

Preliminary communication

X-RAY STRUCTURE OF $\text{Fe}\{\text{C}(\text{CF}_3)_2(\text{OH})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$, A COMPLEX CONTAINING A SUBSTITUTED HYDROXYMETHYL LIGAND

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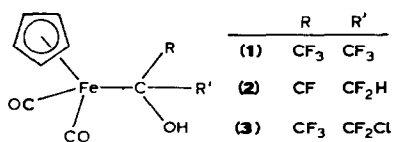
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Summary

An X-ray structure determination on $\text{Fe}\{\text{C}(\text{CF}_3)_2(\text{OH})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$, obtained by protonating the product from $\text{Na}[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ and $(\text{CF}_3)_2\text{CO}$, showed the crystal to contain discrete molecules. There are substantial intramolecular $\text{OH}\dots\text{FCF}_2$ bonds but only weak intermolecular $\text{OH}\dots\text{O}$ interactions. Important distances are: $\text{Fe}-\text{C}$ 2.060(6), $\text{C}-\text{CF}_3$ 1.505(9), $\text{C}-\text{OH}$ 1.435(7), $\text{CF}\dots\text{HO}$ 2.131(6), 2.485(6) Å.

Reactions between polyfluoroacetones and $\text{Na}[\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ afford low yields of the substituted hydroxymethyl complexes $\text{Fe}\{\text{CRR}'(\text{OH})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ ($\text{R} = \text{R}' = \text{CF}_3$ (**1**), $\text{R} = \text{CF}_3$, $\text{R}' = \text{CF}_2\text{H}$ (**2**) and $\text{R} = \text{CF}_3$, $\text{R}' = \text{CF}_2\text{Cl}$ (**3**)) after protonation of the reaction mixture [1]. When first made, these were the first examples of complexes containing σ -bonded hydroxyalkyl ligands; current interest in non-fluorinated hydroxymethyl analogues centres on their intermediacy in the reduction of coordinated CO to methanol or methane in models of the Fischer–Tropsch reaction. A surprising feature of the chemistry of **1** was the lack of reactivity of the hydroxy group. Normally, fluorinated alcohols show enhanced acidity over their non-fluorinated analogues, but no reaction occurred between **1** and LiBu/MeI , CH_2N_2 or $\text{HN}(\text{SiMe}_3)_2$, although H/D exchange occurred in D_2O . We have carried out an X-ray structural study of **1** to determine whether there is any stereochemical reason for its inertness; to our knowledge, this is the second example of a hydroxymethyl-transition metal complex to be structurally characterised, after $[\text{IrH}(\text{CH}_2\text{OH})(\text{PMe}_3)_4][\text{PF}_6]$ [2].



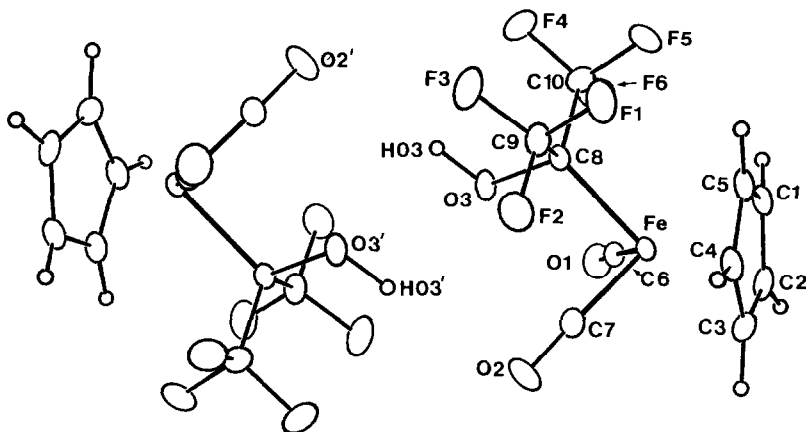


Fig. 1. Centrosymmetrically related molecules in $\text{Fe}\{\text{C}(\text{CF}_3)_2(\text{OH})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ (**I**) showing the numbering scheme used. Hydrogen atoms are labelled according to atom to which they are bonded. Bond distances: Fe–C(8) 2.060(6), Fe–CO 1.755(7), Fe–C(cp) 2.097 (av.), C(8)–CF₃ 1.505(9), C(8)–OH 1.435(7) Å. Bond angles: C(6)–Fe–C(7) 92.3(3), C(6)–Fe–C(8) 89.9(3), C(7)–Fe–C(8) 89.3(3)°, Fe–C(8)–CF₃ 113.8(4), Fe–C(8)–O(3) 107.3(4), C(9)–C(8)–C(10) 109.5(5), CF₃–C(8)–O(3) 106.2(5), 107.3(4)°.

Crystal data: $\text{Fe}\{\text{C}(\text{CF}_3)_2(\text{OH})\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5) \equiv \text{C}_{10}\text{H}_6\text{F}_6\text{FeO}_3$, $M = 344.0$, monoclinic, space group $P2_1/n$ (variant of $P2_1/c$, C_{2h}^5 , No. 14), a 7.920(4), b 11.831(3), c 12.682(8) Å, β 98.96(4)°, U 1173.8 Å³, $Z = 4$, μ 13.21 cm⁻¹, max/min transmission factors for analytical absorption correction 0.7637 and 0.6115, respectively.

A total of 1997 ($1 \leq \theta \leq 22.5^\circ$) reflections were measured on an Enraf–Nonius CAD4F diffractometer with the use of Mo- K_α (graphite monochromator) radiation, λ 0.71073 Å, and the $\omega/2\theta$ scan technique. No decomposition of the crystal occurred during the data collection. Corrections were applied for Lorentz and polarization effects and for absorption [3]. Of the reflections measured, 1543 were unique and of these 1263 satisfied the $I \geq 2.5\sigma(I)$ criterion.

The structure was solved from the interpretation of the Patterson synthesis and refined by a full-matrix least-squares procedure [3]. Hydrogen atoms were located from a difference map. The refinement converged with R 0.060, R_w 0.061 for $w = [\sigma^2(F) + 0.0003|F|^2]^{-1}$ *. The numbering scheme used and selected bond parameters are given in Fig. 1.

As can be seen from the Figure, two centrosymmetrically related molecules (centred about the site 0, 1/2, 1/2) form a loosely associated dimer. As found for many other complexes of this type, the coordination about iron is best described as octahedral [4], with the Fe–C(6), Fe–C(7), and Fe–C(8) vectors being almost perfectly orthogonal. Of the Fe–C(cp) distances (range 2.084–2.120(6), av. 2.097 Å), the longest separation is to C(5), the ring carbon nearest (and between) the two CF₃ groups. A steric origin for the asymmetry in the Fe–C₅ ring interaction seems likely.

* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The Fe–C(sp^3) distance is 2.060(6) Å, which is not significantly different from values of 2.066(6) Å in FeMe(CO)(PR₃)(η -C₅H₅) (PR₃ = PPh₂{NMe(CHMePh)}) [5] or 2.06(2) Å in Fe(CH₂CO₂H)(CO)₂(η -C₅H₅) (a hydrogen-bonded dimer) [6]. There do not appear to be any measurements on complexes containing iron bonded to sp^3 -hybridised carbons bearing F, CF₃ or CN groups; the Fe–C bond length in Fe(CH₂CO₂men)(CO)(PPh₃)(η -C₅H₅) (men = (–)-menthyl) is 2.106(13) Å [7]. The distortions of tetrahedral geometry around the α -carbon [C(8)] e.g. C(9)–C(8)–C(10) 109.5(5), Fe–C(8)–CF₃ 113.8(4), Fe–C(8)–O(3) 107.3(4)°, are consistent with the presence of the bulky CF₃ groups.

While there is only a weak interaction between the two molecules of **1** (closest contacts H(03)...H(03') (2.562 Å), H(03)...O(3') (2.616 Å) and H(03)...O(2') (2.599 Å)), the hydroxy hydrogen atom lies between two F atoms, one from each CF₃ group. The short H(03)...F(3) and H(03)...F(4) contacts of 2.131 and 2.485 Å, respectively, indicate that there is a substantial degree of hydrogen-bonding between these atoms. It is likely that the lack of reactivity of **1** stems from this O–H...F interaction, coupled with the strongly electron-donating character of the Fe(CO)₂(η -C₅H₅) group which counteracts the normal activating effect of the CF₃ groups on the hydroxy group. In addition, approach to the hydroxy group is well shielded by the three bulky groups attached to C(8).

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