

The Formation of $[\text{Ir}(\text{CO})\text{Cl}_2(\text{PEt}_3)_2(\text{NF}_2)]$ and its Rhodium Analogue: Complexes containing the Novel Difluoroamido Ligand

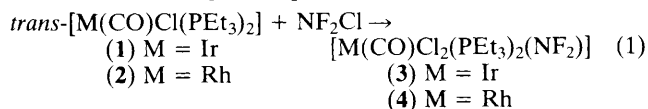
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Chlorodifluoroamine reacts at 190 K in CH_2Cl_2 with $[\text{M}(\text{CO})\text{Cl}(\text{PEt}_3)_2]$ ($\text{M} = \text{Ir}$ or Rh) to give $[\text{M}(\text{CO})\text{Cl}_2(\text{PEt}_3)_2(\text{NF}_2)]$, characterised by ^{19}F and ^{31}P n.m.r. spectroscopy (the ^{15}N derivative was also obtained for $\text{M} = \text{Ir}$); the novel complexes decompose in solution at temperatures above 240 K, the products of decomposition including N_2F_4 .

Transition metal complexes containing fluorinated ligands have been known for many years, but almost all the ligands involved contain carbon (such as CF_3^1 or C_2F_4^2) or phosphorus (such as PF_2^3 , PF_3^4 or PF_4^5). With the exception of $[\text{ReF}_5\text{NF}]^6$ there have been no reports of complexes containing fluorine bound to nitrogen. Here we present spectroscopic evidence to show that NF_2Cl undergoes oxidative addition with $[\text{M}(\text{CO})\text{Cl}(\text{PEt}_3)_2]$ to form novel complexes containing the terminal NF_2 ligand, equation (1).



The $^{31}\text{P}\text{-}\{\text{H}\}^\dagger$ n.m.r. spectrum of a solution of (1) with a slight molar excess of NF_2Cl in CH_2Cl_2 at 190 K showed that all (1) had been consumed; significant amounts of $[\text{Ir}(\text{CO})\text{Cl}_3(\text{PEt}_3)_2]$, identified by its n.m.r. parameters, had been formed, together with a new species whose n.m.r. spectra showed it to be (3). The P resonance of the new species ($\delta -5.83$ p.p.m.) was in the region associated with PEt_3 complexes of Ir^{III} , and it showed a narrow triplet coupling (18 Hz) that we assign to $^3J(\text{PF})$. The F- $\{\text{H}\}$ spectrum showed that significant amounts of N_2F_4 had been formed, and some NF_2Cl remained unreacted; in addition, we

observed a new triplet resonance ($\delta 92.3$ p.p.m., J 18 Hz) in a region associated with NF groups but substantially to high frequency of the F resonances in Ir-F or Rh-F complexes.⁷ Reaction between (2) and NF_2Cl carried out under the same conditions gave very similar results; the P- $\{\text{H}\}$ spectrum showed a resonance ($\delta 23.8$ p.p.m.) with doublet coupling to ^{103}Rh [$^1J(\text{PRh})$ 80 Hz], each line of which showed a narrower triplet splitting (22 Hz) which we assign to $^3J(\text{PF})$. The F- $\{\text{H}\}$ spectrum contained a triplet ($\delta 88.0$ p.p.m., J 22 Hz) with a narrower doublet coupling (7 Hz) that we assign to $^2J(\text{FRh})$.

To confirm that the resonances in the ^{19}F spectra around 90 p.p.m. were due to NF_2 groups, we synthesised 95%-enriched $^{15}\text{NF}_2\text{Cl}$ from $^{15}\text{NF}_2\text{CONH}_2^8$ and aqueous ClO^- ,⁹ and observed its reaction with (1) under the conditions described above. The P- $\{\text{H}\}$ spectrum showed the triplet at -5.85 p.p.m. [$^3J(\text{PF})$ 17 Hz], but each line showed an additional doublet splitting of 4 Hz, assigned to coupling between P and a single ^{15}N nucleus. In the F- $\{\text{H}\}$ spectrum, the resonance at 92.3 p.p.m. showed a wide doublet coupling of 104 Hz, which we assign to $^1J(\text{NF})$, in addition to the triplet coupling due to $^3J(\text{PF})$. The $^{15}\text{N}^\dagger$ spectrum showed a triplet ($J = 104$ Hz) at $\delta 69.2$ p.p.m.; $^2J(\text{NP})$ was not resolved because the signal : noise ratio was not good enough. The magnitude of $^1J(\text{NF})$, which should be compared with the value of 176 Hz observed for $^{15}\text{NF}_2\text{Cl}$, leaves no doubt that the fluorine atoms in the new species are bound to nitrogen. The triplet due to $^3J(\text{PF})$ in the P- $\{\text{H}\}$ spectrum shows that the species contains two equivalent fluorines; the corresponding triplet in the F- $\{\text{H}\}$ spectrum shows that it also contains two equivalent Et_3P groups. The doublet in the P- $\{\text{H}\}$ spectrum of the ^{15}N species,

[†] N.m.r. standards: all n.m.r. shifts are reported as positive to high frequency of 85% H_3PO_4 (for ^{31}P), CCl_3F (for ^{19}F), and MeNO_2 (for ^{15}N).

due to $^2J(\text{PN})$, confirms the presence of a single NF_2 group, and the doublet couplings in P and F spectra of (4) show that one metal atom is present. While we have no direct evidence for the presence of the two Cl and one CO ligands in (3) and (4), the value of $^1J(\text{PRh})$ for (4) is consistent¹⁰ with 6-co-ordinated Rh^{III} but not with 5-co-ordinated Rh^{I} , thus excluding a formulation involving a donor link between NF_2Cl and the metal. The process of oxidative addition of $\text{N}-\text{Cl}$ to the starting materials is logical and natural, even if it has not been reported before.

Unfortunately these products are very unstable thermally, and do not survive for more than a few minutes at temperatures above 240 K, though they are stable indefinitely at 190 K. A major decomposition product is N_2F_4 .

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