The Ferrocenylmethyl Radical

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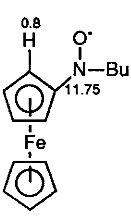
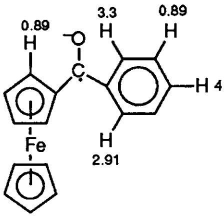
Ferrocenylmethyl, dideuterio(ferrocenyl)methyl and 1′-methylferrocenylmethyl radicals have been prepared by γ-irradiation of the parent ferrocene derivatives in adamantane matrices. Ferrocenylmethyl shows a triplet splitting (14.7 G) in its EPR spectrum attributed to the two α-protons; the couplings from the ring protons are buried in the linewidth. The high *g* value of 2.0200 indicates involvement of the Fe orbitals in the delocalized radical.

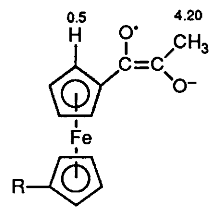
Despite the use of metallocenes as antioxidants, combustion control additives and photoprotecting UV absorbers[1]—areas which clearly involve free-radical chemistry—the ferrocenylmethyl radical, the fundamental metallocene analogue of the benzyl radical, has not hitherto been studied. However, a number of other systems with radical centres α to ferrocene have been reported,[2] for example the aminoxyl[3] **1**, ketyls[4,5] such as **2** and the semidione radical anions[6,7] such as **3**. Ferrocenylmethyl analogues are also clearly implicated in the radical-initiated polymerization of vinylferrocene.[1]



g = 2.0149[3]
1



g = 2.0069[4]
2



g = 2.0071[6]
3

Our interest in benzylic radical stabilization led us to attempt to study the ferrocenylmethyl radical in an adamantane matrix by EPR spectroscopy.

Results and Discussion

Attempts to prepare ferrocenylmethyl radicals in fluid solution by photolysis of solutions of methylferrocene in *tert*-butyl peroxide were unsuccessful: the yellow methylferrocene would be expected to act as a filter for the incident UV light, cutting down the rate of radical production. However, γ-irradiation of methylferrocene, trideuteriomethylferrocene and 1,1′-dimethylferrocene in adamantane matrices at −196 °C followed by warming to −40 °C gave the spectra shown in Fig. 1, with the coupling constants and *g* values shown below.

Assignment of the triplet coupling constant of 14.71 G in **4** to the α-CH_2 protons is confirmed by the EPR spectrum of the deuteriated radical **5**. The single broad line can be analysed[8] in terms of a 1:2:3:2:1 quintet splitting by the two D atoms of 2.18 G which is smaller by a factor of 6.75 (theory[9] 6.51) than that of the CH_2 protons in the protiated radical **4**. The almost identical spectra shown by **6** and **4** show that substitution in the second ring has little effect, a feature also shown[6] by the semidione **3** which has the same methyl splitting (4.20 G) for R = H and R = Bu^t.

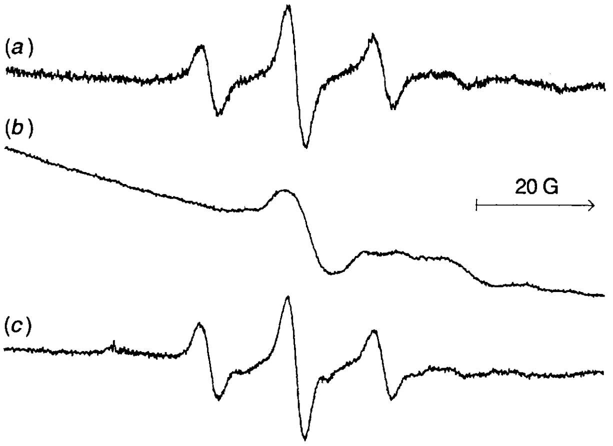
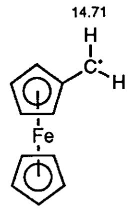
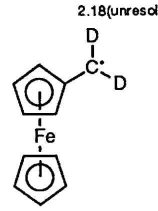


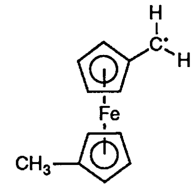
Fig. 1 Adamantane matrix EPR spectra at −40 °C of (*a*) ferrocenylmethyl; (*b*) dideuterio(ferrocenyl)methyl; (*c*) 1′-methylferrocenylmethyl



g = 2.0200
4



g = 2.0201
5

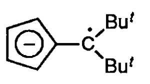


14.69

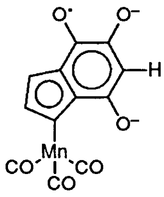
g = 2.0198
6

In radicals of the types **1**–**3**, *ortho* couplings in the region of 0.5–0.8 G are found,[3,6,7] with couplings to the other two protons being too small to be observed. Our results are in accord with *ortho* couplings of this magnitude, undetectable because of the greater linewidths found in adamantane matrix spectra.

The α-CH_2 coupling constant of 14.7 G is significantly less than that of the analogous benzyl radical[8] (16.35 G) implying a greater degree of delocalization. This is in contrast with the ketyl radical anions, where **2** shows greater couplings in the benzene ring than does diphenylketyl,[10] implying that, in this instance, the benzene ring is more efficient in delocalizing spin. The difference may be a result of the different charge types of the two classes of radical. In spite of the delocalization of the spin away from the alkyl group, the cyclopentadienyl ring couplings are small compared with $(cp)^- \dot{C}\,Bu^t_2$ **7**,[11] where couplings of 2.0 and 0.17 G are found in the ring protons, even though the *tert*-butyl groups will be expected to twist the radical centre out of the cyclopentadienyl plane and reduce conjugation. The low (relative to benzyl) coupling constant at the α-position coupled



7



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with the low coupling constants of ring protons implies that a significant amount of spin is delocalized onto the iron atom. The orbitals involved presumably have little s character since no satellites are observed from ^{57}Fe which is present in 2% natural abundance. Manganese couplings of 5.6 G are observed in the radical anion **8**[7] indicating a transfer of spin density to the metal. On account of the greater magnetogyric ratio[9] of ^{55}Mn compared with ^{57}Fe, for radicals with the same spin density on the metal atom and the same degree of s character in the orbital involved, the manganese coupling constant would be 7.6 times greater than that for iron.

Finally, we note that the g value of ferrocenylmethyl (2.0200) is significantly higher than the g values of other ferrocenyl radicals **1**–**3** which have been studied, and which are themselves higher than the values normally found for organic radicals. The high values are doubtless due to involvement of metal-centred orbitals in the delocalized system.

Experimental

Methylferrocene[12] and 1,1′-dimethylferrocene[13] were prepared according to literature procedures. *Trideuteriomethylferrocene* was prepared by reduction of methoxycarbonylferrocene[14] (0.4 g, 1.64 mmol) with $LiAlD_4$ (0.32 g, 7.61 mmol) in absolute THF (5 h reflux) to give dideuterio(ferrocenyl)methanol (0.36 g, 100%, m.p. 96 °C) followed by chlorination and reduction with $AlCl_3$ (0.3 g, 2.25 mmol)/$LiAlD_4$ (0.06 g, 1.43 mmol) in absolute diethyl ether at room temperature. The yellow solid obtained was chromatographed on a SiO_2 (60 g) column with light petroleum (b.p. 50–70 °C), giving as the first fraction trideuteriomethylferrocene (0.27 g, 82%), m.p. 34.5 °C; $\delta_H(CCl_4)$ 3.90 (4 H, s, H_{arom}) and 4.00 (5 H, s, H_{arom}); m/z 203 (M^+). Matrix samples of the above compounds in purified adamantane were γ-irradiated[15,16] to give the corresponding radicals.

Acknowledgements

We thank the British Council for a travel grant (to A. K. Z.).

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Paper 0/05749E
Received 21*st December* 1990
Accepted 21*st January* 1991