

The Preparation and Crystal Structure of the Iridium Thiazylidifluoride Complex $[\text{Ir}(\text{CO})\text{ClF}(\text{NSF}_2)(\text{PPh}_3)_2]$

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The thiazylidifluoride complex $[\text{Ir}(\text{CO})\text{ClF}(\text{NSF}_2)(\text{PPh}_3)_2]$ **2** was prepared by reaction of $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ **1** and NSF_3 and its X-ray crystal structure determined.

Reports of the reactions of main group fluorides with transition metal complexes are rare.¹ However, in the past decade Ebsworth and Holloway have studied the oxidative addition reactions of complexes of the type $[\text{M}(\text{CO})\text{Cl}(\text{PET}_3)_2]$ ($\text{M} = \text{Ir}, \text{Rh}$) with various fluorine containing species.²

NSF_3 is a relatively unreactive compound, reacting with sodium at temperatures greater than 200 °C and hydrolysing only very slowly.⁴ It normally bonds to transition metals to form simple NSF_3 complexes⁵ where the NSF_3 is bonded *via* the nitrogen. Although compounds of the form RNSF_2 are known ($\text{R} = \text{CF}_3, \text{C}_2\text{F}_5, \text{CF}(\text{CF}_3)_2, \text{Cl}$, etc.)⁶, the only reported example of bonding to a metal is the mercury species, $\text{Hg}(\text{NSF}_2)_2$, which was prepared by C–N bond cleavage of $\text{FC}(\text{O})\text{NSF}_2$,⁷ also, only three coordination complexes of iridium containing a fluoride ligand have been structurally characterised to date.⁸ We describe here an oxidative addition reaction of NSF_3 , the first example of oxidative addition across $\text{S}^{\text{VI}}\text{–F}$ that we are aware of, the first example of thiazylidifluoride

as a complex ligand and also a further example of a stable low-oxidation state transition metal fluoride complex.

Typically, reaction of **1** with a four-fold excess of NSF_3 in CH_2Cl_2 in a Schlenk apparatus proceeded rapidly at 0 °C (the temperature at which **1** became soluble) with stirring. The colour changed from a bright yellow slurry to a burgundy solution, indicating oxidation of Ir^{I} to Ir^{III} . Violet crystals of **2** suitable for X-ray analysis† were obtained by recrystallisation from CH_2Cl_2 –diethyl ether. The ^{19}F NMR spectrum‡ shows two resonances as expected; $\delta -337.8$ [t, $^2J(\text{FP}) = 28$ Hz] and $\delta 121$ (br). The first resonance is in the region expected for $\text{Ir}^{\text{III}}\text{–F trans to CO}$,¹ although the second is rather to low field for $\text{S}^{\text{IV}}\text{–F}$. The ^{31}P NMR spectrum consisted of a doublet, $\delta -6.6$ [$^1J(\text{PF}) = 28$ Hz]. The IR spectrum in Nujol shows $\nu(\text{CO})$ at 2022 cm^{-1} , typical for $\text{Ir}^{\text{III}}\text{–CO}$.

The structure is presented in Fig. 1. The molecule has the expected octahedral geometry with Ir–P, Ir–F, Ir–Cl and Ir–C bond lengths of typical values. The F–S–F angle is very low at 83.2° but this is comparable to the value of 88.3° in $\text{Hg}(\text{NSF}_2)_2$.⁷ The appearance of both resonances simultaneously in the NMR spectrum suggests that the reaction may be a concerted oxidative addition. Complex **2** is extremely moisture-sensitive and undergoes ready hydrolysis to the corresponding Ir–NSO complex **3**, Scheme 1.

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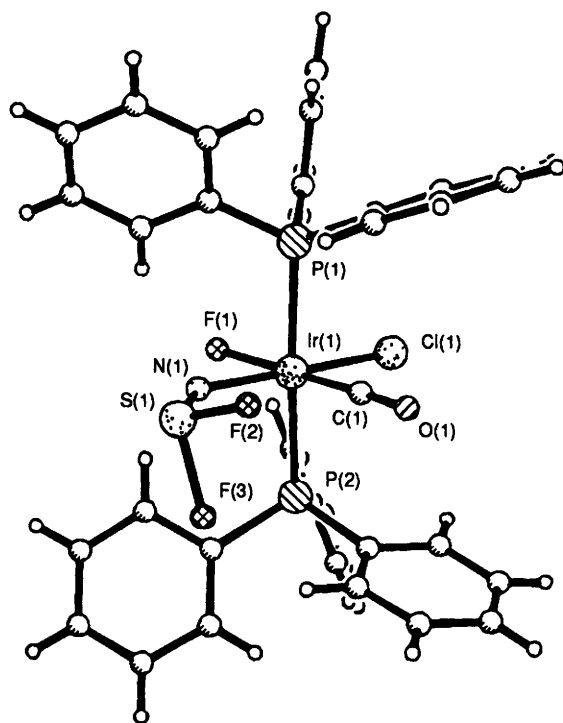
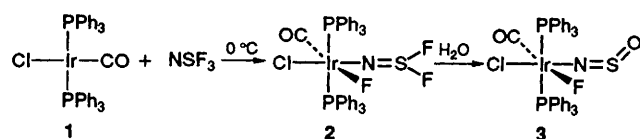


Fig. 1 The molecular structure of $[\text{Ir}(\text{CO})\text{ClF}(\text{NSF}_2)(\text{PPh}_3)_2]$. Important bond lengths (pm) and angles ($^\circ$) are: Ir(1)–F(1) 208.9(4), Ir(1)–N(1) 204.0(7), N(1)–S(1) 143.6(7), S(1)–F(2) 162.1(8), S(1)–F(3) 170.4(12), Cl(1)–Ir(1)–N(1) 178.9(2), Ir(1)–N(1)–S(1) 137.8(4), N(1)–S(1)–F(2) 113.3(4), N(1)–S(1)–F(3) 113.4(5), F(2)–S(1)–F(3) 83.2(6).



Scheme 1

Footnotes

† Crystal data for $\text{C}_{37}\text{H}_{30}\text{ClF}_3\text{IrNOP}_2\text{S}$, crystal dimensions $0.5 \times 0.25 \times 0.1$ mm, $M = 883.3$, space group $P\bar{1}$, triclinic, $a = 10.176(2)$, $b = 12.364(2)$, $c = 13.621(3)$ Å, $\alpha = 97.89(3)^\circ$, $\beta = 93.52(3)^\circ$, $\gamma = 96.74(3)^\circ$, $U = 1680.5(6)$ Å³, $Z = 2$, $D_c = 1.745$ g cm^{−3}, Mo–K α radiation, $\lambda = 0.71073$ Å, $\mu(\text{Mo–K}\alpha) = 42.58$ cm^{−1}, $F(000) = 868$, $R = 0.0474$, $R_w = 0.0508$ for 5747 observed [$F > 4.0\sigma(F)$] diffractometer reflections out of 8251 measured ($0 \leq h \leq 13$, $-15 \leq k \leq 15$, $-17 \leq l \leq 17$, $5.0 \leq \theta \leq 55.0^\circ$) and corrected for absorption empirically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ NMR standards: all NMR shifts are reported as positive to high frequency of 85% H_3PO_4 (for ^{31}P) and CCl_3F (for ^{19}F).

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