

Novel Reaction of an Iridium Carbonyl Complex with Xenon Difluoride: the First Metal Fluoroacyl Complex

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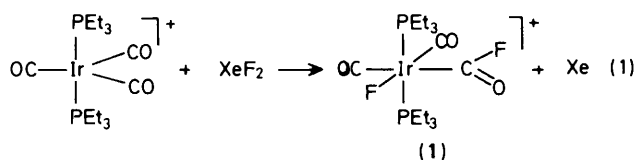
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The cation $[\text{Ir}(\text{CO})_3(\text{PEt}_3)_2]^+$ reacts with XeF_2 in CH_2Cl_2 to give the novel species $[\text{Ir}(\text{CO})_2\text{F}(\text{COF})\text{PEt}_3]_2^+$ (**1**), isolated as BF_4^- and PF_6^- salts and characterised spectroscopically, crystallographically, and by partial elemental analysis.

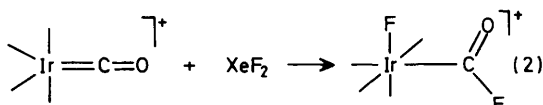
The role of metal carbonyls in formylation reactions is recognised as important,¹ and acyl complexes of metals are well characterised,² but metal complexes containing haloacyl ligands appear to have been unknown up to now. As part of a study of the reactions between XeF_2 and organometallic compounds, we have found that the cation tricarbonylbis(triethylphosphine)iridium(I) reacts smoothly with xenon difluoride at 273 K in dichloromethane to give the novel cation dicarbonylfluoro(fluoroacyl)bis(triethylphosphine)iridium(III) (**1**), in high yield, equation (1).

Compound (**1**), the first fluoroacyl complex described, is stable in solution at room temperature in the absence of air and moisture. It has been isolated as its hexafluorophosphate(v) and tetrafluoroborate salts, as white air-sensitive



solids, and characterised by C and H analysis, ^{19}F , ^{31}P -{H}, and ^{13}C -{H} n.m.r. spectroscopy, i.r. spectroscopy, and by single crystal X-ray crystallography.† The ^{19}F n.m.r. spectrum

† Selected data for (**1**): Satisfactory elemental analysis obtained. I.r.: (cm^{-1}), 2163, 2110, 1815, 1752 (CO). N.m.r.: Chemical shifts given as positive to high frequencies of 85% H_3PO_4 (^{31}P), CCl_3F (^{19}F), and Me_4Si (^{13}C). Crystal data for (**1**): $\text{C}_{15}\text{H}_{30}\text{F}_2\text{IrO}_3\text{P}_2 \cdot \text{BF}_4^-$, monoclinic, $P2_1/c$, $a = 12.8388(10)$, $b = 13.1079(10)$, $c = 14.5327(9)$ Å, $\beta = 107.265(5)^\circ$, $U = 2335.5$ Å³, $D_c = 1.812$ g cm⁻³, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 58.88$ cm⁻¹, 3234 unique data measured to $\theta = 22.5^\circ$ using Mo-K α X-radiation, corrected for absorption using psi scans; refinement based on 2588 data with $F > 6\sigma(F)$. At convergence, R , $R_w = 0.0212$, 0.0297, respectively, for 270 parameters. The Ir position was deduced from a Patterson synthesis and the remaining non-H atoms from iterative rounds of least-squares refinement and difference Fourier synthesis. There is some disorder in the BF_4^- counteranion but the cation is well ordered. All non-H atoms were refined anisotropically and H atoms were included in fixed, calculated positions.⁵ Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



showed two resonances. One was in the region³ associated with F bound to iridium ($\delta -394.6$). It appeared as a triplet [$^2J(\text{FP})$ 32 Hz] of narrower doublets [$^3J(\text{FF})$ 14 Hz]. The other resonance was in a region consistent with F bound to a carbonyl group⁴ ($\delta 132.4$). It appeared as a doublet [$^3J(\text{FF})$ 14 Hz] of slightly broadened lines ($w_{1/2}$ 2 Hz). The $^{31}\text{P}\{-\text{H}\}$ spectrum showed a single resonance $\delta +2.85$ with the expected pattern of a doublet [$^2J(\text{PF})$ 32 Hz] of narrower doublets [$^3J(\text{PF})$ 2 Hz], the couplings corresponding to those observed in the ^{19}F spectrum. There were three resonances in the CO region of the $^{13}\text{C}\{-\text{H}\}$ n.m.r. spectrum. That at intermediate frequency ($\delta 154.5$) showed a wide doublet coupling which we associate with F bound to the acyl carbon [$^1J(\text{CF})$ 423 Hz]. The other two resonances were both doublets, but with much smaller couplings; the one at the lower frequency ($\delta 150.76$) is assigned to the carbonyl *trans* to fluorine, the doublet splitting [$^2J(\text{CF})$ 61 Hz] being the greater; the other resonance ($\delta 162.0$) is assigned to the carbonyl *cis* to fluorine [$^2J(\text{CF})$ 47 Hz]. We did not observe coupling between C and P, presumably because the spectra were not of high enough quality. The i.r. spectrum showed bands in the regions associated with terminal and with ketonic carbonyl groups. The structure was confirmed by the crystallographic results (see Figure 1). Co-ordination round iridium is essentially octahedral, and the acyl fluorine is *cis* to the fluorine bound to iridium, although we cannot exclude at this stage the possibility that there is some disorder between F and O. Bond lengths and angles are reasonably consistent with those observed in alkyl fluoroacyl compounds in the gas phase,⁶ although the C–F bond is shorter and the C–O bond longer in compound (1) (consistent with some disorder between O and F). Principal parameters are given in the figure caption and will be discussed in a full paper.

The reaction leading to the formation of this novel and interesting product appears to be without precedent. In effect, it is an oxidative addition: the metal's oxidation state rises from (I) to (III). However, the addition is not directly across the metal, but across the metal–carbon bond, and can be represented simply if that bond is written as formally double, equation (2).

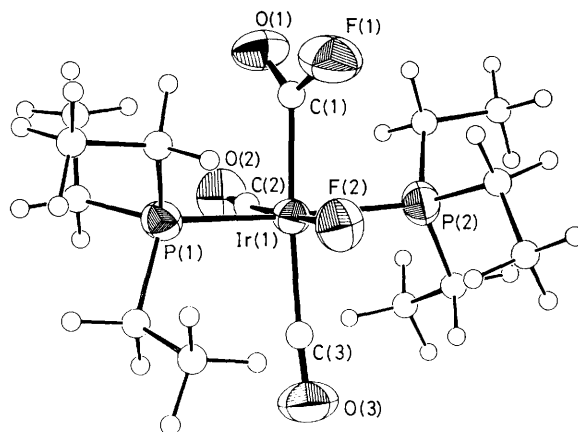


Figure 1. The structure of (1)·BF₄ selected bond lengths (pm) and angles (°): Ir–C(1), 202.8(6); Ir–C(2), 188.3(5); Ir–C(3), 198.9(6); Ir–F(2), 199.8(3); Ir–P, 240.1(1), 240.0(1); C(1)–O(1), 124.9(7); C(1)–F(1), 129.4(7); Ir–C(1)–O(1), 125.4(4); Ir–C(1)–F(1), 118.9(4); O(1)–C(1)–F(1), 115.7(5).

We have no evidence as to the mechanism of the process. The product (1) has considerable potential as a synthetic intermediate. We are exploring both the reactivity of (1) and the reactions between XeF₂ and other metal carbonyls in which a low-valent metal is five-co-ordinated.

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