Fluorination of Tetrairidium Dodecacarbonyl

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Xenon difluoride sequentially fluorinates $Ir_4(CO)_{12}$ dissolved in anhydrous HF yielding initially the novel neutral complexes *mer*- and *fac*-$Ir(CO)_3F_3$, which are characterised by ^{19}F, ^{13}C and $^{13}C\{^{19}F\}$ NMR spectroscopies, and finally $[XeF][IrF_6]$.

The chemistry of organo-transition-metal fluoro-complexes is relatively unexplored,[1] even though potentially interesting synthetic chemistry may be anticipated for such systems when other soft-metal/hard-ligand combinations are considered.[2] Early successes were the transition-metal carbonyl fluorides.[3] The recent application of XeF_2,[4] SF_4,[5] TAS-F [tris(dimethylamino)sulfur(trimethylsilyl) difluoride)],[6] $HBF_4{\cdot}OEt_2$[7] and Olah's reagent[8] to transition-metal systems and synthetic chemistry at the fluoride ligand in $ReF(CO)_3(PPh_3)_2$[9] indicate a resurgence in low-valent transition-metal fluoride chemistry. Until recently only monofluorinated iridium(III) complexes have been known, prepared by oxidative addition to iridium(I) species. We have now reported the first examples of difluorinated iridium(III) complexes,[10] which undergo rearrangement in solution to afford a small quantity of a trifluorinated species. However, all these complexes contain other donor ligands which stabilize the Ir–F bond. Here, we report the sequential fluorination of $Ir_4(CO)_{12}$ affording the first iridium(III) complexes coordinated only by carbonyl and fluoride ligands, and their subsequent fluorination to $[XeF][IrF_6]$.

Tetrairidium dodecacarbonyl was found to be insufficiently soluble in organic solvents to allow an investigation of its reaction with XeF_2 and, in any case, XeF_2 preferentially fluorinates many organic solvents.[11] The reaction between $Ir_4(CO)_{12}$ and XeF_2 occurs in anhydrous HF at *ca.* −40 °C producing xenon as a byproduct. Molar ratios of 1 : 1 through to 26 : 1 $XeF_2 : Ir_4(CO)_{12}$ were investigated. At low ratios, signals due to unconverted $[H_2Ir_4(CO)_{12}]^{2+}$ [12] are observed in both the ^1H and ^{13}C NMR spectra. Above a 6 : 1 ratio, COF_2 is observed in the ^{19}F NMR spectra and in the gas-phase IR spectra of the gases vented from the reaction mixture, and at very high ratios, the ^{19}F NMR signal due to HF broadens significantly owing to the generation of paramagnetic species. At the 26 : 1 ratio, removal of HF afforded a yellow solid, characterised by IR and Raman spectroscopies as $[XeF][IrF_6]$.[13]

Once the $XeF_2 : Ir_4(CO)_{12}$ ratio of 6 : 1 is reached, all the NMR signals due to the $[H_2Ir_4(CO)_{12}]^{2+}$ cation disappeared and, at 25 °C, the ^{19}F NMR spectrum is dominated by three

Table 1 ^1H, ^{13}C and ^{19}F NMR data for iridium carbonyl fluorides[a]

	^{13}C	^{19}F
fac-$Ir(CO)_3F_3$[b]	131.3[c]	−310
mer-$Ir(CO)_3F_3$[b]	130.7(79.7,2.0)[d]	−338(75)[e]
	141.6(6.5,6.5)[d]	−476(75)[e]

[a] Shifts (δ) relative to external $SiMe_4$ or $CFCl_3$. Coupling constants in Hz in parentheses. [b] Recorded at −78 °C. [c] AXX'_2 system, simulated with coupling constants of $^2J_{F_XC}$ 84 Hz, $^2J_{F_{X'}C}$ 5 Hz, $^2J_{F_XF_{X'}}$ 120 Hz, see text. [d] $^2J_{FC}$. [e] $^2J_{FF}$.

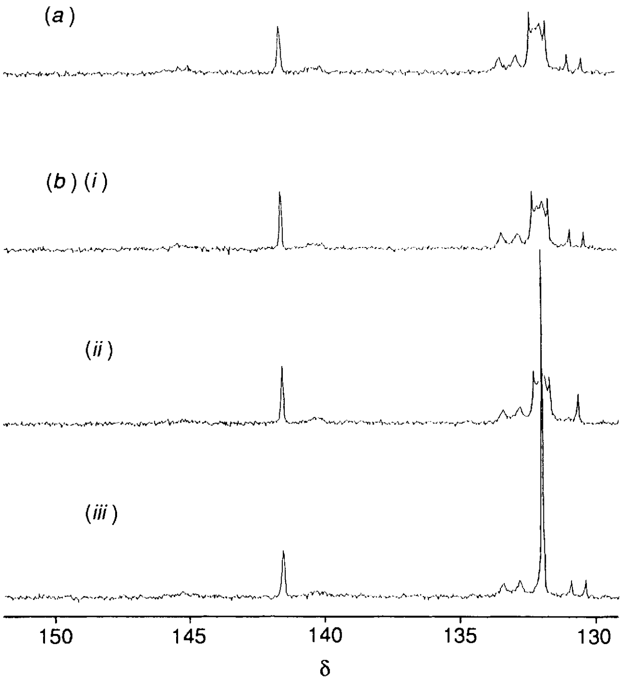

Fig. 1 150 MHz ^{13}C NMR spectra of the iridium carbonyl fluorides. (*a*) Fluorine coupled spectrum. (*b*) Spectrum ^{19}F selectively decoupled at: (*i*) δ −476; (*ii*) δ −338; (*iii*) δ −310.

broad, unresolved, peaks at *ca.* δ −310, −338 and −476. On cooling the system to −78 °C, these resolve into a singlet, triplet and doublet, respectively, the latter two exhibiting $^2J_{FF}$ coupling of 75 Hz. Undoubtedly, the system is slowly exchanging at room temperature, but we are unable to determine the coalescence point because our NMR tubes (perfluoroethylenepropylene copolymer) become porous to HF above room temperature. The peaks at δ −310 and −338 are in a region of the spectrum characteristic[5] of F_{trans}–CO while the peak at δ −476 occurs in a region characteristic[10] of F_{trans}–F. We, therefore, assign these peaks to the 18 electron *fac*- and *mer*-Ir(CO)$_3$F$_3$ species. ^{13}C NMR spectra at 25 and −78 °C support this assignment. The predominant peak at *ca.* δ 131 is a broad unresolved multiplet with two additional features at δ 130.7 and 141.6, which appear to be doublets of triplets (Table 1). Assignment of these signals to the *fac*- and *mer*-Ir(CO)$_3$F$_3$ species was aided by recording selective ^{13}C{^{19}F} NMR spectra (Fig. 1) at the SERC ultra-high-field NMR service. Irradiation at δ −476 removed the triplet couplings on the peaks at δ 130.7 and 141.6 while irradiation at δ −338 removed the doublet couplings on the same peaks. These resonances are, therefore, assigned to the CO_{trans}–F and CO_{trans}–CO in *mer*-Ir(CO)$_3$F$_3$. Irradiation at δ − 310 collapsed the multiplet at *ca.* δ 131 to a sharp singlet, and this resonance is, therefore, assigned to CO_{trans}–F in *fac*-Ir(CO)$_3$F$_3$. The ^{13}C NMR spectrum for the *fac*-isomer is expected to be an AXX'_2 system, and the broad multiplet may be simulated using the coupling constants given in Table 1.

Removal of the solvent from the 6 : 1 ratio sample leaves a pale-yellow solid, which, when redissolved in HF, shows only the ^{13}C and ^{19}F NMR signals due to the *fac*-isomer, suggesting that this isomer has thermodynamic stability over the *mer*-isomer. Dry powder IR spectra of the pale-yellow solid show two bands assignable as ν(C–O) at 2213 and 2165 cm^{-1} as expected for *fac*-Ir(CO)$_3$F$_3$.

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