DALTON
COMMUNICATION

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

Brett R. Pool, Chee-Chung Sun and Jonathan M. White *,†

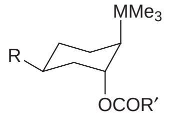
School of Chemistry, The University of Melbourne, Parkville, VIC 3052, Australia

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.

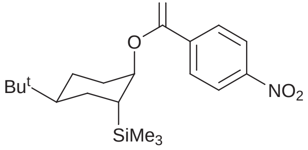
The interaction of electron-rich C–M metal σ bonds with electron-deficient centres in organic molecules manifests in many interesting chemical and physical properties.[1–10] The C–Si, C–Ge and C–Sn bonds are examples of strong σ donors which have a remarkable stabilising effect on carbenium ions in β 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 $10^{12}:10^{13}:\geqslant 10^{14}$ 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 suggested[17] 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**.

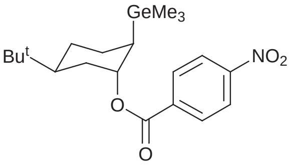
1-Ferrocenylethanol[19] was prepared by lithium aluminium hydride reduction of acetyl ferrocene,[20] and the ester derivatives were prepared by reaction of 1-ferrocenylethanol with the appropriate acid chloride in pyridine.‡



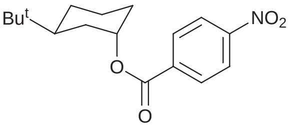
	R	M	R′
1	Bu^t	Si	CF$_3$
2	H	Ge	CF$_3$
3	Bu^t	Sn	CF$_3$



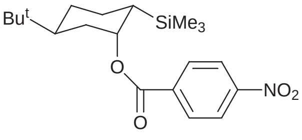
4



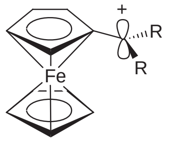
5



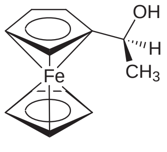
6



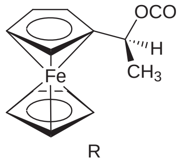
7



8



9



	R
10	*p*-NO$_2$Ph
11	Ph

---

‡ 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 N_2 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 ($MgSO_4$) 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).

† E-Mail: J.White@mail.chemistry.unimelb.edu.au

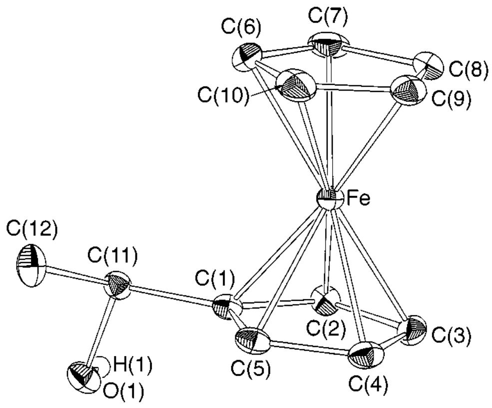


Fig. 1 Thermal ellipsoid plot for compound **9**. Ellipsoids are at the 30% probability level

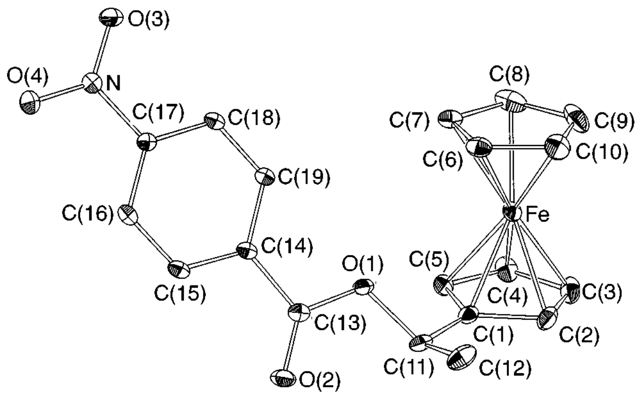


Fig. 2 Thermal ellipsoid plot for compound **10**. Details as in Fig. 1

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).

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)

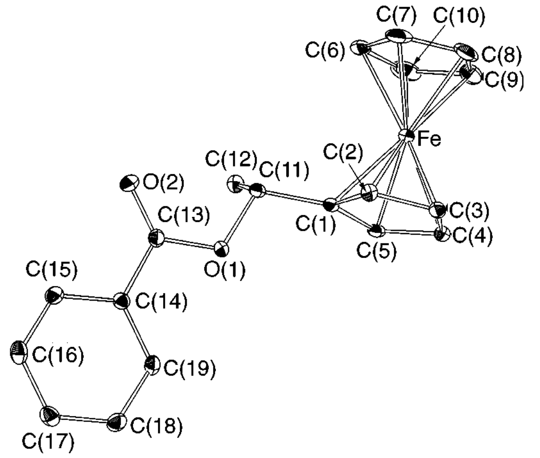


Fig. 3 Thermal ellipsoid plot for compound **11a**. Details as in Fig. 1

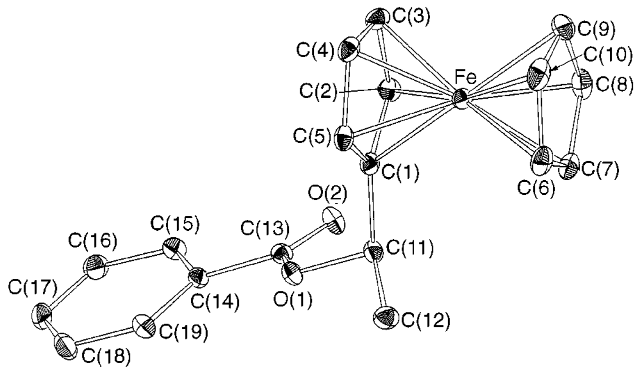


Fig. 4 Thermal ellipsoid plot for compound **11b**. Details as in Fig. 1

Carbon–oxygen bond distances in the structural fragment R_3C–OR depend on the substituents attached to the carbon and upon the electron demand of the oxygen substituent (OR) as indicated by the pK_a value for the parent acid ROH.[21,22] A linear relationship between C–OR bond distance and pK_a for secondary alcohols and esters has been determined as: r(C–OR, Å) = (1.475–2.90) × 10^{-3} pK_a (ROH). This equation 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–$OCOC_6H_4NO_2$ distance 1.465 Å (using pK_a values of H_2O, $PhCO_2H$ and *p*-$NO_2C_6H_4CO_2H$ 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–OH 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

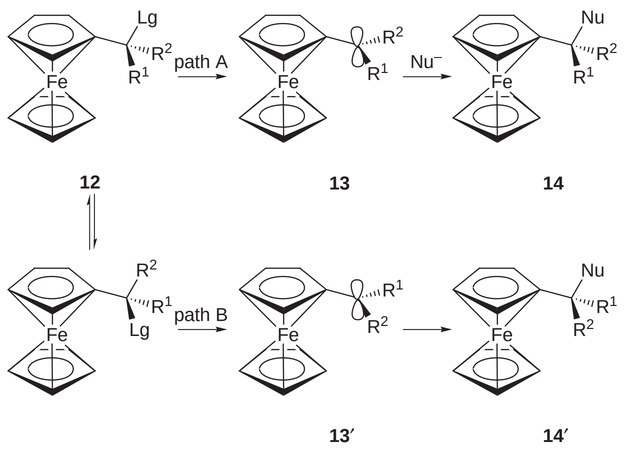
---

§ Crystal data for **9**: $C_{12}H_{14}FeO$, $M = 230.08$, tetragonal, space group $I4_1cd$ (no. 110), $a = 23.132(2)$, $c = 7.5720(10)$ Å, $U = 4051.7(7)$ Å^3, $Z = 16$, $\mu = 1.449$ mm^{-1}, $T = 130.0$ K, $R1 = 0.0225$ for 1476 unique data with $I > 2\sigma(I)$.

Crystal data for **10**: $C_{19}H_{17}FeNO_4$, $M = 379.19$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.325(2)$, $b = 7.2810(10)$, $c = 17.488(4)$ Å, $\alpha = 88.76(2)$, $\beta = 79.26(2)$, $\gamma = 61.31(2)°$, $U = 801.4(3)$ Å^3, $Z = 2$, $\mu = 0.966$ mm^{-1}, $T = 130.0$ K, $R = 0.0377$ for 3777 unique data with $I > 2\sigma(I)$.

Crystal data for **11a**: $C_{19}H_{18}FeO_2$, $M = 334.18$, monoclinic, space group, $P2_1/c$ (no. 68), $a = 9.415(2)$, $b = 19.390(4)$, $c = 8.845(3)$ Å, $\beta = 109.87(2)°$, $U = 1518.6(7)$ Å^3, $\mu = 0.997$ g cm^{-3}, $T = 130.0$ K, $R = 0.0362$ for 2144 unique data with $I > 2\sigma(I)$.

Crystal data for **11b**: $C_{19}H_{18}FeO_2$, $M = 334.18$, monoclinic, space group $P2/c$ (no. 68), $a = 7.8523(9)$, $b = 9.7282(9)$, $c = 20.154(3)$ Å, $\beta = 92.720(10)°$, $U = 1537.8(3)$ Å^3, $\mu = 0.984$ g cm^{-3}, $T = 130.0$ K, $R = 0.0336$ for 2936 unique data with $I > 2\sigma(I)$. CCDC reference number 186/932. See http://www.rsc.org/suppdata/dt/1998/1269/ for crystallographic files in .cif format.



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 σ_{C-Fe}–σ^*_{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 σ_{C-Fe}–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.

References

1 W. Hanstein and T. G. Traylor, *Tetrahedron Lett.*, 1967, **45**, 4451.
2 J. M. White, *Aust. J. Chem.*, 1995, **48**, 1227.
3 J. B. Lambert, *Tetrahedron*, 1990, **46**, 2677.
4 A. N. Egorochkin, *Russ. Chem. Rev.* (*Engl. Transl.*), 1984, **53**, 445.
5 R. P. Arshinova, *Organomet. Chem. USSR*, 1990, **3**, 581.
6 J. B. Lambert, G. Wang, R. B. Finzel and D. H. Teramura, *J. Am. Chem. Soc.*, 1987, **109**, 7838.
7 J. B. Lambert, G. Wang and D. H. Teramura, *J. Org. Chem.*, 1988, **53**, 5422.
8 J. B. Lambert, R. W. Embledge and S. Malany, *J. Am. Chem. Soc.*, 1993, **115**, 1317.
9 J. B. Lambert and E. C. Chelius, *J. Am. Chem. Soc.*, 1990, **112**, 8120.
10 J. B. Lambert and X. Zhao, *J. Organomet. Chem.*, 1996, **521**, 203.
11 A. R. Bassindale, C. Eaborn, D. R. M. Walton and D. J. Young, *J. Organomet. Chem.*, 1969, **20**, 49.
12 D. D. Davis, *J. Organomet. Chem.*, 1981, **206**, 21.
13 J. M. White and G. B. Robertson *J. Org. Chem.*, 1992, **57**, 4638.
14 A. J. Green, Y. L. Kuan and J. M. White, *J. Org. Chem.*, 1995, **60**, 2734.
15 V. Y. Chan, C. I. Clark, J. Giordano, A. J. Green, A. Karalis and J. M. White, *J. Org. Chem.*, 1996, **61**, 5227.
16 J. M. White and G. B. Robertson, *Acta Crystallogr.*, *Sect. C*, 1993, **49**, 347.
17 T. G. Taylor and J. C. Ware, *J. Am. Chem. Soc.*, 1967, **89**, 2304.
18 G. Wadner and R. Herrmann, in *Ferrocenes*, eds. A. Togni and T. Hayashi, VCH, Weinheim, 1995.
19 F. S. Arimoto and A. C. Haven, jun., *J. Am. Chem. Soc.*, 1955, **77**, 6296.
20 M. Rosenblaum and R. B. Woodward, *J. Am. Chem. Soc.*, 1958, **80**, 5448.
21 R. D. Amos, N. C. Handy, P. G. Jones, A. J. Kirby, J. K. Parker, J. M. Percy and M. D. Su, *J. Chem. Soc.*, *Perkin Trans. 2*, 1992, 549.
22 F. H. Allen and A. J. Kirby, *J. Am. Chem. Soc.*, 1984, **106**, 6197.
23 G. Gokel, P. Hoffmann, H. Klusacek, D. Marquarding, E. Ruch and I. Ugi, *Angew. Chem.*, *Int. Ed. Engl.*, 1970, **9**, 64.
24 G. W. Gokel, D. Marquarding and I. K. Ugi, *J. Org. Chem.*, 1972, **37**, 3052.

Received 27*th February* 1998; *Communication* 8/01652E