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Novel reactions of thiazyl fluorides with transition metal complexes

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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 [M(CO)Cl(PEt$_3$)$_2$] (M = Ir, Rh) with various fluorine-containing species [2].

Inert NSF$_3$ normally complexes to metals to form simple NSF$_3$ complexes where the NSF$_3$ is bonded via the nitrogen [3]. However, we have observed that oxidative addition of NSF$_3$ to [Ir(CO)Cl(PPh$_3$)$_2$] [4] occurs in CH$_2$Cl$_2$ or CHCl$_3$ at 0 °C. This is the first example of oxidative addition across an S^{VI}–fluorine bond, as well as the first example of NSF$_2$ as a complex ligand.

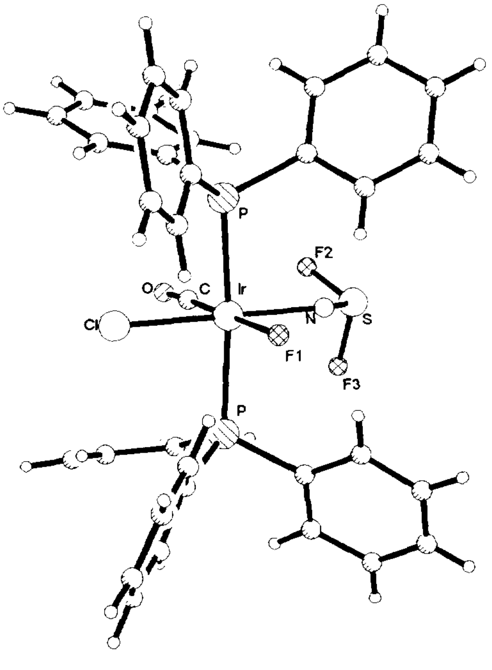
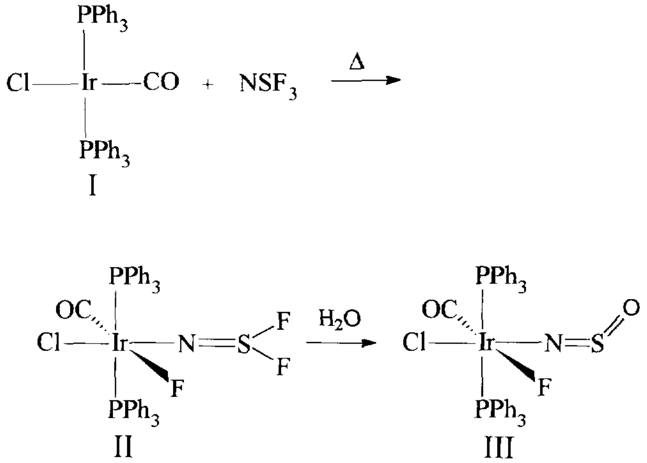


Fig. 1. X-Ray crystal structure of [Ir(CO)ClF(PPh$_3$)$_2$(NSF$_2$)].



Scheme 1.

The complex was recrystallized from CH$_2$Cl$_2$/diethyl ether and the single-crystal X-ray structure solved 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 quite small at 83.2° but this is comparable to the value of 88.3° in Hg(NSF$_2$)$_2$ [5]. The ^{19}F NMR spectrum shows two resonances as expected; δ −337.8 (t, ^{2}J(FP) = 28 Hz) ppm in the region expected for Ir^{III}–F *trans* to CO [1], and δ 121 (broad) ppm; although rather too low field for S^{IV}–F, this does lie between the values observed for TAS^{+}NSF$_2^{-}$ (δ 162.3 ppm) and Br–NSF$_2$ (δ 57.6 ppm). The ^{31}P NMR spectrum consists of a doublet δ −6.6 (^{1}J(PF) = 28 Hz) ppm. The IR spectrum in Nujol shows ν(CO) at 2022 cm^{-1}, typical for Ir^{III}–CO.

Complex **II** is extremely moisture-sensitive and undergoes ready hydrolysis to the corresponding Ir–NSO complex (**III**) (Scheme 1), characterized by NMR and IR spectroscopy, and by X-ray crystal structure.

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