Iridium Complexes

An Iridium Difluoroketene Complex: Synthesis and Isolation[**]

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Dedicated to Professor John E. Bercaw
on the occasion of his 60th birthday

Despite substantial research on the chemistry of ketenes, efforts to isolate or characterize the electron-deficient difluoroketene ($F_2C{=}C{=}O$) have met with little success.[1] While an early claim of the preparation of $F_2C{=}C{=}O$ exists,[2] attempts to repeat this synthesis were not success-

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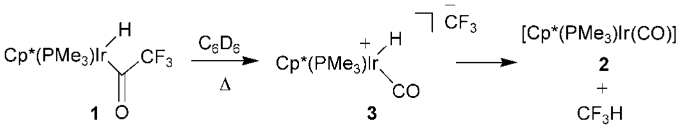
ful.[3] Difluoroketene has been generated transiently by zinc-induced dehalogenation of bromodifluoroacetyl halides, but its formation was only inferred from the isolation of a cycloaddition product with acetone and from the detection of CO and $F_2C{=}CF_2$, the presumed products of difluoroketene dissociation.[3] Experiments designed to trap [2+2] adducts of cyclopentadiene and fluorinated ketenes generated in situ were successful with methylfluoroketene, phenylfluoroketene, and trifluoromethylfluoroketene, but failed when attempted with difluoroketene.[4] Difluoroketene ethyl trimethylsilyl ketal, a masked variant of difluoroketene, has been employed in organic synthesis as a reagent for making fluoroorganic compounds.[5–7]

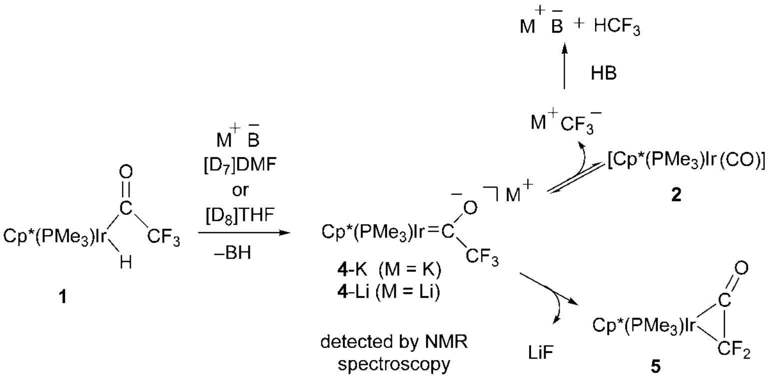
In 1998, the generation and IR characterization of difluoroketene in a CO_2-doped argon matrix at 30 K was reported.[8] This highly reactive ketene was also detected in the gas phase by mass spectrometry after ionization of perfluoromethylvinyl ether.[9] However, until now neither the free ketene nor its metal complexes have been obtained on a preparative scale. Herein we report that research on the electron-rich organometallic fragment [Cp*(PMe$_3$)Ir] (Cp* = η^5-C_5Me_5), has led to the discovery of an isolable difluoroketene complex.

Recently, we reported that upon heating a solution of [Cp*(PMe$_3$)Ir(H){C(O)CF$_3$}] (**1**) in C_6D_6 at 105 °C, [Cp*(PMe$_3$)Ir(CO)] (**2**) and CF_3H were generated in quantitative yield.[10] The proposed mechanism for this elimination involves CF_3^- dissociation from **1** to give the intermediate ion pair **3** (scheme 1). Rapid proton transfer from the iridium carbonyl cation to the CF_3^- ion yields the observed products (Scheme 1).[10] While investigating the mechanism of this transformation, we discovered two different base-induced elimination reactions from **1**.



Scheme 1. Proposed mechanism for CF_3H loss from **1**.

Upon vacuum transferring [D$_7$]DMF to an NMR tube containing **1** and a catalytic amount of potassium *tert*-butoxide (0.2 equiv) at −196 °C, only **2**, CF_3H, and potassium *tert*-butoxide were detected in quantitative yield, by NMR spectroscopy upon warming to 22 °C. Using [D$_8$]THF as solvent gave similar results. The proposed mechanism for this transformation involves rapid deprotonation of **1** to generate the potassium iridate **4**-K. Elimination of CF_3^- from **4**-K followed by deprotonation of *tert*-butanol, produces **2** and CF_3H, which regenerates the base (Scheme 2). Treatment of **1** with a base which would irreversibly deprotonate it, gave an unexpected result.



Scheme 2. Deprotonation of **1** leading to **2** and difluoroketene adduct **5**.

Compound **1** and 1.4 equivalents of *tert*-butyllithium were dissolved in [D$_8$]THF at low temperature and the subsequent reaction was monitored by NMR spectroscopy as the solution was warmed from −80 to 22 °C. At −80 °C one major species, assigned as the lithium iridate **4**-Li was detected in the ^{19}F NMR spectrum at $\delta = -69.2$ ppm and in the $^{31}P\{^1H\}$ NMR spectrum at $\delta = -39.9$ ppm. Upon warming, the chemical shifts of all intermediates shifted slightly upfield. At −13 °C only the acyl iridate **4**-Li was detected;[11] at −6 °C new products began to form. As the reaction mixture was warmed above 0 °C, elimination of CF_3Li gave iridium carbonyl **2**, and surprisingly, LiF elimination from **4**-Li furnished difluoroketene iridium adduct **5** in a 1:1 ratio (Scheme 2).

Isolation of the difluoroketene adduct **5** was by multiple precipitations and crystallizations from a mixture containing **2** and **5** in a solution of diethyl ether and pentane at −38 °C (ca. 30 % yield).[12] As a solid at 22 °C under a N_2 atmosphere, the difluoroketene adduct **5** showed no signs of decomposition after two weeks. Heating a C_6D_6 solution of **5** at 75 °C resulted in slow decomposition to **2** and unidentifiable products which contained the {Cp*(PMe$_3$)Ir} fragment.

The characterization of **5** began with heteronuclear NMR spectroscopy experiments on the four NMR active nuclei. The ^1H NMR spectrum showed a singlet at $\delta = 1.75$ ppm for the Cp* ligand, and a doublet at $\delta = 1.01$ ppm with $^2J_{H,P} = 10.4$ Hz for the PMe$_3$ ligand. In the ^{19}F NMR spectrum, two inequivalent signals were observed in the region typical of fluorine atoms bound to a sp^2-hybridized carbon atoms. The signal at $\delta = -123.4$ ppm was coupled to both phosphorus and fluorine atoms to give a doublet of doublets with $^2J_{F,F} = 187$ Hz and $^3J_{F,P} = 33$ Hz. The more upfield signal at $\delta = -132.1$ ppm was coupled only to the other fluorine atom with $^2J_{F,F} = 188$ Hz. The $^{31}P\{^1H\}$ NMR spectrum showed the signals for the PMe$_3$ ligand as a doublet coupled to one fluorine atom at $\delta = -41.6$ ppm with $^3J_{P,F} = 33$ Hz. In the $^{13}C\{^1H\}$ NMR spectrum, only singlets for the methyl and quaternary carbon atoms of the Cp* ligand at $\delta = 10.0$ ppm and 96.1 ppm, respectively, and a doublet for the PMe$_3$ ligand at $\delta = 18.3$ ppm with $^2J_{C,P} = 42.3$ Hz were found.

The difluoroketene carbon atom signals of **5** were observed in a ^{19}F-detected 2D $^{19}F,^{13}C$ heteronuclear single- and multiple-bond correlation (HSMBC) experiment.[13,14] This NMR experiment revealed ^{13}C signals at $\delta = 178.0$ and 207.2 ppm, through correlation peaks with each of the ^{19}F signals (see Figure 1), mediated by $^1J_{C,F}$ (320–340 Hz) and $^2J_{C,F}$ (5–10 Hz), respectively. Specifically, the $^{19}F_a$ signal at −123.4 ppm appeared as a ddd ($^1J_{F_a,C} = 344$, $^2J_{F_a,F_b} = 187$,

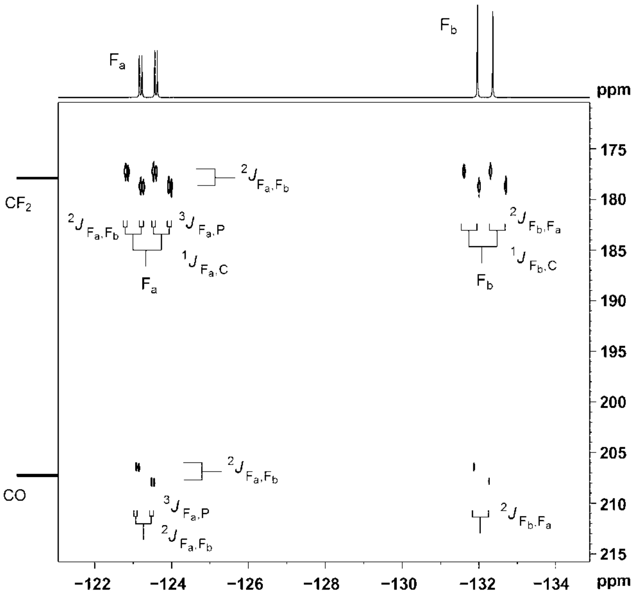


Figure 1. The 2D ^{19}F,^{13}C HSMBC spectrum of **5** in C_6D_6, recorded at 11.7 T and 19 °C. (The 1D ^{19}F NMR spectrum of **5** is displayed at the top.) The HSMBC experiment was carried out using a Bruker Avance 500 spectrometer equipped with a 5 mm (^{1}H,X,^{31}P) triple-resonance probehead with an actively shielded *z*-gradient coil. The inner (^{1}H) coil was tuned to the ^{19}F frequency (470.6 MHz), and the outer (X) coil to the ^{13}C frequency (125.8 MHz). The experiment used a gradient-enhanced 2D HMBC pulse sequence without a low-pass filter, allowing for observation of both $^1J_{\mathrm{F,C}}$ and $^2J_{\mathrm{F,C}}$ mediated correlations in one experiment. No ^{13}C-decoupling was applied during the detection period. For further experimental conditions see ref. [19].

$^3J_{\mathrm{F_a,P}} = 34$ Hz) in its correlation peak with the signal at 178.0 ppm, which therefore arises from the CF$_2$ carbon atom; and as a dd ($^2J_{\mathrm{F_a,F_b}} = 187$, $^3J_{\mathrm{F_a,P}} = 34$ Hz, $^2J_{\mathrm{F_a,C}}$ unresolved, that is, < 10 Hz) in the cross peaks with the CO signal at $\delta = 207.2$ ppm. Analogously, the ^{19}F$_b$ fluorine signal at $\delta = -132.1$ ppm appeared as a dd ($^1J_{\mathrm{F_b,C}} = 327$, $^2J_{\mathrm{F_b,F_a}} = 187$ Hz) in its cross peaks with the CF$_2$ signal, and as a doublet ($^2J_{\mathrm{F_b,F_a}} = 187$ Hz; $^2J_{\mathrm{F_b,C}}$ unresolved, that is, < 8 Hz,) in its correlation peaks with the CO signal. All four cross-peak patterns in the 2D spectrum are displaced by the $^2J_{\mathrm{F_a,F_b}}$ coupling in both the ^{13}C and ^{19}F dimension. Reported ^{13}C NMR spectroscopic data for the η^2-(C,C) carbon atoms of related phenyl- and diphenylketene iridium complexes were significantly upfield from these values.[15] The downfield resonances for the η^2-(C,C) carbon atoms are likely a result of the deshielding effects of the fluorine atoms.

Solid-state ZnSe attenuated total reflectance (ATR) FTIR spectroscopy of difluoroketene **5** showed strong bands at 1725, 1172, 954, 938, and 837 cm^{-1}. Medium to weak bands were recorded at 1424, 1384, and 1287 cm^{-1}. Using X-ray analysis and isotopic ^{18}O and ^{13}C labeling, Grotjahn and coworkers showed that the IR absorptions for a series of six bisphosphine chloro-iridium and rhodium ketene complexes were dependent on the coordination mode.[15] When the ketene was coordinated through the carbonyl C–O bond an intense IR band, assigned to the C=O stretch, was found between 1632 and 1651 cm^{-1}. Alternatively, when the ketene was coordinated through the C–C bond, a strong absorption was located between 1728 and 1802 cm^{-1}. Based on these data and the absorption at 1725 cm^{-1} for **5**, the coordination mode of our difluoroketene **5** was inferred to be η^2-(C,C).

Pale yellow pyramidal crystals suitable for X-ray analysis were grown from a concentrated solution of difluoroketene **5** in diethyl ether at −38 °C. The ketene adduct crystallized in the *C*2/*c* space group with one molecule in the asymmetric unit.[16] Coordination of the difluoroketene to iridium was confirmed to be η^2-(C,C) (Figure 2). An unusually short C–O bond of 1.11(1) Å for **5** compared to other iridium and rhodium η^2-(C,C)-bound ketene complexes suggests that back-donation from the metal center to the ketene does not elongate the C–O bond.[15,17] However, shorter Ir–C and C–C bonds were also measured, which indicate that the difluoroketene binds more closely than diphenyl- or phenylketene to iridium.[18]

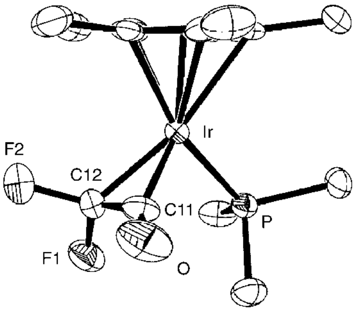


Figure 2. ORTEP diagram of **5** (thermal ellipsoids set at 50% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir-C11 1.799(9), Ir-C12 1.994(10), Ir-P 2.256(2), C12-F2 1.37(1), C12-F1 1.39(1), C12-C11 1.38(1), C11-O 1.11(1); P-Ir-C11 92.9(3), P-Ir-C12 91.1(3), Ir-C12-C11 61.3(5), Ir-C11-C12 76.6(6), C12-Ir-C11 42.1(4), F2-C12-C11 117.2(9), F1-C12-C11 124.1(8), F1-C12-F2 103.3(8), O-C11-C12 138(1), Ir-C11-O 143.9(9).

Overall loss of fluoride rather than the CF$_3^-$ ion, when *tert*-butyllithium is used as the base to deprotonate **1**, may be attributed to reversible CF$_3^-$ loss from iridate **4**. When **1** is deprotonated with KO*t*Bu to give iridate **4**-K and HO*t*Bu, CF$_3^-$ loss followed by protonation to yield CF$_3$H and **2** is irreversible. However, in the absence of a proton source, F$^-$ loss becomes competitive with CF$_3^-$ loss to give **5** (Scheme 2). Unfortunately, attempts to increase the yield of **5** by adding reagents which might assist in fluoride elimination were unsuccessful.

Difluoroketene iridium complex **5** joins an important group of complexes containing reactive organic fragments that are stabilized by coordination to transition-metal centers. The robust character of adduct **5** is attributed to the donating ability of the electron-rich organometallic fragment that coordinates to the electron-deficient difluoroketene. To our knowledge, this is the first example of a dihaloketene complex and the only structural data available for the difluoroketene fragment in any form.

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[11] This intermediate could be trapped with the electrophile MeI, to generate the methyl acyl compound [Cp*(PMe$_3$)Ir(Me){C(O)CF$_3$}], see ref. [10].

[12] The synthesis of **5** was achieved on a larger scale as follows: A 250-mL thick-walled, resealable flask equipped with a stir bar was charged with **1** (125 mg, 0.25 mmol) and *tert*-butyllithium (22 mg, 0.35 mmol, recrystallized from pentane at −38 °C until white). The flask was attached to a vacuum manifold and cooled to −196 °C. THF (10 mL) was vacuum transferred from Na/benzophenone into the flask. The frozen reaction mixture was warmed to −78 °C and then allowed to warm to room temperature over 15 h. The volatile materials were removed in vacuo to give a reddish-brown residue. Analysis of the crude reaction mixture by NMR spectroscopy revealed a 1:1 mixture of difluoroketene adduct **5** and iridium carbonyl **2** with a small amount of **1**. In a N$_2$ filled glove box, the crude material was filtered through a pad of silica gel on a medium-pore fitted glass frit eluting with diethyl ether. The resulting orange solution was concentrated in vacuo to 1 mL, layered with pentane, and allowed to stand at −38 °C for crystallization. Dark reddish-brown clusters of crystals grew after 1 week. The mother liquor was removed by pipette and the solid was washed with pentane. Excess solvent was removed under reduced pressure. Yield: 38 mg (32 %) EI HRMS: m/z calcd for $C_{15}H_{24}F_2OPIr$ 482.1162 $[M]^+$; found 482.1152.

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[16] CCDC-244081 (**5**) contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[18] In a separate experiment, compound **5** was co-crystallized with **2**. X-ray analysis of this crystal revealed a 2:1 mixture of **5** to **2** with the iridium carbonyl lying along the mirror plane of the unit cell. CCDC-244082 (**5/2**) contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[19] The delay Δ was set to 25 ms; acquisition times t_2 and t_1 were 218 ms (^{19}F spectral width 9400 Hz, 4 K complex data points) and 5 ms (^{13}C spectral width 12,575 Hz, 128 real data points), respectively. The relaxation delay was 1 s; 128 scans were accumulated per t_1 increment. Gradient ratios G_1:G_2:G_3 were 3:1:3. The total acquisition time of the ^{19}F,^{13}C HSMBC experiment on the difluoroketene sample ($\approx$20 mg of **5** in 0.6 mL C_6D_6) was 5 h 45 min. ^{19}F Chemical shifts are referenced to external CFCl$_3$ at 0 ppm, ^{13}C chemical shifts to internal TMS at 0 ppm.