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The redox behaviour of ferrocene derivatives

III *. Ferrocenylacyl complexes $(\eta^5\text{-}C_5H_5)\ Fe(\eta^5\text{-}C_5H_4\text{–}COER_3)$, E = C, Si or Ge; R = Me or Ph

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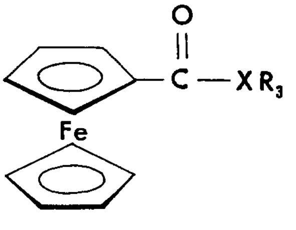
Abstract

The electrochemical behaviour of the ferrocenylacyl derivatives $[FcCOER_3]$ (E = C, Si or Ge; R = Me or Ph) is examined. One-electron oxidations to the substantially stable monocations $[FcCOER_3]^+$ occur at potentials significantly higher than that observed with ferrocene, but only minor differences hold within the series, independent of the nature of both E and R. In contrast the EPR spectra of the monocations for E = C show that the unpaired electron resides mainly on the iron, whereas for E = Si or Ge the electron density is essentially localized on the $C_5H_4COER_3$ fragment.

1. Introduction

The Group 14 elements represent an almost unique opportunity to evaluate periodic trends in the chemical properties of the elements. All the elements possess a significant chemistry in the formally +4 oxidation state and all possess isostructural characteristics in this regard. We recently reorted [2,3] a systematic structural analysis of ferrocenyl substituted acylsilanes and germanes $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4\text{–}CO\text{–}ER_3)]$, $[FcCOER_3]$, (E = Si or Ge; R = Me or Ph) plus a subsequent analysis [4] of the corresponding C analogue, $ER_3 = CMe_3$. It was clear that the Fc portion of these molecules determines the properties of the various molecules.



	X	R_3
1	C	Me_3
2	Si	Me_3
3	Si	Me_2Ph
4	Si	$MePh_2$
5	Si	Ph_3
6	Ge	Me_3
7	Ge	Ph_3

Given this dominance, and profiting from the fact that we have recently started a programme devoted to the redox behaviour of ferrocene molecules and the kinetic stability of their ferrocenium complexes [1], it seemed of interest to analyse the effect of the various $COER_3$ groups on the one-electron oxidation process

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of [FcCOER$_3$] to give the corresponding ferrocenium species.

2. Results and discussion

2.1. Electrochemistry

Figure 1 shows the typical cyclic voltammetric responses exhibited by the complexes [FcCOER$_3$] in dichloromethane solution.

All show an oxidation peak directly associated with a reduction peak in the reverse scan, suggesting chemical reversibility in the short time scale of cyclic voltammetry. Controlled potential coulometry ($E_w = +0.7$ V) at ambient temperature indicates the consumption of one electron per molecule, even if some residual current still persists after the exhaustive generation of the monocations. This means that the electrogenerated ferrocenium species are not indefinitely stable in solution, and that they slowly decompose to by-products, further oxidizable at the applied potential. Upon one-electron oxidation, the initial yellow-orange solutions turn blue.

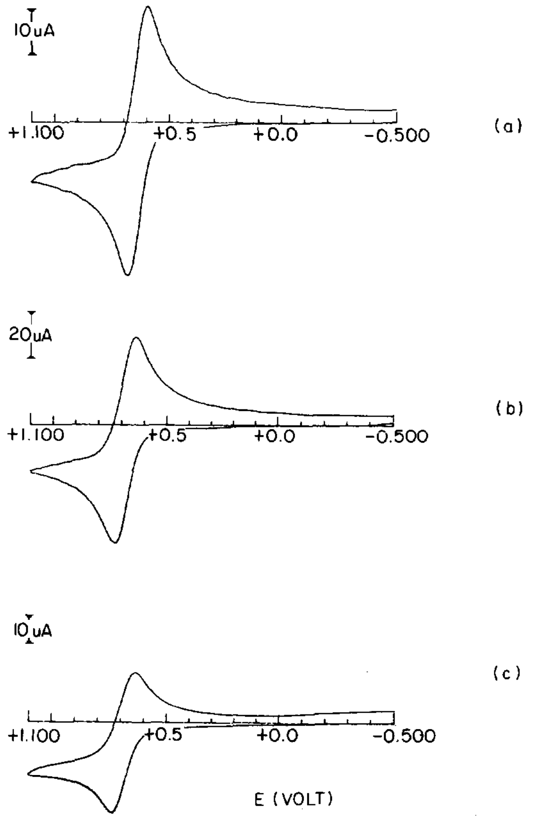

Fig. 1. Cyclic voltammograms recorded at a platinum electrode from CH$_2$Cl$_2$ solutions containing [NBu$_4$][ClO$_4$] (0.2 mol dm^{-3}) and: (a) **1** (2.0×10^{-3} mol dm^{-3}); (b) **2** (2.3×10^{-3} mol dm^{-3}); (c) **6** (1.5×10^{-3} mol dm^{-3}). Scan rate 0.2 V s^{-1}.

TABLE 1. Electrochemical characteristics of the one-electron oxidation of the ferrocenylacyl derivatives 1–7, in dichloromethane solution

Complex	$E^{\circ\prime}$(V)	ΔE_p [a] (mV)
(1)[FcCOCMe$_3$]	+0.64	78
(2)[FcCOSiMe$_3$]	+0.68	84
(3)[FcCOSiMe$_2$Ph]	+0.67	80
(4)[FcCOSiMePh$_2$]	+0.68	72
(5)[FcCOSiPh$_3$]	+0.70	78
(6)[FcCOGeMe$_3$]	+0.69	92
(7)[FcCOGePh$_3$]	+0.71	70
[FcCOH]	+0.73	86
[FcCOCH$_3$]	+0.79 [b]	
[FcH]	+0.45	72
PhCOSiMe$_3$	+1.83 [c]	
PhCOSiMe$_2$Ph	+1.97 [c]	
PhCOGeMe$_3$	+1.63 [c]	
PhCOGePh$_3$	+1.85 [c]	

[a] Measured at 0.1 Vs^{-1}. [b] from Ref. 7. [c] peak potential value for the irreversible process in MeCN solution. From Ref. 8.

As a typical analysis [5] of the electrochemical features of such neutral/monocation steps, let us consider the cyclic voltammetric responses exhibited by **1** as a function of the scan rate v, varying from 0.02 V s^{-1} to 10.24 V s^{-1}. The cathodic-to-anodic peak current ratio, i_{pc}/i_{pa}, is constantly equal to 1; the current function $i_{pa} \cdot v^{-1/2}$ remains essentially constant; the peak-to-peak separation, ΔE_p, increases progressively from 72 to 304 mV.

Even if a ΔE_p value of 59 mV independent of scan rate is theoretically expected for an electrochemically reversible one-electron step [6] uncompensated solution resistances may compete with the effects of structural reorganizations in causing departure from such a value, particularly at high scan rates.

Table 1 summarizes the redox potentials of the complexes, together with those of a few related species.

The data indicate that one-electron oxidation is more difficult than in ferrocene, mainly due to the electronic effects of the acyl group, rather than the peripheral ER$_3$ moieties. In fact, on substituting the CMe$_3$ by SiMe$_3$ and GeMe$_3$, electron-donating Me$_3$ groups for electron-withdrawing Ph$_3$ groups, only minor variations are induced in the redox potential. In addition, the peak-to-peak separations relevant to the ferrocenylacyl complexes are not significant by different from that of ferrocene. Therefore, one-electron oxidation causes no significant structural reorganization.

Finally, the oxidation process is governed by the ferrocenyl moiety, in that the complexes RCOER$'_3$ (E = Si or Ge) are much more difficult to oxidize and their redox potentials are notably sensitive to the inductive effects of the R, R′ substituents *.

2.2. EPR spectra of the ferrocenium cations

In order to characterize the present ferrocenium species, the monocations [**1**]$^+$, [**2**]$^+$, [**7**]$^+$ were selected for EPR investigation. They were prepared by exhaustive macroelectrolysis in dichloromethane-tetrabutylammonium-hexafluorophosphate (0.1 mol dm^{-3}) solution. Figure 2 shows the relevant liquid-helium EPR spectra of powder samples obtained after solvent evaporation.

The spectrum of [**1**]$^+$ displays more features than expected for a ferrocenium species, with absorptions at X-band frequency ranging from 0 to 7000 G. The intensity of these signals rapidly decreases on increasing the temperature. It is apparent that more than one species is present in the solid state, presumably due to slow decomposition reactions following the one-electron oxidation. Although an accurate analysis is not possible, the two features at $g = 1.8$ and 1.6, respectively, correspond to the x and y components of g for $S = 1/2$, which can be associated with $g_z = 3.2$. These values are typical of a ferrocenium complex in low-symmetry environment, and compare well with those previously reported [11] for similar compounds. The signals which are left unassigned are both at low (300 G) and high (6400 g) field and they may correspond to fine structure of a S = 1 species. Weaker features are observed at 1000 and 1500 G.

The spectra of [**2**]$^+$ and [**7**]$^+$ show essentially one quasi-isotropic feature at $g \approx 2.03$. This is evidence for a species having the unpaired electron essentially localized on the organic moiety, but experiencing interaction with the metal ion, as shown by the broad line ($\Delta H_{[2]^+} = 370$ G; $\Delta H_{[7]^+} = 320$ G). Some impurities are present also in these cases, but in concentrations notably smaller than those observed in [**1**]$^+$.

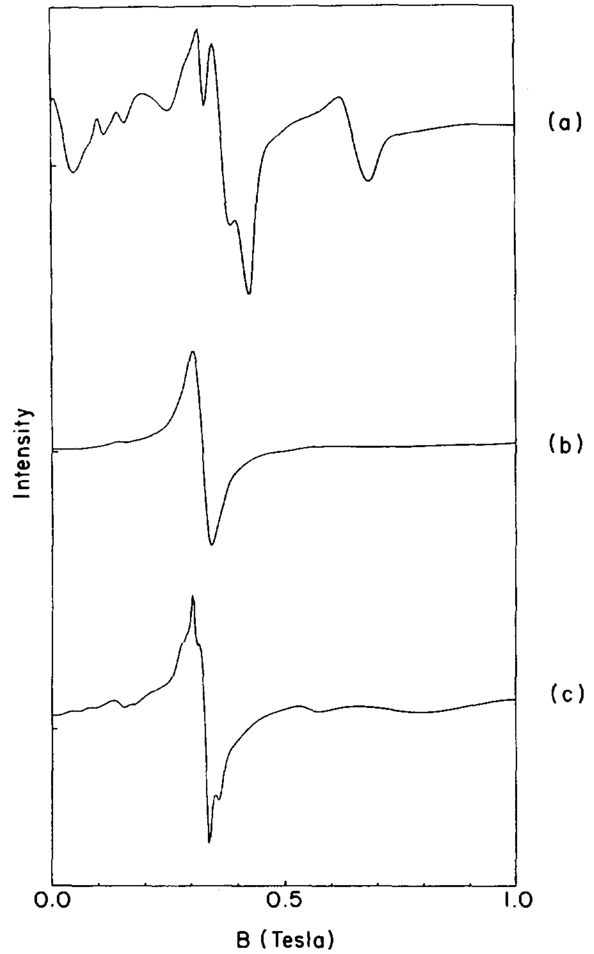

Fig. 2. X-band EPR spectra recorded at 4.2 K from polycrystalline powder hexafluorophosphate samples of: (a) [**1**]$^+$; (b) [**2**]$^+$; (c) [**7**]$^+$.

The EPR data suggest that, with respect to the carbon atom of the alkyl group, the silicon and germanium atoms exert a significant polarizability upon the iron centre and withdraw electrons from Fe towards the COER$_3$ group better than expected on the basis of the various redox potentials alone.

3. Experimental details

Complexes **1**–**7** were prepared according to literature references [2–4].

Materials and apparatus for electrochemical techniques have been described elsewhere [12]. All the potential values are referred to the saturated calomel electrode (S.C.E.).

Electron paramagnetic resonance spectra were recorded with a Varian E9 spectrometer operating at X-band frequency (9.24 GHz). Liquid-helium temperature spectra were recorded with an Oxford Instruments ESR9 liquid-helium continuous-flow cryostat.

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* A referee asked us to correlate the redox potentials with Hammett-type parameters for the XR$_3$ fragment. It is commonly accepted that the electronic effects of the substituents present in the cyclopentadienyl rings of ferrocene are mainly inductive [9]. This seems to hold in the present case, simply from considering the homologues **1**,**2**,**6** (a plot of the inductive constant F (or σ_I) [10] *vs.* E°′ gives a correlation coefficient of 0.98). Nevertheless, the inclusion of the remaining species destroys the linear relationship (correlation coefficient 0.21). Considering both inductive and resonance effects the σ_p parameter, which is the sum of the inductive F and the resonance R constants [10], gives a correlation coefficient of 0.75. Even if this is not sufficient to demonstrate a linear correlation, it is likely that a proper balance of the two effects may improve the correlation. Hence, it seems plausible to assume that for the derivatives studied resonance effects prevail over inductive effects.

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