Organometallics **2008,** *27,* 67–71

Synthesis of the Electron-Poor Dicationic Arene Complex [Cp*Ir(η^6-*p*-bis(difluoromethyl)benzene)][BF_4]$_2$ and Ring Attack by Hydroxide in Attempted Deprotonation: Synthesis, Structures, and C−H···F Hydrogen Bonding

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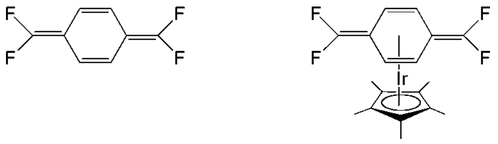
Received July 27, 2007

Treatment of *p*-bis(difluoromethyl)benzene, *p*-CF_2H-C_6H_4-CF_2H, with [Cp*Ir(acetone)$_3$][OTf]$_2$ (prepared in situ) along with $BF_3 \cdot 2H_2O$ provided the target compound [Cp*Ir(η^6-*p*-CF_2H-C_6H_4-CF_2H)][BF_4]$_2$ (**3**) in good yield, which was fully characterized, and its X-ray molecular structure was determined. Interestingly the usual π-complexation procedure in the absence of $BF_3 \cdot 2H_2O$ did not lead to complex **3**; instead, the hydroxypentadienyl complex [Cp*Ir(η^5-$CH_2C(Me)CHC(OH)CH_2$)][OTf] (**2**) was formed. The latter was also identified by X-ray analysis. Reaction of **3** with a base such as LiOH or Ag_2CO_3 did not yield the neutral tetrafluoro-*p*-xylylene complex [Cp*Ir(η^4-*p*-CF_2-C_6H_4-CF_2)] (**4**), in which the reactive intermediate tetrafluoro-*p*-xylylene (**1**) would be stabilized by Cp*Ir coordination. Instead the dinuclear iridium complex [{Cp*Ir(η^5-*p*-CF_2H-C_6H_4-CF_2H)}$_2$O][BF_4]$_2$ (**5**) was obtained. Complex **5**, with two η^5-cyclohexadienyl moieties bridged by an oxygen atom, is the net result of water or hydroxide attacking two molecules of the arene complex **3**. A mechanism for this transformation is discussed.

Introduction

(Pentamethylcyclopentadienyl)iridium (Cp*Ir) is a very stabilizing entity, and its coordination chemistry toward arenes has been the focus of intense investigation, thus providing thermodynamically stable π-complexes of the type [Cp*Ir(η^6-arene)]-[BF_4]$_2$.[1–5] Recent studies in our laboratory have shown the capacity of this metal to stabilize reactive intermediates such as *o*-quinone methides,[2,3a] *o*-dithiobenzoquinone,[6] and *p*-dithiobenzoquinone[7] where these reactive quinone derivatives are η^4-π-bonded to the iridium metal center following the general formula [Cp*Ir(η^4-intermediate)]. Interestingly the metal-stabilized quinone methides showed unusual reactivity compared to that of the free *o*-quinone methide intermediates. On the other hand, the metalated dithiobenzoquinone showed such high stability relative to the parent molecules that they could be used as organometallic linkers to construct supramolecular coordination assemblies.



(1) **(4)**

Figure 1

Tetrafluoro-*p*-xylylene (**1**) is a highly reactive molecule and has been generated by flash vacuum pyrolysis of octafluoro[2,2] paracyclophane and subsequent trapping of the products in solid argon at 9 K.[8–11] Thus molecule **1** cannot be isolated or

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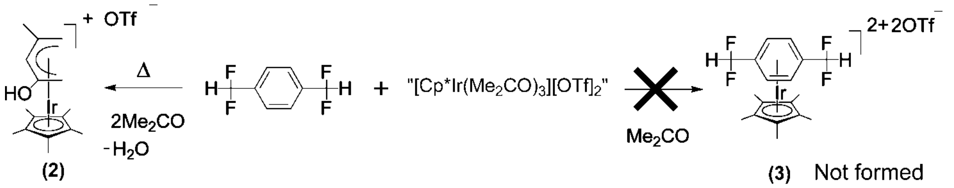
Scheme 1



identified by spectroscopic methods at room temperature. To overcome this difficulty, we envisaged stabilization of **1** by a Cp*Ir moiety, as in tetrafluoro-*p*-xylylene complex [Cp*Ir(η^4-*p*-CF_2-C_6H_4-CF_2)] (**4**) (Figure 1).

Our synthetic approach started by preparation of the organometallic precursor *p*-bis(difluoromethyl)benzene complex [Cp*Ir(η^6-*p*-CF_2H-C_6H_4-CF_2H)][BF_4]$_2$ (**3**). Subsequent deprotonation of the two acidic protons of the difluoromethyl moieties attached to the 1,4-positions of the arene ring would provide the target complex with tetrafluoro-*p*-xylylene coordinated to the Cp*Ir moiety (Figure 1). In this work we report a novel synthetic procedure for the complexation of electron-poor arenes. To this end, the synthesis and X-ray molecular structure of [Cp*Ir(η^6-*p*-CF_2H-C_6H_4-CF_2H)][BF_4]$_2$ (**3**) was successfully achieved. Interestingly the usual complexation procedure did not lead to the target complex **3**; instead, the hydroxypentadienyl complex [Cp*Ir(η^5-$CH_2C(Me)CHC(OH)CH_2$)][OTf] (**2**) was formed. The latter was fully characterized by spectroscopic data, and its structure was confirmed by X-ray analysis.

Treatment of **3** by a base such as Ag_2CO_3 or LiOH in THF did not lead to the formation of the target complex [Cp*Ir(η^4-*p*-CF_2-C_6H_4-CF_2)] (**4**), but unexpectedly the dinuclear compound [ηCp*Ir(η^5-*p*-CF_2H-C_6H_4-CF_2H)η_2O][BF_4]$_2$ (**5**) was obtained, where an oxygen atom is inserted between two metalated arene monomers. A mechanism describing the formation of **5** and its X-ray molecular structure are reported.

Results and Discussions

Synthesis, Characterization, and X-ray Molecular Structures of Hydroxypentadienyl Complexes [Cp*Ir(η^5-$CH_2C(Me)CHC(OH)CH_2$)][OTf] (2) and [Cp*Ir(η^6-*p*-CF_2H-C_6H_4-CF_2H)][BF_4]$_2$ (3). The outstanding π-complexing ability of the Cp*Ir moiety allows an efficient direct method to prepare highly electron-deficient arene π-complexes featuring halogenated and fluorinated arenes. Thus, we were surprised to find that the reaction of *p*-bis(difluoromethyl)benzene, *p*-CF_2H-C_6H_4-CF_2H, with [Cp*Ir(acetone)$_3$][OTf]$_2$[12,13] prepared in situ in acetone did not lead to the π-complexation of the electron-poor arene ligand. Repeating the previous experiment but under reflux in acetone for several hours produced a deep brown solution. Reaction workup allowed us to isolate a yellow-brownish complex in 76% yield. The ^1H NMR spectrum of the latter was recorded in CD_2Cl_2 and showed the presence of a singlet at δ 2.03 ppm attributed to the Cp*Ir protons, along with four doublets visible at δ 1.32, 1.56, 3.18, and 3.65 ppm and a singlet at 6.53 ppm attributed to the dienyl C-H protons. Moreover a singlet was also observed at 2.18 ppm attributed to a $-CH_3$ group and a broad singlet at δ 9.21 ppm attributed to the $-OH$ group. It is noteworthy that this complex was also obtained upon attempting to place the Cp*Ir^{2+} moiety on other electron-poor arenes such as 1,2- and 1,4-dichloroarene ligands[6,7] (Scheme 1).

To ascertain the structure of compound **2**, an X-ray study was performed on suitable crystals. The structure shows the formation of a hydroxypentadienyl iridium complex obtained as a triflate salt, [Cp*Ir(η^5-$CH_2C(Me)CHC(OH)CH_2$)][OTf] (**2**) (Figure 2). Complex **2** crystallizes in the monoclinic unit cell space group $P2_1/n$. A view of the molecule with selected bond distances and angles is shown in Figure 2. The structure shows indeed that the Cp*Ir is coordinated to five carbons of an open pentadienyl ligand bearing a hydroxyl and a methyl group at the 2- and 4-positions. Such a compound was previously observed by Maitlis and co-workers upon refluxing of an acetone solution of the tris-solvated species [Cp*Ir(acetone)$_3$][PF_6]$_2$.[14,15] In their paper the authors suggested that the hydrolysis of the hexafluorophosphate anion gives the dimer [(Cp*Ir)$_2$(μ-η^2-OPF_2O)$_3$][PF_6] and that subsequent reaction with the product formed via aldol condensation of acetone produced the metalated cyclopentadienyl iridium complex. The product was isolated by conversion to [Cp*Ir(η^5-$CH_2C(Me)CHC(OH)CH_2$)][BPh_4]; however no X-ray structure was reported. More recently the synthesis and X-ray structure of half-open rhodocenium and iridocenium with oxodienyl ligands but no X-ray structure of the related hydroxy-iridium complexes was reported.[16] Thus **2** represents the first example of this type stabilized by a Cp*Ir moiety to be characterized structurally.

Interestingly in our work the solvated iridium species is [Cp*Ir(acetone)$_3$][OTf]$_2$, which contains triflate anions that are stable toward hydrolysis, yet the aldol condensation reaction occurs. Acid catalyst for the aldol reaction could come from traces of triflic acid in the AgOTf or from the acidifying effect of Cp*Ir^{2+} complexation on traces of water in the mixture. To overcome this obstacle, we report in this paper an efficient and novel method for the complexation of electron-poor arene rings (vide infra).

As usual, [Cp*Ir(acetone)$_3$][OTf]$_2$ was prepared in acetone, and to it was added *p*-bis(difluoromethyl)benzene, *p*-CF_2H-C_6H_4-CF_2H. Then, solvent was removed under vacuum and the residue treated with excess $BF_3 \cdot 2H_2O$ for 30 min followed by addition of diethyl ether to give a white precipitate. Reaction workup to eliminate the excess of $BF_3 \cdot 2H_2O$ provided the target compound [Cp*Ir(η^6-*p*-CF_2H-C_6H_4-CF_2H)][BF_4]$_2$ (**3**) in 68% yield as a white, microcrystalline powder (Scheme 2). Complex **3** was fully characterized by spectroscopic methods and elemental analysis. The infrared spectrum recorded from KBr discs shows the presence of a large band at 1071 cm^{-} assigned to BF_4 anions. The ^1H NMR spectrum recorded in acetonitrile-d_3 showed the presence of a singlet at δ 2.36 ppm attributed to the methyl protons of the η^5-Cp*Ir moiety, a triplet ($J_{H\text{-}F}$ =

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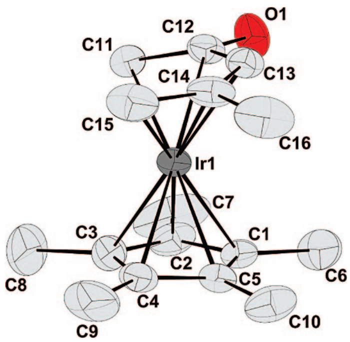
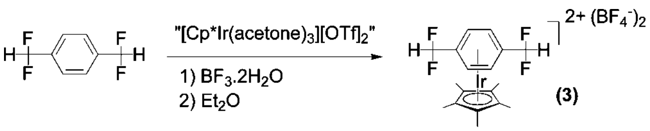


Figure 2. X-ray molecular structure of the cationic part of **2** with atom-numbering system. Selected bond distances (Å) and angles (deg): Ir1−C13 = 2.223(5), Ir1−C14 = 2.182(3), Ir1−C15 = 2.170(1), Ir1−C12 = 2.231(8), Ir1−C11 = 2.189(2), C11−C12 = 1.417(0), C12−C13 = 1.421(4), C13−C14 = 1.445(2), C14−C15 = 1.412(1), C14−C16 = 1.510(4), C12−O1 = 1.350(2), C11−C12−C13 = 123.5(6), C12−C13−C14 = 125.1(7), C13−C14−C15 = 120.9(7), C11−C12−O1 = 121.9(6), C13−C14−C16 = 116.7(8).

Scheme 2



50.6 Hz) to $-CHF_2$ attributed to the difluoromethyl proton at δ 7.09 ppm, and a singlet at δ 7.67 ppm attributed to the arene protons.

To confirm the structure of **3**, suitable crystals for an X-ray structural determination were obtained from CH_3CN/Et_2O by slow evaporation. A view of the cation of compound **3** together with selected bond distances and angles is shown in Figure 3. Complex **3** crystallizes in the orthorhombic $Pna2_1$ space group.

The structure of **3** (Figure 3) was determined and shows that the Cp*Ir moiety is coordinated symmetrically to the fluorinated arene. Interestingly, we note the formation of three types of C−H···F hydrogen bonding: between the free BF_4 anions and (i) two acidic protons of the difluoromethyl moieties attached to the 1,4-positions of the benzene rings, (ii) the arene C-H protons (iii), and the C-H methyl protons of η^5-Cp*Ir moieties. Such noncovalent interaction has been widely employed in supramolecular chemistry and crystal engineering.[17,18]

The reason for the beneficial effect of $BF_3 \cdot 2H_2O$ on the complexation reaction is unclear, but unmistakable: when reactions were conducted in its absence, analysis of the reaction mixtures by ^1H NMR spectroscopy showed peaks for unreacted free arene and a Cp*Ir species, presumably a tris(solvento) complex or a partially aquated form. The appearance of two BF_4 anions in the product suggests that some of the BF_3 reagent must be consumed, but the nature of boron-containing side products was not investigated further. The excess of $BF_3 \cdot 2H_2O$ may serve to trap acetone (as some enol derivative) or its aldol product(s) (cf. formation of **2** in the absence of $BF_3 \cdot 2H_2O$) as borate esters and force complexation to the electron-poor arene as the acetone is consumed.

We then sought the deprotonation of the two acidic protons ($-CHF_2$) in order to obtain the target complex [Cp*Ir(η^4-*p*-CF_2-C_6H_4-CF_2)] (**4**) (Scheme 3).

Thus treatment of **3** with LiOH or Ag_2CO_3 in THF provided a colorless solution. Extraction by acetonitrile and reaction workup provided an off-white microcrystalline material in 70% yield. The use of KO*t*-Bu led to decomposition. The new complex was identified by elemental analysis and IR and NMR spectroscopy as {(Cp*Ir)$_2$(μ-η^5:η^5- *exo*:*exo*-1,1′-(O)-[CF_2H-C_6H_4-CF_2H]$_2$[BF_4]$_2$} (**5**). The ^1H NMR spectrum of **5** recorded in CD_3CN solution showed the presence of a singlet at δ 2.10 ppm, attributed to the methyl protons of the two η^5-Cp*Ir moieties, and two triplets ($J_{H\text{-}F} = 50.6$ Hz) at δ 6.09 and 6.39 ppm assigned to the two different CHF_2 groups. A further four multiplets attributed to the aromatic protons are visible at δ 4.30, 4.85, 5.75, and 6.74 ppm. These data are in accord with the proposed formula where loss of symmetry has occurred relative to the starting material **3**. To ascertain the structure of **5**, an X-ray crystal structural study was performed. Crystals of **5** were obtained by slow crystallization from CH_3CN/ether solution. Complex **5** crystallizes in the orthorhombic $Pna2_1$ space group. The structure of **5** (Figure 4) shows the formation of a binuclear complex in which two Cp*Ir[η^5-(CF_2H-C_6H_4-CF_2H)] units are linked by an oxygen bridge. In each unit the Cp*Ir is coordinated to only five carbon centers of the coordinated arene. The hinge angle is about 38° for the Ir(1) unit and of 41° for the Ir(2) unit. The two $-CF_2H$ moieties in the Ir(2) unit are almost oriented in the same direction, while in the Ir(1) unit, this is not the case. We also note, similar to that observed for complex **3**, the presence of several types of of C−H···F hydrogen bondings: between the two free BF_4 anions and (i) two acidic protons of the difluoromethyl moieties attached to the 1,4 -positions of the benzene rings, (ii) the arene C-H protons, and (iii) and the C-H methyl protons of η^5-Cp*Ir moieties.

The spectroscopic data as well as the X-ray molecular structure of **5** confirm a dimer iridium complex and not the hypothetical [Cp*Ir(η^4-*p*-CF_2-C_6H_4-CF_2)]. The formation of **5** can be explained as a nucleophilic addition to carbon at an *ortho*-position relative to the $-CF_2H$ substituents, rather than a deprotonation of the two $-CF_2H$ groups by a base, as observed with previous Cp*Ir-arene complexes. It seems that this acidic hydrogen center is highly protected by the two fluorine groups, which prevent any approach of a base reagent to undergo a deprotonation reaction, but favors a double nucleophilic attack by a hydroxide ion at the *ortho*-position of the $-CF_2H$ group and leads to the formation of the dinuclear complex {(Cp*Ir)$_2$(μ-η^5:η^5-*exo*:*exo*-1,1′-(O)-[CF_2H-C_6H_4-CF_2H]$_2$[BF_4]$_2$} (**5**) (Scheme 4). It may be also that hydroxide ions are produced from carbonate and water when Ag_2CO_3 was used as a base.

In summary we report a novel method to coordinate electron-poor arene ligands such as *p*-CF_2H-C_6H_4-CF_2H with the Cp*Ir moiety, resulting in a high yield of fluorinated π-arene complex **3**. Reaction of **3** with a base (Ag_2CO_3, LiOH) did not lead to the desired complex [Cp*Ir(η^4-*p*-CF_2-C_6H_4-CF_2)] (**4**), which would be the result from deprotonation of each of the two acidic $-CHF_2$ protons; instead a double *ortho*-nucleophilic addition reaction occurred, yielding the dinuclear iridium complex **5**, an unusual example in the chemistry of metal arene complexes. Other methods will have to be tried in order to prepare the tetrafluoro-*p*-xylylene complex [Cp*Ir(η^4-*p*-CF_2-C_6H_4-CF_2)] (**4**).

Experimental Section

General Considerations. All manipulations were carried out under argon atmosphere using Schlenk tube techniques. Solvents were purified and dried prior to use by conventional distillation techniques. Acetone was distilled over K_2CO_3, diethyl ether and THF were distilled over Na, and CH_3CN was distilled over CaH_2.

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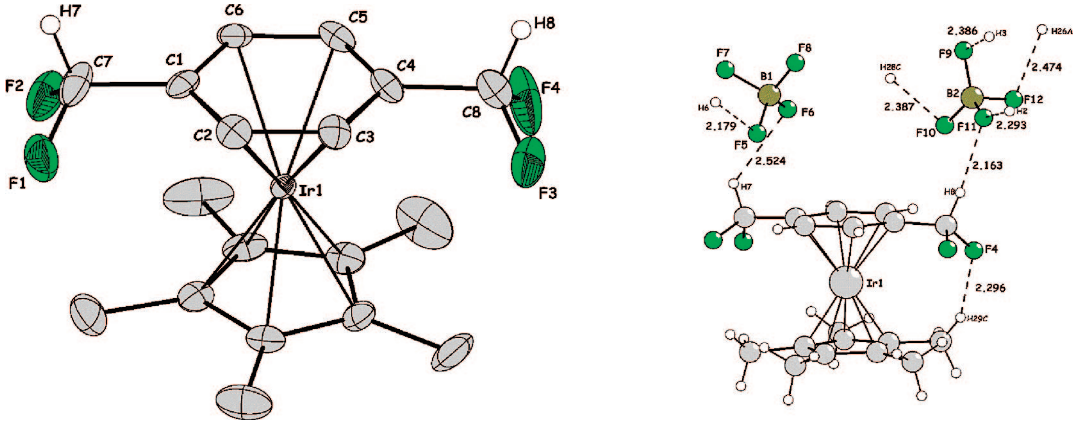
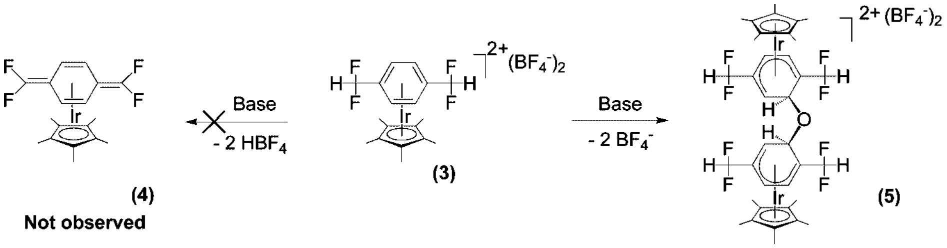


Figure 3. X-ray molecular structure of the cationic part of **3** and the whole complex showing the hydrogen bonding C−H---F with the two free BF_4 anions. Selected bond distances (Å) and angles (deg): Ir1−C1 = 2.248(6), Ir1−C2 = 2.261(6), Ir1−C3 = 2.257(6), Ir1−C4 = 2.261(7), Ir1−C5 = 2.260(7), Ir1−C6 = 2.248(7), C2−C1−C6 = 118.98(56), C3−C4−C5 = 118.93(63), C6−C1−C7 = 119.58(58), C3−C4−C8 = 121.23(68).

Scheme 3



All reagents obtained from commercial sources were used without further purification. IR spectra were recorded from KBr discs on a Biorad FTS 161 or directly from the sample on a Bruker Tensor 27 equipped with a Harricks ATR. NMR spectra were recorded on Bruker AM 300 and 400 MHz instruments.

Synthesis of [Cp*Ir(η^5-CH$_2$C(Me)CHC(OH)CH$_2$)][OTf] (2). A solution of $AgCF_3SO_3$ (260 mg, 1.00 mmol) in acetone (10 mL) was added to [Cp*Ir(μ-Cl)Cl]$_2$ (200 mg, 0.25 mmol) in acetone (10 mL), to give rapidly a white precipitate of AgCl. The reaction mixture was stirred for 10 min. Then the resulting yellow solution of [Cp*Ir(acetone)$_3$][CF$_3$SO$_3$]$_2$ was filtered into a dry Schlenk tube kept under argon containing *p*-bis(difluoromethyl)benzene (0.7 mL, 2.7 mmol), and the mixture was refluxed for 12 h, during which the solution became dark brown. Then the solvent was removed under vacuum and the residue washed with ether and then extracted with CH_2Cl_2 (2 × 15 mL). The solvent was removed to give a yellow-brownish solid material, which was washed with ether and dried under vacuum to give 218 mg (76%).

Spectroscopic data for **2**: IR (KBr disk)/cm^{-1} $\nu(CF_3SO_3)$ 1263, 1033. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.03 (s, 15H, Cp*), 2.18 (s, 3H, Me), 1.32 (d, $^2J_{H\text{-}H} = 4$ Hz, 1H, C-H dienyl), 1.56 (d, $^2J_{H\text{-}H} = 6$ Hz, 1H, C-H dienyl), 3.18 (d, $^2J_{H\text{-}H} = 4$ Hz, 1H, C-H dienyl), 3.65 (d, $^2J_{H\text{-}H} = 6$ Hz, 1H, C-H dienyl), 6.53 (s, 1H, C-H dienyl), 9.28 (br, 1H, O-H). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ 132.88 (s, C-dienyl), 96.59 (s, Cp*, C=C), 96.31 (s, C-dienyl), 85.61 (s, C-dienyl), 43.96 (s, C-dienyl), 35.36 (s, C-dienyl), 22.78 (s, CH_3, dienyl), 8.50 (s, Cp*, CH_3). Anal. Calcd for $C_{17}H_{24}O_4F_3SIr \cdot 2CH_2Cl_2$: C, 29.86; H, 3.70. Found: C, 30.69; H, 3.80.

Synthesis of [Cp*Ir(η^6-*p*-CF$_2$H-C$_6$H$_4$-CF$_2$H)][BF$_4$]$_2$ (3). A solution of $AgCF_3SO_3$ (260 mg, 1.00 mmol) in acetone (10 mL) was added to [Cp*Ir(μ-Cl)Cl]$_2$ (200 mg, 0.25 mmol) in acetone (5 mL), to give rapidly a white precipitate of AgCl. The reaction mixture was stirred for 10 min. Then the resulting yellow solution of [Cp*Ir(acetone)$_3$][CF$_3$SO$_3$]$_2$ was filtered into a dry Schlenk tube kept under argon containing *p*-bis(difluoromethyl)benzene (1.0 mL, 5.4 mmol). Then the solvent was removed under vacuum, and

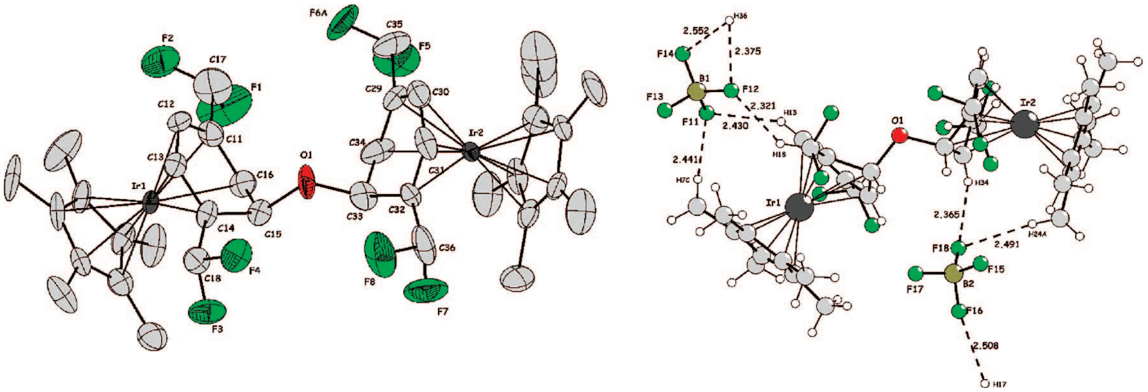
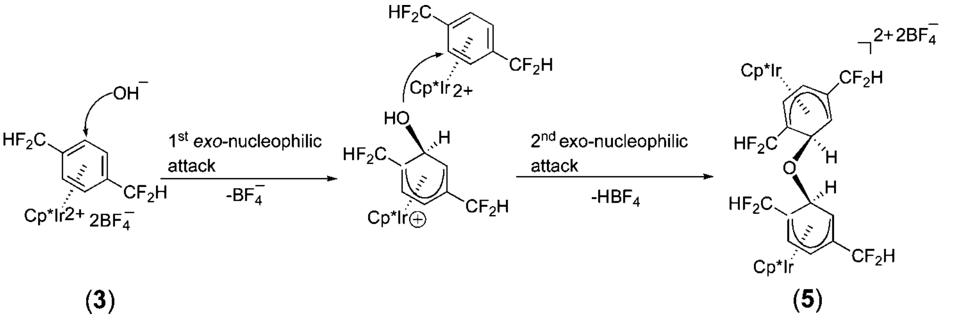


Figure 4. X-ray molecular structure of the cationic part of **5** as well as the whole complex showing the hydrogen bonding C−H---F interactions with the two free BF_4 anions. Selected bond lengths (Å) and angles (deg): Ir1−C11 = 2.185(12), Ir1−C12 = 2.240(11), Ir1−C13 = 2.195(8), Ir1−C14 = 2.199(6), Ir1−C15 = 2.721(10), Ir1−C16 = 2.242(12), C15−O1 = 1.504(13), C33−O1 = 1.496(15), C11−C12−C13 = 117.5(10), C14−C15−C16 = 105.0(8), C15−O1−C33 = 111.74(80).

Scheme 4. Proposed Mechanism to Explain the Formation of 5



$BF_3 \cdot 2H_2O$ (1 mL) was added to the residue. This mixture was allowed to react at room temperature for 30 min. Subsequent addition of Et_2O (50 mL) afforded a white precipitate, which was separated and washed several times with Et_2O and dried under vacuum, leaving **3** (230 mg, 68%). Spectroscopic data for **3**: IR (KBr disk)/cm^{-1} ν(B−F) 1071. ^{1}H NMR (CD_3CN, 400 MHz): δ 2.36 (s, 15H, Cp*), 7.09 (t, $^2J_{H\text{-}F}$ = 50.6 Hz, 2H, CF_2H), 7.67 (s, 4H, aromatic). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_3CN): δ 111.59 (t, $^1J_{F\text{-}C}$ = 246.9 Hz, CF_2H), 110.03 (s, Cp*, C═C), 109.79 (t, $^2J_{F\text{-}C}$ = 24.4 Hz, aromatic, C═C), 96.56 (s, aromatic, C═C), 10.98 (s, Cp*, CH_3). Anal. Calcd for $C_{18}H_{21}B_2F_{12}Ir \cdot 2H_2O$: C, 30.23; H, 3.52. Found: C, 30.00; H, 2.93.

Synthesis of {(Cp*Ir)$_2$(μ-η^5:η^5-*exo*:*exo*-1,1′-(O)-[CF_2H-C_6H_4-CF_2H]$_2$[BF_4]$_2$} (5). Method A. A suspension of **3** (67 mg, 0.10 mmol) in THF (15 mL) was added to a suspension of Ag_2CO_3 (64 mg, 0.20 mmol) in THF (5 mL). The reaction mixture was stirred for 1 h, and the solvent was removed under vacuum. The residue was dissolved in acetonitrile (5 mL) and filtered through Celite, and slow evaporation of diethyl ether into this solution gave off-white crystals of **5** (53 mg, 83%). Spectroscopic data for **5**: IR (KBr disk)/cm^{-1} ν(B−F) 1083. ^{1}H NMR (CD_3CN, 400 MHz): δ 2.36 (s, 15H, Cp*), 7.09 (t, $^2J_{H\text{-}F}$ = 50.6 Hz, 2H, CF_2H), 7.67 (s, 4H, aromatic). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_3CN): δ 114.87 (t, $^1J_{F\text{-}C}$ = 241.4 Hz, CF_2H), 12.11 (t, $^1J_{F\text{-}C}$ = 242.7 Hz, CF_2H), 101.72 (s, Cp*, C═C), 97.12 (t, $^2J_{F\text{-}C}$ = 26.9 Hz, aromatic C═C), 85.12 (s, aromatic, C═C), 65.78 (s, aromatic C═C), 56.06 (t, $^2J_{F\text{-}C}$ = 24.4 Hz, aromatic C═C), 47.20 (s, C-O), 10.19 (s, Cp*, CH_3). Anal. Calcd for $C_{18}H_{21}B_2F_{12}Ir \cdot 4H_2O$: C, 33.97; H, 3.96. Found: C, 33.47; H, 3.44.

Synthesis of {(Cp*Ir)$_2$(μ-η^5:η^5-*exo*:*exo*-1,1′-(O)-[CF_2H-C_6H_4-CF_2H]$_2$[BF_4]$_2$} (5). Method B. This compound was also obtained by treatment of a suspension of **3** in THF with LiOH. The spectroscopic data obtained for this compound were similar to those observed for complex **5**.

X-ray Structural Analysis of 2, 3, and 5. Crystals of **2**, **3**, and **5** suitable for X-ray studies were grown from CH_3CN/Et_2O or CH_2Cl_2/Et_2O. In all cases X-ray data collections with Mo Kα radiation were carried out at 250 K using an Enraf-Nonius diffractometer equipped with a CCD area detector. A single crystal of either **2**, **3**, or **5** was selected, mounted onto a glass fiber, and transferred in a cold nitrogen gas stream. Intensity data were collected with a Bruker-Nonius Kappa-CCD with graphite-monochromated Mo Kα radiation. Unit-cell parameters determination, data collection strategy, and integration were carried out with the Nonius EVAL-14 suite of programs (A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J. Appl. Crystallogr.* **2003**, *36*, 220). The structure was solved by direct methods using the SIR92 program (Giacovazzo et al., 1993) and refined anisotropically by full-matrix least-squares methods using the SHELXL-97 software package (G. M. Sheldrick, University of Göttingen, Germany, 1997).

Table 1. Crystal Data and Structure Refinement Details for Compounds 2, 3, and 5

	2	**3**	**5**
formula	$C_{16}H_{24}IrO \cdot CF_3SO_3$	$C_{18}H_{21}F_4Ir \cdot 2BF_4$	$C_{36}H_{42}F_8Ir_2O \cdot 2BF_4$
fw (g mol^{-1})	573.62	679.17	1200.72
unit cell	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	$Pna2_1$	$Pna2_1$
a (Å)	10.0140(4)	12.3940(10)	31.8950(12)
b (Å)	15.4210(17)	13.8910(14)	9.0050(11)
c (Å)	12.9970(11)	12.7840(5)	13.8630(16)
α (deg)	90.00	90.00	90.00
β (deg)	96.651(7)	90.00	90.00
γ (deg)	90.00	90.00	90.00
volume (Å^3)	1993.6(3)	2201.0(3)	3981.7(7)
Z	4	4	4
λ(Mo Kα) (Å)	0.710730	0.710730	0.710730
ρ_{calc} (g/cm^3)	1.911	2.050	2.003
T (K)	250(2)	250(2)	250(2)
μ (mm^{-1})	6.847	6.170	6.782
$R(F_o)^a$	0.0393	0.0281	0.0459
$R_w(F_o)^b$	0.0823	0.0738	0.0995

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Acknowledgment. This work was supported by the CNRS and by the Université Pierre et Marie Curie-Paris 6 and is part of an ongoing collaboration (DRI) between SDSU and UPMC-Paris 6, which we gratefully acknowledge.

Supporting Information Available: Crystallographic data for **2**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700760Y