Letters to the Editor

1-(2-Chloro-1,1,1,3,3,3-hexafluoroprop-2-yl)ferrocene as the first stable representative of chloromethylferrocenes

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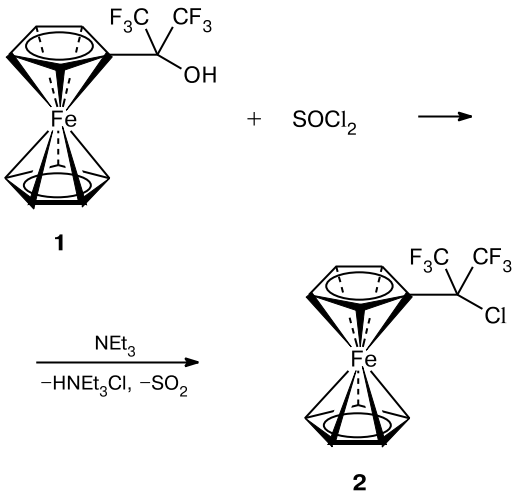
Chloromethylferrocene, as well as its α-substituted derivatives, are unstable.[1—3] 1-(1-Chloroethyl)ferrocene was synthesized by the addition of HCl to vinylferrocene and characterized.[4] However, it has been later reported that this compound undergoes decomposition within several hours.[5] Attempts to synthesize chloromethylferrocene in the pure form by either the reaction of ferrocenylmethanol with PCl_3 (see Ref. 3) or the reaction of ferrocene with dichloromethane[6] have failed. Hence, this compound is generally used *in situ* in reactions.[7]

We synthesized the first stable representative of this series, *viz.*, 1-(2-chloro-1,1,1,3,3,3-hexafluoroprop-2-yl)ferrocene (**2**), by the reaction of 1-ferrocenyl-1-trifluoromethyl-2,2,2-trifluoroethanol (**1**)[8] with thionyl chloride in toluene in the presence of triethylamine (Scheme 1).

Scheme 1



The OH group is easily replaced by the chlorine atom in the reaction at an equimolar ratio of the reagents at −5—0 °C. The conversion of **1** occurs almost immediately and is completed with the addition of the last drop of thionyl chloride (TLC data) to give compound **2** in quantitative yield. After the conventional treatment of the reaction mixture with a 5% sodium carbonate solution and water, the drying of the organic layer with anhydrous $CaCl_2$, and the removal of the solvent, we obtained a spectrally pure red-orange oil, which spontaneously crystallized upon cooling.

Apparently, the stability of chloromethylferrocene **2**, unlike other analogs, is associated with the *I* effect of CF_3 groups.

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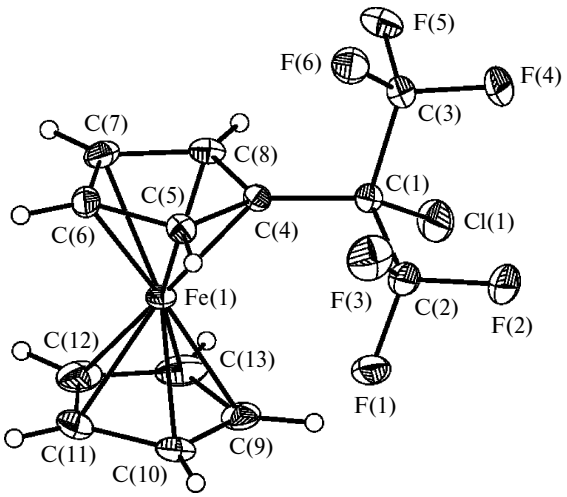

Fig. 1. Molecular structure of compound **2**. The atoms are represented as probability displacement ellipsoids ($p = 0.5$).

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance^{TM} 600 instrument (600.22 and 150.93 MHz) in $CDCl_3$, and the ^{19}F NMR spectrum was measured on a Bruker Avance^{TM} 300 instrument (282.40 MHz); Me_4Si was used as the internal standard (^{1}H and ^{13}C); CF_3CO_2H (^{19}F), as the external standard. The mass spectrum was obtained on a Finnigan MAT INCOS 50 quadrupole mass spectrometer using a direct inlet system; the ionization energy was 70 eV.

1-(2-Chloro-1,1,1,3,3,3-hexafluoroprop-2-yl)ferrocene (2). The yield was 95% (preparative), m.p. 72—73 °C (petroleum ether). ^{1}H NMR, δ: 4.30 (br.s, 5 H, C_5H_5); 4.35 (br.s, 2 H, 2 CH); 4.47 (br.s, 2 H, 2 CH). ^{19}F NMR, δ: –7.24 s. ^{13}C NMR, δ: 68.86 (2 CH—Cp); 69.27 (2 CH—Cp); 70.15 (5 CH—Cp); 70.23 (q, C*—CF_3, $^2J_{C,F} = 31$ Hz); 79.62 (C*—$C(CF_3)_2Cl$ (Cp)); 121.75 (q, CF_3, $^1J_{C,F} = 287$ Hz). MS, *m/z* (I_{rel} (%)): 370, 372 (3 : 1) $[M]^+$ (15), 335 (4), 316 (3), 214 (6), 195 (33), 176 (10), 156 (100), 145 (44), 140 (10), 91 (42), 69 (7), 56 (5). Found (%): C, 41.98; H, 2.29; Cl, 9.17; F, 30.54. $C_{13}H_9ClF_6Fe$. Calculated (%): C, 42.14; H, 2.45; Cl, 9.57; F, 30.77.

According to the X-ray diffraction data, the ferrocenyl moiety has an almost eclipsed conformation (the angle of rotation of the Cp rings with respect to each other is 6.5°, the angle between the planes of the Cp rings is 177.60(18)°). The average Fe—C distance is 2.043 Å; the Fe(1)—C(4) bond is slightly shortened (2.025(1) Å), which is apparently attributed to the presence of the electron-withdrawing substituent. The introduction of the $CCl(CF_3)_2$ group also leads to a slight shortening of the Fe—centroid distance for the substituted Cp ring (1.639(2) Å *versus* 1.647(2) Å). The distribution of the C—C bond lengths in the Cp rings and the C(1)—C(4) bond length (1.500(2) Å) are similar to those observed in (1,1,1,3,3,3-hexafluoro-2-hydroxyisopropyl)ferrocene.[9] The isopropyl moiety deviates from the plane of the Cp ring toward the metal atom by 0.179(3) Å. In the crystal structure, the molecules are held together by weak C—H...F (C...F, 3.2—3.6 Å) and C—H...π (C...C, 3.6—3.8 Å) interactions.

The single-crystal X-ray diffraction study of compound **2** was carried out on a Bruker Smart APEX II diffractometer equipped with a CCD detector.

At 100 K, crystals of **2** are monoclinic, space group $P2_1/c$, $a = 10.5086(6)$ Å, $b = 7.2784(4)$ Å, $c = 17.3020(11)$ Å, $\beta = 97.6395(11)°$, $V = 1311.61(13)$ Å^3, $Z = 4$ ($Z' = 1$), $d_{calc} = 1.876$ g cm^{-3}, $\mu(MoK\alpha) = 1.70$ cm^{-1}, $F(000) = 736$. The intensities of 8655 reflections were measured at 100 K on a SMART APEX II CCD diffractometer ($\lambda(Mo\text{-}K\alpha) = 0.71072$ Å, ω-scanning technique, $2\theta < 60°$); 3827 independent reflections ($R_{int} = 0.0182$) were used in the refinement. The crystal structure was solved by direct methods and refined anisotropically by the full-matrix least-squares method based on F^2_{hkl}. The hydrogen atoms were positioned geometrically and refined isotropically with fixed thermal parameters $U_{iso} = 1.2C_{iso}$. The final R factors for **2** are $R_1 = 0.0268$ (calculated based on F_{hkl} for 3360 reflections with $I > 2\sigma(I)$), $wR_2 = 0.0712$ (calculated based on F^2_{hkl} for all 3827 reflections), GOOF = 1.048. All calculations were carried out with the use of the SHELXTL 5.10 complex package.[10]

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