Novel Ligand Transformations in Cluster Complexes. Activation of C–F Bonds in a Perfluorovinyldiiron(I) Complex by Primary and Secondary Amines

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Reactions of primary amines with the perfluorovinyl complex $[\{Fe(CO)_3\}_2\{\mu\text{-}C(SMe)(CF_3)CCF_2\}]$ **1** proceed with cleavage of two C–F bonds to give **2**, whereas with secondary amines fluorine migration and C–F bond rupture afford the novel organometallic complex **3**; both **2** and **3** have been characterized by X-ray analysis.

Interest in organofluorine compounds and their technological applications owes much to the great thermal and chemical stability of these materials. The chemical modification and functionalization of perfluorocarbons thus provide a challenge for the synthetic chemist.[1] The ability of transition metal cluster compounds to produce unusual ligand transformations by multicentre processes[2] may be used to activate robust C–F bonds. A few reports on C–F activation in coordinated ligands, mainly fluoroalkenes, have appeared.[3] C–F bond activation involving more saturated substrates has been virtually unexplored, though intramolecular migration of fluorine from a CF_3 group to the metal has been observed in mononuclear η^2-vinyl molybdenum or tungsten complexes, the transition metal centre acting as an internal Lewis acid.[4] We now report the cleavage of C–F bonds in fluorovinylic ligands by a multicentre activation process, with concomitant fluorine migration along the carbon chain of the ligand, to give diiron complexes of novel neutral 6-electron donor ligands.

As shown in Scheme 1, the complex **1**[5] reacted quantitatively in chloroform solution at room temperature with the primary amine Bu^tNH_2 to give **2** and with the secondary amine Me_2NH to give **3**. These compounds were characterized by ^1H, ^{13}C and ^{19}F NMR and mass spectroscopy.† The spectroscopy of **2** is similar to that of the starting compound **1**, suggesting that the basic structure of **1** is conserved in the product of its reaction with primary amines. This conclusion has been confirmed by X-ray analysis‡ which indicates that **2** can be formulated as $[\{Fe(CO)_3\}_2\{\mu\text{-}C(CNBu^t)C(CF_3)SMe\}]$, establishing that two C–F bonds have been cleaved (Fig. 1). The C(9)–C(10) and C(10)–N(1) distances [1.344(5), 1.195(5) Å] in the C=C=NBu^t unit suggest orders of at least two for both bonds. Compound **2** may be alternatively regarded as a μ^3-C$^-$–C≡N$^+$–CMe$_3$ complex: this view would explain the shortness of the C(10)–N(1) bond but not the acuteness of the C(10)–N(1)–C(11) angle [138.0(4)°] which is closer to 120 than 180°. The Fe(1)–C(10) distance is extremely long [2.465(4) Å].

The ^{19}F NMR spectrum of **3** exhibited a doublet at δ −59.20 for the CF_3 group and a resonance at δ −152.65, indicating the presence of a single fluorine bond to a carbon atom.† Complex **3** was isolated as small, red–orange crystals which proved on X-ray analysis‡ to contain $[\{Fe(CO)_3\}_2\{\mu\text{-}C(NMe_2)CFC(CF_3)SMe\}]$, thus establishing both that one C–F

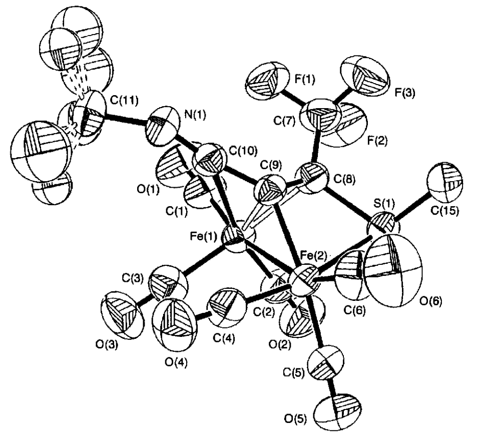


Fig. 1 View of a molecule of complex **2**. Hydrogen atoms are omitted and 50% probability ellipsoids are displayed. Each of the three methyl groups attached to C(11) is disordered over two sites. Selected bond distances (Å) and angles (°) are as follows: Fe(1)–Fe(2) 2.591(1), Fe(1)–C(8) 2.020(4), Fe(1)–C(9) 2.004(4), Fe(1)–C(10) 2.465(4), Fe(2)–S(1) 2.324(1), Fe(2)–C(9) 1.970(3), C(10)–N(1) 1.195(5), N(1)–C(11) 1.475(6), C(7)–C(8) 1.493(5), C(8)–C(9) 1.435(5), C(9)–C(10) 1.344(5), C(9)–C(10)–N(1) 160.8(4), C(10)–N(1)–C(11) 138.0(4).

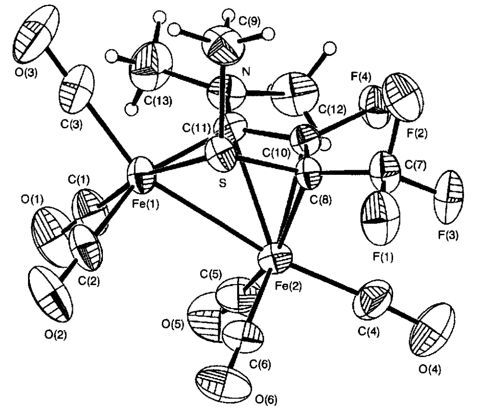
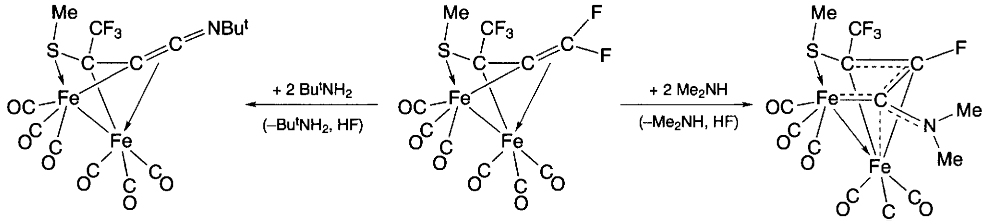


Fig. 2 View of a molecule of complex **3**. Hydrogen atoms are shown as spheres of arbitrary radius but for other atoms 30% probability ellipsoids are displayed. Selected bond distances (Å) are as follows: Fe(1)–Fe(2) 2.643(1), Fe(1)–S(1) 2.262(2), Fe(1)–C(11) 1.998(4), C(7)–C(8) 1.493(6), C(8)–C(10) 1.435(5), C(10)–C(11) 1.405(5), Fe(2)–C(8) 2.007(4), Fe(2)–C(10) 2.033(4), Fe(2)–C(11) 2.379(4), N–C(11) 1.351(5), N–C(12) 1.475(6), N–C(13) 1.454(6).

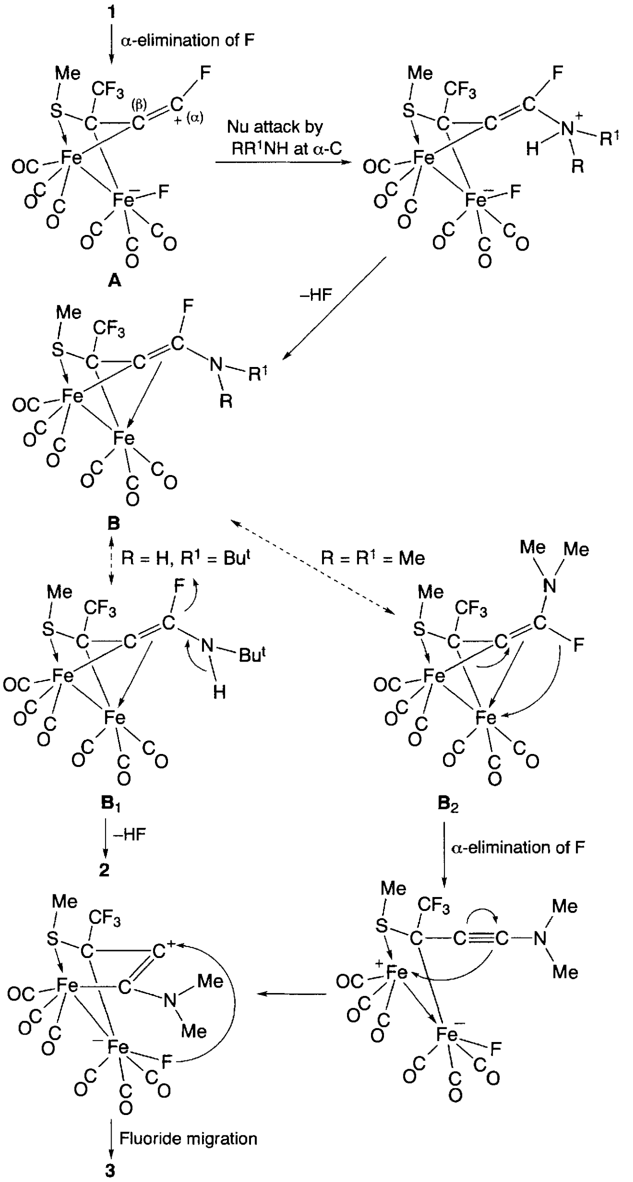


2 **1** **3**

Scheme 1

bond has been cleaved and that the remaining vinylic fluorine substituent has undergone a 1,2-shift from C(8) to C(10) (Fig. 2). In **3** the sulfur and the three carbon atoms C(8), C(10) and C(11) are ligated to the iron frame; the nitrogen atom has a planar environment. In order to achieve a count of 18 electrons around each iron the complex may formally be regarded as a metallated Fe(1)=C(11)–C(10)=C(8) butadiene-like unit π-bonded to Fe(2); however, there is extensive electron delocalization along the Fe(1)–C(11)–C(10)–C(8) chain, as shown by the sequence of distances 1.998(4), 1.405(5) and 1.435(5) Å. C(11) is in conjugation with its NMe_2 substituent [C(11)–N 1.351(5) Å] and the Fe(2)–C(11) interaction [2.379(4) Å] is thereby greatly weakened.

The formation of **3** is an unusual example of a C–F bond cleavage reaction and fluorine migration along a carbon chain under mild conditions to give a novel ligand. A plausible mechanism to account for the formation of **2** and **3** from reactions of **1** with RR^1NH is outlined in Scheme 2. It is based on the possible role of a vacant coordination site on Fe(2) in **1**. This centre acts as an internal Lewis acid in the α-elimination of fluoride to generate **A** which is then activated towards attack at the α-carbon by the amine RR^1NH. Subsequent elimination of HF affords the intermediate **B**. When R = H and $R^1 = Bu^t$ a second elimination of HF gives the observed product **2**. When $R = R^1 = Me$ a similar elimination of a second molecule of HF from **B** is not possible. However, a second α-elimination of fluoride onto Fe(2) and concomitant internal rearrangement gives a zwitterionic intermediate which undergoes an internal migration of the fluoride to the β-carbon to afford complex **3**. Evidence for the formation of HF has been obtained; it has been characterized in the form of the corresponding amine hydrofluoride in the reactions of **1** with Me_2NH and Bu^tNH_2.



Scheme 2

The results described here suggest that metal-catalysed transformations of fluorinated organic molecules may be considered as a practical synthetic tool despite the great strength of the carbon–fluorine bond.

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Footnotes

† *Selected spectroscopic data* for **2**: ^{19}F NMR ($CDCl_3$) δ −65.58 (s, CF_3). MS *m/z*: 503 (M^+). For **3**: ^{19}F NMR ($CDCl_3$) δ −152.65 (q, C*F*, $^4J_{F-F}$ 12 Hz), −59.20 (d, C*F*$_3$, $^4J_{F-F}$ 12 Hz). MS *m/z*: 495 (M^+).

‡ *Crystal data* for **2** and **3**: For both compounds, crystallographic measurements were made at room temperature on an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation, λ = 0.71073 Å, a graphite monochromator and ω/2θ scans. The structures were solved by direct methods and refined on F^2 by the full-matrix least-squares procedure. For **2**: $C_{15}H_{12}F_3Fe_2NO_6S$, $M = 503.01$, monoclinic, space group $P2_1/c$, $a = 15.027(1)$, $b = 9.704(1)$, $c = 15.295(1)$ Å, $\beta = 116.79(1)°$, $V = 1991.0(3)$ Å^3, $D_{calc} = 1.678$ g cm^{-3}, $Z = 4$. For reflections with $\theta < 27.5°$, $R(F) = 0.052$ for 2685 observed reflections [$I > 2\sigma(I)$] and $wR(F^2) = 0.137$ for all 3922 reflections used in refinement. For **3**: $C_{13}H_9F_4Fe_2NO_6S$, $M = 494.97$, monoclinic, space group $P2_1/c$, $a = 9.871(2)$, $b = 10.621(1)$, $c = 17.248(2)$ Å, $\beta = 94.81(1)°$, $V = 1801.8(4)$ Å^3, $D_{calc} = 1.825$ g cm^{-3}, $Z = 4$. For reflections with $\theta < 27°$, $R(F) = 0.042$ for 2231 observed reflections [$I > 2\sigma(I)$] and $wR(F^2) = 0.099$ for all 3535 reflections used in refinement. 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.

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