slowly dissipate over the course of formation of **III** and isomerization to **V**, whereas heating a toluene solution of mainly **I** at 150 °C rapidly generates **III** without observation of **II**. In conjunction, when a solution concentrated in **II**, formed from ^{iPr}PCPIrH$_4$ and AP-F_5 at room temperature, is heated at 150 °C for 1 h, complete

DOI: 10.1021/acs.organomet.7b00466
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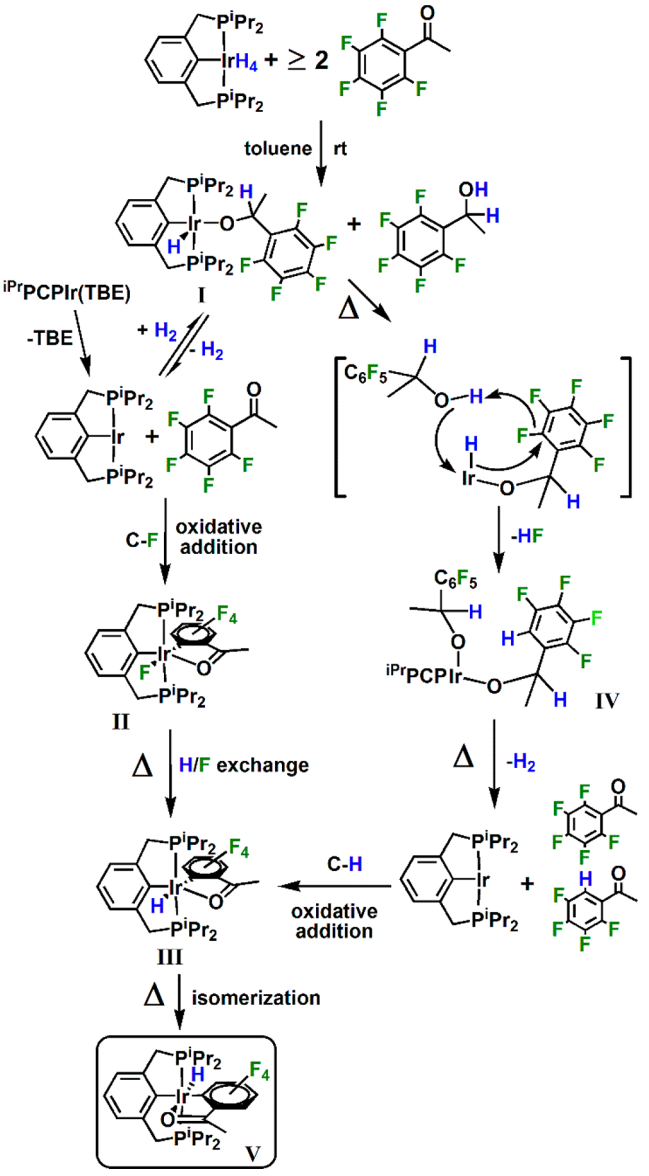
disappearance of **II** is seen with **III** becoming the major product (~64%) and **V** representing the majority of other species in solution (~26%). These results indicate that formation of **III** is accelerated by 1-(pentafluorophenyl)-ethanol, though clearly it is not necessary. As a final effort, rigorous measures were taken to ensure that all sources of O−H and easily activated C−H bonds were as low as possible. ^{iPr}PCPIr(CH_2CH_2) was used as Ir(I) precursor, and AP-F_5 was stored for 3 days over 3 Å molecular sieves activated by heating for 12 h at 230 °C under high vacuum. The solvent used was *para*-xylene-d_{10} distilled from a purple solution containing Na and benzophenone, and passed through a column of freshly activated alumina before use. These materials were combined in an oven-dried Teflon NMR-tube liner within a flame-dried J-Young NMR tube. These efforts did not prevent the formation of **V**, but after 11 days at 150 °C, **II** was still detectable by ^{31}P NMR spectroscopy in a 1-to-10 ratio with **V**. Under these conditions, **III** was never observed to be the major species in solution, and after 80 h of reaction, **III** was no longer detectable. For the remainder of the reaction, the concentration of **II** slowly decreased as **V** increased. This may be explained by the rate of isomerization of **III** to **V** outpacing the formation of **III** from **II** as the hydride source is depleted. Evidently, **II** is able to scavenge even the slightest traces of hydrogen containing compounds in order to form the, apparently, thermodynamically preferred products **III** and **V**. Though the nature of the F−H exchange process is not entirely clear, based on these observations, we can propose a mechanism for the transformation of ^{iPr}PCPIrH_4 or ^{iPr}PCPIr into products **II**, **III**, and **V** when reacted with AP-F_5 (Scheme 6).

As can be seen in Scheme 6, and described earlier, addition of ≥2 equiv of AP-F_5 to ^{iPr}PCPIrH_4 leads to formation of **I** and an equivalent of 1-(pentafluorophenyl)ethanol. When left to react at room temperature overnight, **II** becomes the major species in solution, possibly due to **I** existing in equilibrium with free ^{iPr}PCPIr and AP-F_5. If instead this mixture is heated at 150 °C shortly after mixing reactants, the rapid formation of **III** as a major product is observed. This is believed to proceed through (bis)alkoxide intermediate **IV** via the concerted metalation deprotonation reaction shown. Similar reactivity has been reported by Hughes and Rheingold in the defluoroprotonation or methylation of CF_2R_F moieties (where R_F = perfluoroalkyl) bound to Cp*Ir(PMe_3)H or Cp*Ir(PMe_3)CH_3, respectively.[45,46] Once formed, **IV** can undergo double *β*-hydride elimination, and release of H_2, to give free ^{iPr}PCPIr, AP-F_5, and 2,3,4,5-tetrafluoroacetophenone. Preferential C−H oxidative addition of 2,3,4,5-tetrafluoroacetophenone would then lead to **III**. This route would help to explain the fact that the 1-(pentafluorophenyl)ethanol initially generated upon reaction of ^{iPr}PCPIrH_4 and AP-F_5 is seen to dissipate over the course of the reaction, leaving only AP-F_5, iridium based products, and a small amount of unknown side products at the end of the reaction as observed by ^{19}F NMR spectroscopy. When **II**, formed from ^{iPr}PCPIrH_4 and ≥2 equiv of AP-F_5 at room temperature (i.e., in the presence of 1-(pentafluorophenyl)-ethanol), is heated at 150 °C, the rapid disappearance of **II** and formation of **III** is also noted, presumably by a similar pathway. However, when **II** is generated by the reaction of ^{iPr}PCPIr precursors ^{iPr}PCPIr(TBE) or ^{iPr}PCPIr(CH_2CH_2) and AP-F_5, longer reaction times are noted as well as the persistence of **II** for most, or all, of the reaction progress in forming **V**. This supports the assistance of excess 1-(pentafluorophenyl)ethanol

Scheme 6. Proposed Mechanism for the Formation of Products II, III, and V Starting from Either ^{iPr}PCPIrH_4 or ^{iPr}PCPIr(TBE) and AP-F_5 Showing the Variation of Mechanism Based on the Presence or Absence of Initial Heating



in formation of **III** from **I** or **II**. The even longer reaction times noted under extremely dry conditions in Teflon lined NMR tubes indicates that other O-H sources such as water or Si-OH functionalities of glass may play a role as well. In any case, once **III** is formed, both routes follow the same course of isomerization to **V**, consistent with our previous findings with benzophenone.[23]

CONCLUSIONS

The reactions of ^{iPr}PCPIrH_4, ^{iPr}PCPIr(TBE), and ^{iPr}PCPIr-(CH_2CH_2) with fluorinated aryl-ketones to form cyclometalated *cis* C−H addition products by monodefluorination have been demonstrated. Depending on the conditions, the reaction proceeds via *ortho* C−F oxidative addition, followed by H/F exchange and isomerization, or by a proposed concerted metalation deprotonation mechanism, which ultimately leads to

DOI: 10.1021/acs.organomet.7b00466
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the same products by selective C−H activation. The C−F oxidative addition products have been characterized by NMR spectroscopy, and the first crystal structure of an iridium-fluoride formed by C(sp^2)−F oxidative addition is reported. Fluoride loss from C−F oxidative addition products is believed to be assisted by the presence of O-H groups from, possibly, water or hydrated glass, but in particular fluorinated aryl alcohols formed by the initial reaction of ^{iPr}PCPIrH$_4$ with fluorinated aryl ketones. The extension of this reactivity to catalytic defluorofunctionalization is currently under investigation in our lab.

EXPERIMENTAL SECTION

General. All manipulations were carried out under an argon atmosphere either in a Vacuum Atmospheres glovebox or by modified Schlenk techniques. All NMR spectra were collected on a Bruker AMX 400 MHz spectrometer, except for low temperature experiments which were conducted on a Bruker AMX 500 MHz spectrometer. All ^{31}P NMR spectra were referenced to external H_3PO_4. For quantitative ^{31}P NMR spectra, an inverse-gated decoupling sequence was used in conjunction with a relaxation delay of 4 s. Proton NMR spectra were referenced to residual deuterated solvent signal. External trifluoroacetic acid was used as reference for ^{19}F NMR spectra. All aromatic solvents were dried over sodium/benzophenone, distilled from the resultant purple solution prior to use, and stored over 3 Å molecular sieves. All other reagents were used as received from commercial sources without further purification unless noted. X-ray structure collection was conducted on a Bruker SMART APEX II CCD platform diffractometer. The ^{iPr}PCPH ligand and ^{iPr}PCPIrH$_4$ complex were synthesized by literature methods,[42,47] or slight variations thereof.

General Procedure for Reactions of ^{iPr}PCPIrH$_4$ and Fluorinated Aryl Ketones. To a J-Young NMR tube, 5−15 mg (9.4−28.1 μmol) of ^{iPr}PCPIrH$_4$ was added, followed by 0.5 mL of toluene or benzene, and 2−3 equiv of the appropriate aryl ketone was then added. The sealed tube was then mixed at room temperature in a rotary spinning device, or heated in an aluminum block at 120−150 °C for varying periods of time. Reaction progress was monitored by ^{31}P, ^{1}H, and ^{19}F NMR spectroscopy. In the case of **V**, crystals were obtained by removing volatiles in vacuo, extracting the residue with pentane, and storing at −17 °C. Best yields (85−90%) were obtained when this solution was allowed to slowly evaporate. The product was found to cocrystallize with pentane. For **V**: ^{31}P{^{1}H} NMR (C_6D_6): δ 46.88 (s). ^{1}H NMR (C_6D_6): δ 7.21 (overlapping d and t, partially obscured by solvent, 3H, *meta* and *para* PCP), 3.14 (app qvt, J_{HH} = 16 Hz, J_{PH} = 4 Hz, 4H, CH_2-PCP), 2.50 (d, J_{FH} = 5.2 Hz, 3H, CH_3-ketone), 1.58 (m, 4H, CH-PCP), 0.90 (m, overlaps with pentane, 12H, iPr-PCP), 0.57 (app q, J = 6.8, 6H, iPr-PCP), 0.49 (app q, J = 6.8, 6H, iPr-PCP), −24.5 (td, J_{PH} = 15.4 Hz, J_{FH} = 8.8 Hz, 1H, Ir-H). ^{19}F NMR (C_6D_6): −105.5 (overlapping ddd, J_{HF} = 8.7 Hz, 1F, *ortho* to Ir-C), −133.1 (tvt, J_{FF} = 20.7 Hz, 1F), −147.4 (app ddd, 1F), −165.3 (t, J_{FF} = 21.1 Hz, 1F). Anal. Calcd: **V** + 0.5 pentane; C = 48.34%, H = 5.98%. Found: C = 48.07%, H = 5.81%.

Preparation of ^{iPr}PCPIr(TBE) and ^{iPr}PCPIr(CH_2CH_2). The desired amount of ^{iPr}PCPIrH$_4$ was added to a J-Young NMR tube, followed by ∼0.3 mL of toluene. For the TBE adduct, 4−6 equiv of *tert*-butylethylene was then added and the contents mixed, upon which the solution took on a deep red color. All volatiles were then removed under high vacuum, leaving behind a red residue of ^{iPr}PCPIr(TBE) which was then employed as usual. For the ethylene complex, a toluene solution of ^{iPr}PCPIrH$_4$ in a J-Young NMR tube was degassed by 3 freeze−pump−thaw cycles and exposed to 1 atm ethylene. The solution was then heated at 60 °C for several minutes, after which the color had changed to brown. NMR spectroscopy was consistent with previous reports,[48] and the volatiles were then removed under high vacuum and the residue employed as usual.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00466.

Supplementary data including selected ^{1}H, ^{19}F, and ^{31}P NMR spectra (PDF)

Accession Codes

CCDC 1556151−1556154 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jones@chem.rochester.edu.

ORCID

William W. Brennessel: 0000-0001-5461-1825

William D. Jones: 0000-0003-1932-0963

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the NSF under the CCI Center for Enabling New Technology through Catalysis (CENTC), CHE-1205189.

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DOI: 10.1021/acs.organomet.7b00466
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