

Influence of the ferrocene substituent on C–O bonds at the α position. Results from low-temperature X-ray structural studies

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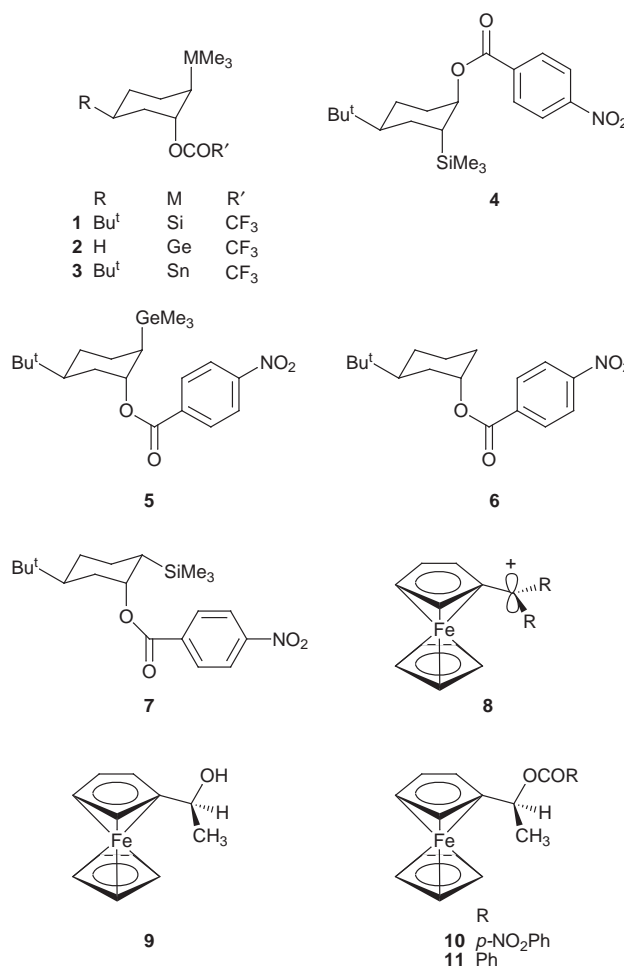
Results from structural studies have demonstrated that the ferrocenyl substituent lengthens C–O bonds at the α position provided that the C–O bond is antiperiplanar with respect to the C–Fe bond, these structural effects parallel the known solution behaviour of α -ferrocenyl esters.

The interaction of electron-rich C–M metal σ bonds with electron-deficient centres in organic molecules manifests in many interesting chemical and physical properties.^{1–10} The C–Si, C–Ge and C–Sn bonds are examples of strong σ donors which have a remarkable stabilising effect on carbenium ions in β positions. The strong donor abilities of these bonds are apparent from the Hammett σ^+ values for the R_3MCH_2 substituted benzene derivatives which are -0.62 , -0.63 and -0.82 for $M = Si$, Ge and Sn respectively.^{11,12} The magnitude of stabilisation of β positive charge by these substituents is exemplified by the relative rates of unimolecular solvolysis of the β -trimethylmetal esters **1–3** which are 10^{12} : 10^{13} : $\gg 10^{14}$ relative to the corresponding non-metallated analogs.^{6–9} The strong dependence of the solvolysis rates upon the dihedral angle between the Group 4 metal substituent and the departing leaving group (Lg) whereby maximum effects are seen when the M–C–C–Lg dihedral angle is 180° and minimum effects are observed when this angle is 90° , is consistent with hyperconjugation between the C–M σ bonding orbital and the carbocation p orbital being the important mode of stabilisation in these systems.¹⁰ In addition to these large enhancements of reactivity seen in β -trimethylmetal esters towards unimolecular solvolysis, significant effects on the ground-state structure are also seen. For example the C (alkyl)–O (ester) bond is significantly lengthened, and hence weakened, by the presence of the β Group 4 substituent;^{13–16} the C (alkyl)–O (ester) bond distances in the β -trimethylsilyl and β -trimethylgermyl *p*-nitrobenzoates **4** and **5** are $1.483(3)$ ¹³ and $1.485(2)$ ¹⁵ Å respectively which are both significantly lengthened compared with the unsubstituted analog **6** for which the corresponding distance is $1.473(2)$ Å.¹⁶ The origin of the bond lengthening in **4** and **5** is believed to be the σ – σ^* interaction between the high lying C–M ($M = Si$ or Ge) σ orbital and the vacant low lying C–O σ^* orbital.

Consistent with this interpretation is the absence of any significant effects on the C–O bond distance in the *gauche* β -silyl *p*-nitrobenzoate ester **7**,¹³ for which σ_{C-Si} – σ^*_{C-O} overlap is negligible. The ferrocenyl substituent is also a strong donor substituent as is apparent from the σ_p^+ constant for the ferrocenyl substituent which has been determined to be -0.70 from both the carbonyl stretching frequencies of substituted acetophenones, and from the rates of unimolecular solvolyses of substituted phenethyl chlorides.¹⁷ α -Ferrocenylcarbenium ions (e.g. **8**) have a similar stability to the triphenylmethyl cation,¹⁸ and it is suggested¹⁷ that this remarkable stability is due mainly to carbon–iron hyperconjugation. As part of our studies on the effects of strong donor substituents on ground-state structures, we were interested to establish whether a

ferrocenyl substituent in α -ferrocenyl alcohols and esters would result in any significant effects on the C (alkyl)–O (ester) bond distance in the ground state. To this end we carried out a low-temperature X-ray structural study of 1-ferrocenylethanol **9** and its esters **10** and **11**.

1-Ferrocenylethanol¹⁹ was prepared by lithium aluminium hydride reduction of acetyl ferrocene,²⁰ and the ester derivatives were prepared by reaction of 1-ferrocenylethanol with the appropriate acid chloride in pyridine.[‡]



[‡] Complex **10**. A solution of complex **9** (0.337 g, 1.3 mmol) stirred in py (2 ml) at 0 °C was treated with *p*-nitrobenzoyl chloride (0.37 g, 2 mmol). The resulting mixture was stirred at 0 °C under N₂ for 3 h then quenched by the addition of water (0.5 ml) and stirred for a further 15 min. The mixture was diluted with water (20 ml) and extracted with diethyl ether (3 × 30 ml). The combined extracts were washed sequentially with HCl (1 M, 20 ml), sodium bicarbonate (10%, 20 ml) and water (20 ml), dried (MgSO₄) and evaporated under reduced pressure to an orange solid. Recrystallisation from ether–pentane gave **10** as yellow plates (0.38 g 76%), m.p. 138–140 °C (decomp.).

Complex **11**. Prepared as above using complex **9** (0.2 g, 0.87 mmol), py (1.5 ml) and benzoyl chloride (0.18 g, 1.28 mmol) to give an orange solid (0.2 g, 70%). Recrystallisation from pentane gave **11** as a mixture of rods (m.p. 75–76 °C) and plates (m.p. 74–75 °C).

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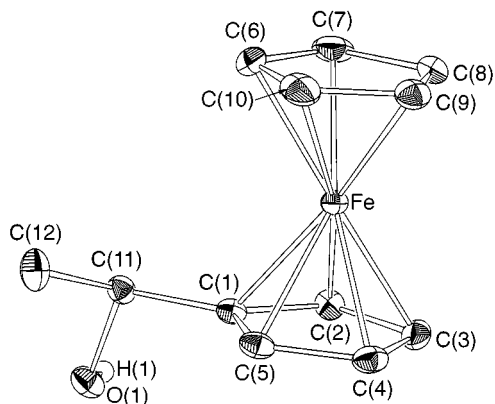


Fig. 1 Thermal ellipsoid plot for compound **9**. Ellipsoids are at the 30% probability level

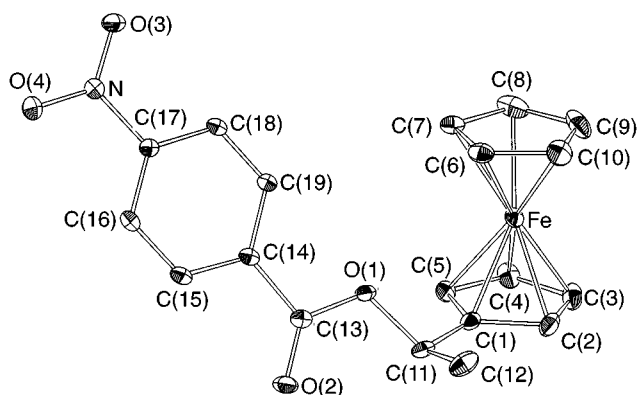


Fig. 2 Thermal ellipsoid plot for compound **10**. Details as in Fig. 1

The thermal ellipsoid plot for 1-ferrocenylethanol **9**, the *p*-nitrobenzoate derivative **10**, and the two crystal modifications for the benzoate ester **11** (**11a** and **11b**) are shown in Figs. 1–4 respectively. Selected bond distances, angles, and dihedral angles are presented in Table 1. In the alcohol **9** and the two crystal modifications **11a** and **11b** the Fe–C(1)–C(11)–O(1) dihedral angle (Table 1) is close to antiperiplanar (the ester substituent is *exo* to the ferrocenyl substituent), whereas for the *p*-nitrobenzoate derivative **10** the Fe–C(1)–C(11)–O(1) dihedral angle is close to *gauche* (the ester substituent is *endo* to the ferrocenyl substituent).

Carbon–oxygen bond distances in the structural fragment R₃C–OR depend on the substituents attached to the carbon and upon the electron demand of the oxygen substituent (OR) as indicated by the p*K*_a value for the parent acid ROH.^{21,22} A linear relationship between C–OR bond distance and p*K*_a for secondary alcohols and esters has been determined as: $r(\text{C–OR}, \text{\AA}) = (1.475 - 2.90) \times 10^{-3} \text{ p}K_a(\text{ROH})$. This equation

§ Crystal data for **9**: C₁₂H₁₄FeO, *M* = 230.08, tetragonal, space group *I*4₁*cd* (no. 110), *a* = 23.132(2), *b* = 7.2810(10), *c* = 7.5720(10) Å, *U* = 4051.7(7) Å³, *Z* = 16, μ = 1.449 mm^{−1}, *T* = 130.0 K, *R*1 = 0.0225 for 1476 unique data with *I* > 2σ(*I*).

Crystal data for **10**: C₁₉H₁₇FeNO₄, *M* = 379.19, triclinic, space group *P*1̄ (no. 2), *a* = 7.325(2), *b* = 7.2810(10), *c* = 17.488(4) Å, α = 88.76(2), β = 79.26(2), γ = 61.31(2)°, *U* = 801.4(3) Å³, *Z* = 2, μ = 0.966 mm^{−1}, *T* = 130.0 K, *R* = 0.0377 for 3777 unique data with *I* > 2σ(*I*).

Crystal data for **11a**: C₁₉H₁₈FeO₂, *M* = 334.18, monoclinic, space group *P*2₁/*c* (no. 68), *a* = 9.415(2), *b* = 19.390(4), *c* = 8.845(3) Å, β = 109.87(2)°, *U* = 1518.6(7) Å³, μ = 0.997 g cm^{−3}, *T* = 130.0 K, *R* = 0.0362 for 2144 unique data with *I* > 2σ(*I*).

Crystal data for **11b**: C₁₉H₁₈FeO₂, *M* = 334.18, monoclinic, space group *P*2₁/*c* (no. 68), *a* = 7.8523(9), *b* = 9.7282(9), *c* = 20.154(3) Å, β = 92.720(10)°, *U* = 1537.8(3) Å³, μ = 0.984 g cm^{−3}, *T* = 130.0 K, *R* = 0.0336 for 2936 unique data with *I* > 2σ(*I*). CCDC reference number 186/932. See <http://www.rsc.org/suppdata/dt/1998/1269/> for crystallographic files in .cif format.

Table 1 Selected distances (Å), angles (°) and dihedral angles (°) for **9**, **10**, **11a** and **11b**

	9	10	11a	11b
O(1)–C(11)	1.444(3)	1.471(2)	1.483(3)	1.481(2)
C(1)–C(11)	1.509(3)	1.498(3)	1.500(4)	1.498(2)
Fe–C(1)	2.038(2)	2.042(2)	2.036(3)	2.0414(17)
C(11)–C(1)–Fe	128.00(14)	129.76(13)	124.08(18)	126.96(12)
O(1)–C(11)–C(1)	109.7(2)	107.82(14)	105.5(2)	108.56(14)
Fe–C(1)–C(11)–C(12)	−73.8(3)	−75.8(2)	70.8(3)	63.4(2)
Fe–C(1)–C(11)–O(1)	165.88(13)	45.2(2)	−169.99(16)	179.98(11)

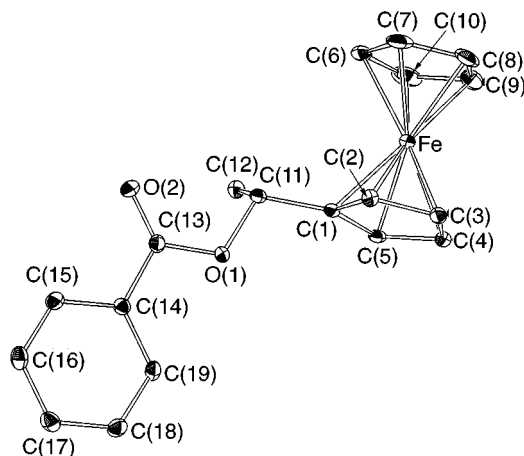


Fig. 3 Thermal ellipsoid plot for compound **11a**. Details as in Fig. 1

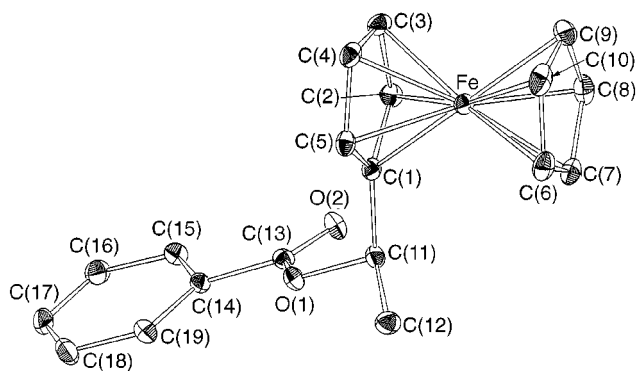
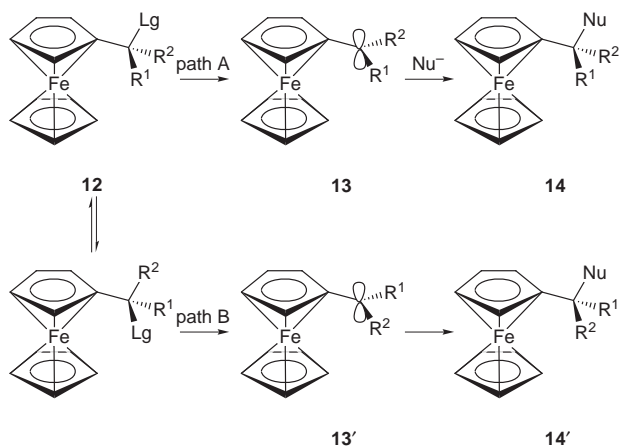


Fig. 4 Thermal ellipsoid plot for compound **11b**. Details as in Fig. 1

leads to the prediction that a secondary C–OH distance should be 1.428 Å, a secondary C–OCOPh distance 1.463 Å and a secondary C–OCOC₆H₄NO₂ distance 1.465 Å (using p*K*_a values of H₂O, PhCO₂H and *p*-NO₂C₆H₄CO₂H as 16, 4.2, 3.42 respectively). Comparison between the predicted C–OR bond distances and those which are observed for structures **9–11** (Table 1) reveal that those structures which have the OR substituent *exo* with respect to the ferrocene substituent have C–O bond distances which are significantly lengthened relative to the predicted value. For example the observed C–O bond distance is the alcohol **9** is 1.444(3) Å which is 0.016 Å longer than predicted for a typical secondary alcohol (1.428 Å). In the more highly electron demanding benzoate derivatives **11a** and **11b** the C–OCOPh distances are 1.483(3) and 1.481(2) Å respectively; while these do not differ from each other, they are lengthened even further (0.019 Å) relative to that predicted (1.463 Å) for a secondary alkylbenzoate ester. In contrast, in the *p*-nitrobenzoate ester derivative **10**, for which the Fe–C–C–O dihedral angle is close to *gauche*, the observed C–O bond distance is



Scheme 1 Lg = leaving group, Nu = nucleophile

1.471(2) Å which is within experimental error of the predicted distance which is 1.465 Å. These structural effects whereby significant C–O bond lengthening (and hence weakening) is observed in the antiperiplanar structures **9**, **11a** and **11b** but no significant lengthening is observed for the *gauche* structure **10** suggest the presence of a $\sigma_{\text{C-Fe}}-\sigma^*_{\text{C-O}}$ interaction between the C(1)–Fe(11) σ bonding orbital and the C(11)–O(1) σ^* antibonding orbital. These structural effects are consistent with the stereospecificity which is observed in the unimolecular solvolysis of optically active α -ferrocenyl alkyl derivatives which occur with greater than 99% retention of configuration.^{18,23,24} Solvolysis of the chiral α -ferrocenyl substituted ester **12** can conceivably follow either of the two pathways shown in Scheme 1. Reaction of the substrate **12** from the *exo* conformation (path A) provides the chiral carbocation **13** which does not rotate due to $\sigma_{\text{C-Fe}}-\text{p}$ hyperconjugation, capture of this carbocation by a nucleophile preferentially from the *exo* face would give the product **14** with retention of configuration. In contrast, reaction from the *endo* conformation (path B) would result in the configuration being inverted (if capture occurs from the *exo* direction) with the formation of **14'**. The observation of retention of configuration in the solvolyses of α -ferrocenyl esters suggests that the reaction proceeds *via* path A. This is readily

understood on the basis of these structural results which predict that the C–O bond of esters in the *exo* conformation is weaker and hence more likely to react than esters in the *endo* conformation.

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