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An ESR and electrochemical approach to the unusual reactivity of ferrocenoylsilanes with organometallic compounds

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ABSTRACT: ESR studies carried out during the reaction of ferrocenoylsilanes with Grignard reagents at low temperature led to the detection of the radical anions of the former compounds. Cyclic voltammetric experiments indicate that the observed radical anions are likely to originate through an inner-sphere electron transfer process. Different radical species were observed upon annealing, originating from destruction of the ferrocenyl moiety. Paramagnetic species were also detected on reacting ferrocenoylsilanes with $LiAlH_4$. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: ferrocenoylsilanes; Grignard reagents; electron spin resonance; ESR; cyclic voltammetry; single electron transfer; SET; radical anions

INTRODUCTION

The reaction of aldehydes and ketones with Grignard reagents is of very broad scope, and is reported in every textbook of organic chemistry as a well established method for the preparation of alcohols (see, for example, Ref. 1). In a recent paper,[2] we described the unusual reactivity of ferrocenoylsilanes towards Grignard reagents. Actually, as outlined in Scheme 1, the reaction of Grignard reagents with ferrocenoylsilanes **1** afforded as main product ketones **2**, where the silyl moiety has been replaced by the alkyl group from the Grignard reagent, instead of the expected tertiary alcohols. In all cases ketones **2** were formed in very low yields, i.e. 11–15% depending on the individual ferrocenoylsilane and Grignard reagent used. The yields could be substantially improved (up to 60% in the most favourable case) by adding cerium trichloride to the system, that is when working under Imamoto conditions.[3] This behaviour was rationalized by admitting that the expected alcohols are actually formed in a first stage but are quickly converted to the recovered carbonyl compounds via the formal loss of a silane unit that in the aqueous medium is converted to a silanol.[2]

The unusual behaviour of ferrocenoylsilanes towards nucleophilic addition is not unique to Grignard reagents. Indeed, the reactions of ferrocenoylsilanes **1** with alkyllithium derivatives also resulted in the formation of ketones **2** with 50–60% yields, whereas that with lithium aluminium hydride led to ferrocenecarboxaldehyde in a similar yield.[2] Puzzled by the low yields of these reactions and reminiscent of previous studies in which it was shown that hydrides and Grignard reagents may react with organic compounds via single electron transfer (SET) processes,[4–7] we undertook a combined ESR and cyclic voltammetric (CV) study of the reactions of ferrocenoylsilanes **1a** and **b** and methylmagnesium chloride in order to investigate the possibility of the occurrence of SET processes as one of the factors leading to the peculiarly low yields.

RESULTS

ESR studies

When MeMgCl was added at 223 K to an argon-purged THF solution of **1a** contained in a quartz tube located inside the cavity of an ESR spectrometer, a single line could be observed with $\Delta H_{pp} \approx 0.50\,mT$ and a g-factor

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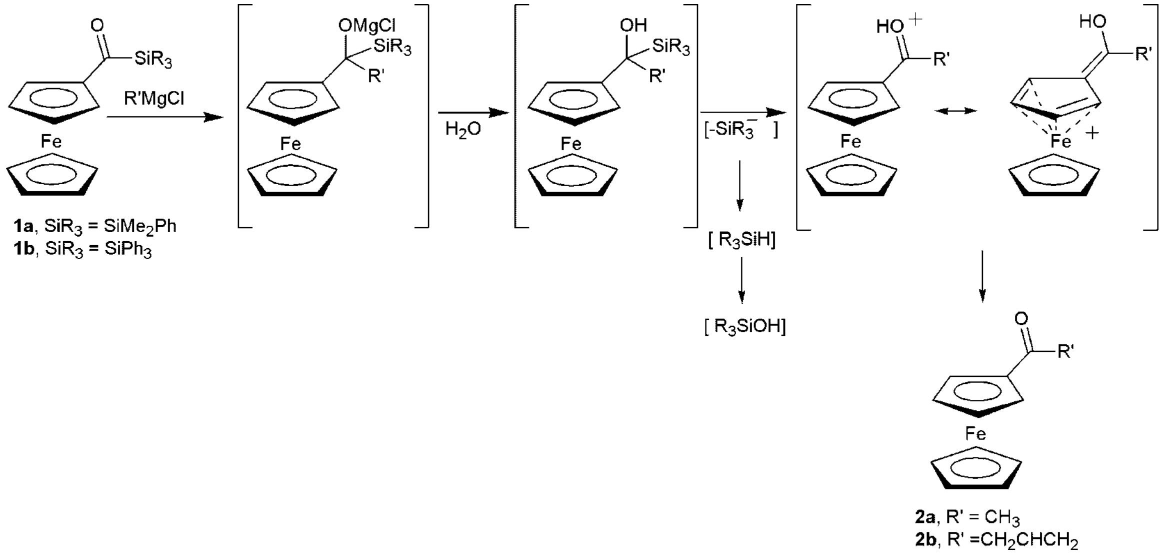


Scheme 1

value of 2.0123$_5$ [see Fig. 1(a)]. Raising the temperature resulted in an initial increase in the spectral intensity that reached a maximum at ca 253 K. Further heating of the system resulted in a rapid intensity decrease and at or above 273 K the original signal completely disappeared, to be replaced by a more complex signal [see Fig. 1(b) and 1(c)]. The new spectrum was centred at higher field ($g = 2.0029_9$) and could be satisfactorily reproduced by assuming coupling of the unpaired electron with five different hydrogen atoms ($a_H = 0.095$, 0.228, 0.595, 0.746 and 1.692 mT). When **1b** was similarly reacted with MeMgCl a partially resolved 1:2:1 triplet ($a_{2H} = 0.121$ mT, $g = 2.0133_0$) was observed [see Fig. 2(a)] instead of the broad single line, the hyperfine structure indicating coupling of the unpaired electron with two magnetically equivalent hydrogen atoms. When the spectrum was recorded at higher receiver gain it also exhibited satellite lines on the two wings of the main signal [see Fig. 2(b)] due to the ^{29}Si isotope present in natural abundance (n.a. 4.7%, $I = ½$, $a_{^{29}\text{Si}} = 0.988$ mT). An almost identical ESR spectrum could be observed by reducing **1b** over a sodium mirror in the presence of some dibenzo-18-crown-6 ether in THF solution ($a_{2H} = 0.110$ mT, $a_{29Si} = 1.000$ mT, $g = 2.0126_5$) at ca 250 K. At variance with **1a**, heating the reaction mixture of **1b** did not result in any major change of the spectral pattern, and at room temperature the ill-resolved triplet with its small satellite lines remained the only observable signal. On the other hand, attempts to perform the electrochemical reduction of either **1a** or **1b** at room temperature in DMF or DMSO solutions containing TBAP as supporting electrolyte failed to lead to the detection of any ESR signal whatsoever. Also, no ESR signals were detected on reacting **1a** and **b** with methylmagnesium bromide in the presence of cerium trichloride,[2,3] or on treatment with methyllithium at low temperature.

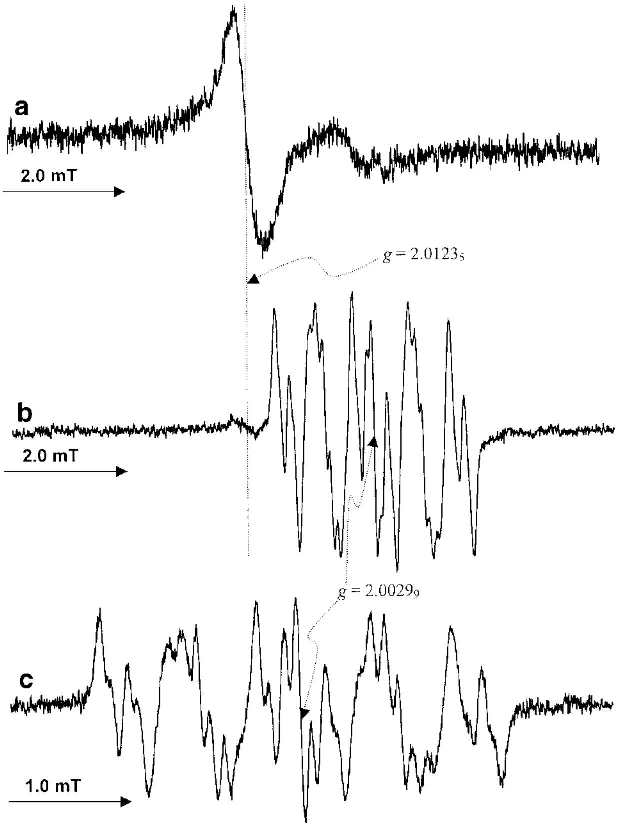


Figure 1. ESR spectra observed on reaction of MeMgCl with **1a**: (a) in THF at 233 K; (b) in THF at 298 K; (c) same as (b) but recorded on a narrower magnetic field scan width with a 7-fold decrease of the modulation amplitude (0.0075 mT)

For the sake of comparison, **1b** was also reacted with $^{\cdot}SiPh_3$, $^{\cdot}GePh_3$ and $^{\cdot}SnBu_3$ radicals by photolysing a solution of **1b** in di-*tert*-butyl peroxide containing the

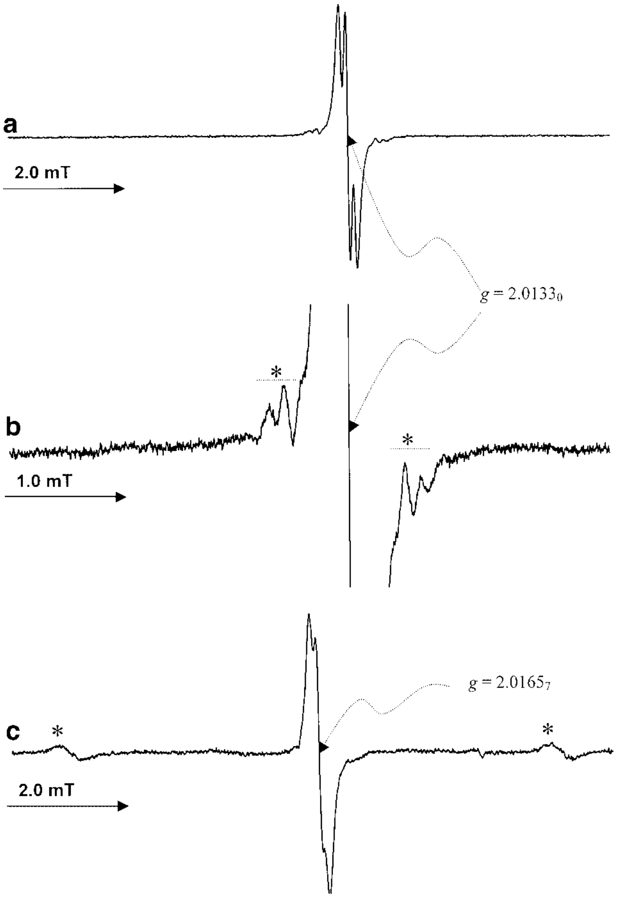


Figure 2. ESR spectra observed on reaction of **1b**: (a) with MeMgCl in THF at 233 K; (b) same as (a) but recorded on a narrower magnetic field scan width with a 20-fold increase of the receiver gain (marked lines are ^{29}Si satellites); (c) with hexabutylditin under UV irradiation at 298 K (marked lines are $^{117/119}$Sn satellites)

appropriate Group 14 hydride or ditin compound. In all cases (see Table 1) this led to radicals whose spectra were closely reminiscent [see Fig. 2(c)] of that observed on reaction of **1b** with MeMgCl, although with larger *g*-factor values. These signals were fairly persistent even at room temperature and could be observed for minutes after interrupting the UV irradiation.

When an argon-purged THF solution of **1a** was treated with $LiAlH_4$ at 193 K, an ESR signal consisting of a broad single line ($\Delta H_{pp} \approx 0.70$ mT) with a *g*-factor of 2.027_9 was observed. The line, the intensity of which decreased as the temperature was raised, was undetectable above 223 K and could not be further resolved. An analogous spectral behaviour (single line, $\Delta H_{pp} \approx 0.70$ mT, $g \approx 2.0280$) was exhibited by **1b**. In some experiments with either **1a** or **1b**, weak new signals identical with those already observed on treating the same compounds with a Grignard reagent could be detected between 223 K and 263 K. These new signals disappeared as the temperature was further increased.

Electrochemical studies

Relying on the fact that **1a** and **1b** exhibited very similar ESR and voltammetric behaviour, the electrochemical studies were focused only on the latter compound. The electrochemical investigation was carried out in THF at room and low temperature under highly aprotic conditions by means of CV, and the same voltammetric pattern was observed independent of the working electrode material used (platinum and glassy carbon). Whereas at room temperature the monoelectronic reduction process was apparently reversible, the irreversibility of the process became fully evident when working below room temperature.

The low temperature CV curve for the negative potential region (see Fig. 3) consisted of a cathodic peak I having a peak potential E_{pc} of -2.2 V (vs SCE) and of an anodic peak II at -1.3 V that, on the other hand, varied drastically with the scan rate. Basically the same behaviour was observed at room temperature, but with peaks less far apart. The cathodic peak was rather broad in comparison with an electrochemically reversible process, with a separation E_p–$E_{p/2}$ of 140 mV after uncompensated ohmic drop correction. The anodic peak II was even broader, and its corresponding charge was smaller than that of the cathodic peak. The latter corresponds to a one-electron process, since it shows the same charge as that of the one-electron oxidation.[8] The lower current corresponding to anodic peak II is consistent with the occurrence of a subsequent chemical reaction after reduction (see below).

The electrochemical irreversibility was assessed varying the sweep rate over several orders of magnitude (from 0.1 to 1000 V s^{-1}), the higher scan rates resulting in a larger cathodic–anodic peak separation and in a broadening of the peaks themselves, a feature typical of a sluggish electron transfer. The occurrence of a chemical

Table 1. ESR spectral parameters of the radicals observed when reacting **1b** under different conditions

Reagent	Radical	a_{2H}	a_{other}	g	T (K)
Na/THF DB18C6	$\mathbf{1b}^{\cdot -}$	0.110	1.000 ($^{29}Si_\alpha$)	2.01265	250
MeMgCl THF	$\mathbf{1b}^{\cdot -}$	0.121	0.988 ($^{29}Si_\alpha$)	2.01330	253–298
$HSiPh_3$ BOOB/*hν*	**3**	0.113	2.317 ($^{29}Si_\beta$)	2.02160	298
$HGePh_3$ BOOB/*hν*	**4**	0.117	0.520 (^{73}Ge)	2.02083	298
$Bu_3SnSnBu_3$ *hν*	**5**	0.124	16.40 (^{119}Sn) 15.76 (^{117}Sn)	2.01657	298

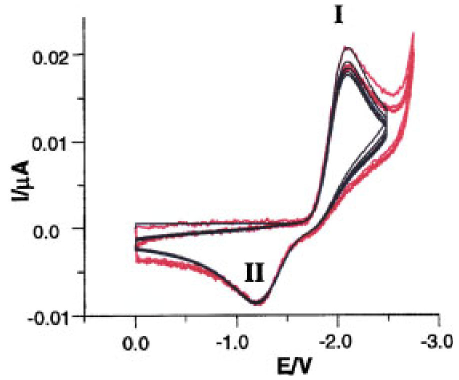


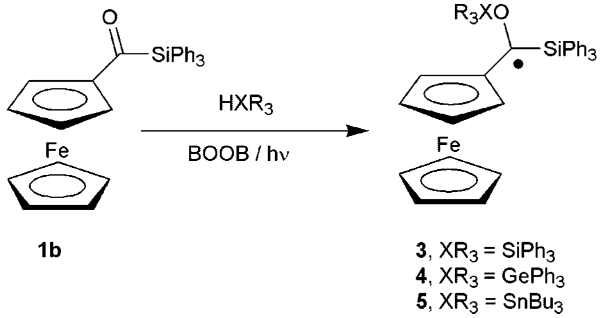
Figure 3. Experimental and simulated (see text) multiscan cyclic voltammetric curves for **1b** (10^{-3} M) in THF solution containing TBAH (5×10^{-2} M) at 203 K. Working electrode, Pt 125 μm; scan rate, 1 V s^{-1}. The experimental trace is shown in grey

reaction following the electron transfer process was also substantiated by the appearance in the positive potential region of a reversible redox couple with a much lower current (roughly 5%) than that corresponding to a one-electron process: this new voltammetric wave, which was not present in the voltammetric curve relating to the oxidation of the starting material, could be attributed to ferrocene on the basis of its $E_{1/2}$ potential.

DISCUSSION

We attribute the ESR signals observed in the course of the reaction of **1a** and **b** with Grignard reagents to the corresponding radical anions **1a**$^{\cdot-}$ and **b**$^{\cdot-}$ (or the ion pairs between these radical anions and a magnesium counterion) on the basis of previous ESR investigations focused on the reduction of alkyl- and arylferrocenyl ketones[9,10] and on the radical anion of nitroferrocene.[9] In particular, the multiplicity of the signal of **1b**$^{\cdot-}$, the values of its splitting and *g*-factor and the detection at high gain of ^{29}Si satellites with a splitting similar to that found in the radical anion of benzoyl triphenylsilane[11] make its identification unambiguous. Further, the identity of **1b**$^{\cdot-}$ could be substantiated by generating the authentic radical anion by alkali metal reduction of **1b** in the presence of an appropriate crown ether. In the spectra of **1a**$^{\cdot-}$ the small unresolved splitting from the hydrogen atoms of the two methyl groups bonded to the silicon atom makes it impossible to resolve the small triplet from the ring hydrogen atoms in positions 2 and 5.

The addition of Group 14 organometallic radicals to carbonyl compounds has been widely investigated, and is known to lead to radical adducts structurally related to the ketyl radical anions (Scheme 2) (for a comprehensive collection of ESR data, see Ref. 12). Thus the spectra observed on reacting **1b** with silyl, germyl or stannyl radicals can be safely attributed to radicals **3**–**5**. The similarity of these spectra with those observed when reacting **1b** with MeMgCl provides, if needed, further support to the identification of the radical anion **1b**$^{\cdot-}$.



Scheme 2

The identification of the species responsible for the spectrum observed when the reaction mixture of **1a** and MeMgCl was allowed to warm to room temperature [see Fig. 1(b) and 1(c)] is intriguing. The value of the *g*-factor is much lower than that of the radical anion **1a**$^{\cdot-}$ and seems indicative of the destruction of the ferrocene moiety. The hyperfine coupling constants derived from computer simulation are consistent with a semicyclic pentadienylic radical and on this basis we tentatively assign the observed spectrum to radical **6** (see Fig. 4).

It is unclear what the fate of the radical anions **1a**$^{\cdot-}$ and **1b**$^{\cdot-}$ may be and how radical **6** is formed. Although the resulting ferrocenoyl radical could not be detected by ESR, the possibility that at low temperature **1a**$^{\cdot-}$ and **1b**$^{\cdot-}$ evolve by loss of a R_3Si^- anion cannot be ruled out *a priori*. Indeed, this decay route via loss a R_3Si^- anion seems to find support in the remarkably higher persistence of the neutral silyl, germyl and stannyl adducts **3**–**5**, for which the loss of the R_3Si^- anion is not a likely event.

We believe it worthwhile stressing that the observation of the spectra of radical anions **1a**$^{\cdot-}$ and **1b**$^{\cdot-}$ suggests the occurrence to a greater or lesser extent of a SET process involving the ferrocenoyl silanes and the Grignard reagent, in a fashion similar to the widely documented formation of ketyl radical pairs in the reactions between ketones and Grignard reagents.[1,13,14] The electrochemical results have particular implications as to the possibility of such a SET process taking place in the initial stage of these reactions. The successive CV traces, obtained without renewal of the diffusion layer, were satisfactorily reproduced through simulations (the simulations were carried out using the Marcus theory instead of the Butler–Volmer equation for the heterogeneous electron transfer

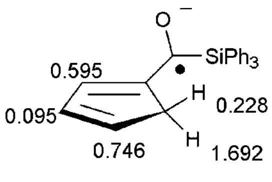


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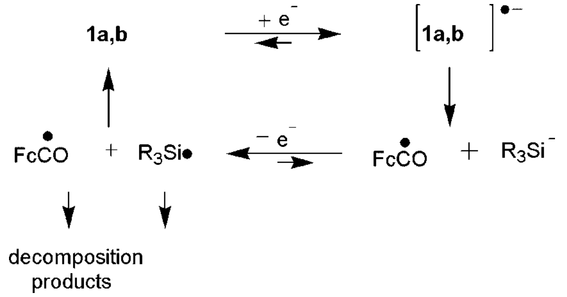
Figure 4. Assignment of the hyperfine coupling constants (mT) for radical **6**



Scheme 3

step) based on the mechanism outlined in the square Scheme 3, according to which in the forward scans a slow electron transfer reduction process would lead to the observed cathodic peak I (see Fig. 3). Cleavage of the silicon–carbonyl bond of the resulting radical anion would afford the ferrocenoyl radical and silyl anions. Slow oxidation of the latter, in the reverse scans, would lead to silyl radicals[15] that might quickly recombine following two equivalent pathways, i.e. coupling either with the ferrocenoyl radicals in the diffusion layer to regenerate the starting ferrocenoylsilanes or with another silyl radical giving a disilane as by-product.[16]

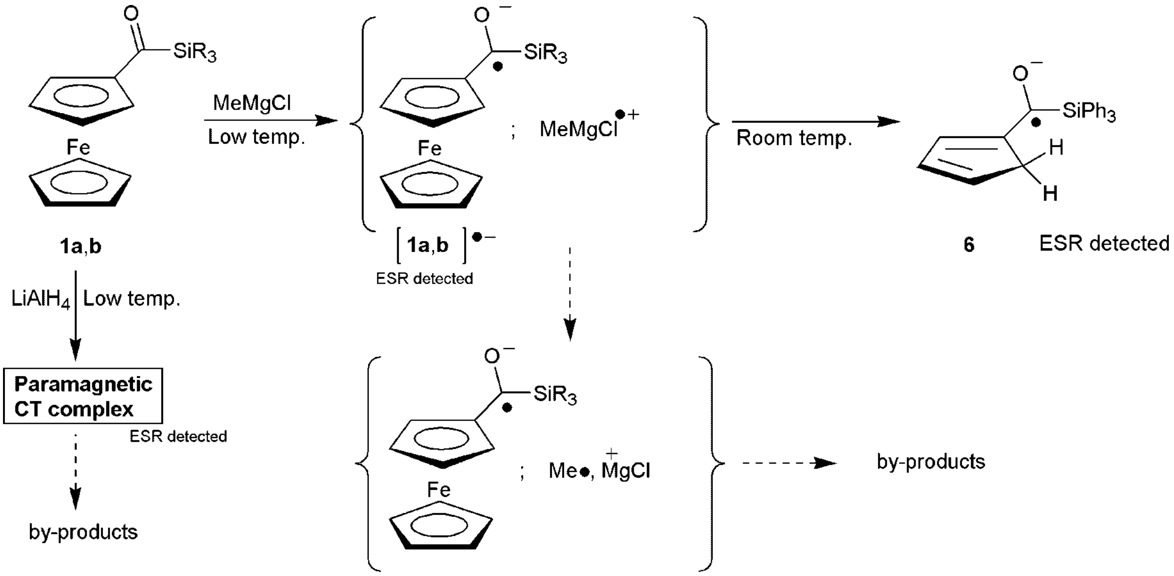
Peak II would therefore be the result of two concomitant processes: (i) the re-oxidation of the ferrocenoylsilane radical anion, that is displaced so far from the cathodic peak because the heterogeneous electron transfer process is intrinsically slow, and (ii) the oxidation of the triphenylsilyl anion. The detection of the small ferrocene oxidation wave may be explained by decarbonylation of ferrocenoyl radical, a very slow process because of the aromaticity of the pentaatomic rings. [It should be emphasized that although a simple slow electron transfer process can simulate the cathodic wave I of Fig. 3, it is completely faulty with anodic peak II. Furthermore, the hypothesis of a simpler electrochemical mechanism not involving any chemical reaction cannot justify the appearance of ferrocene in the positive potential region, after the reduction process. Other mechanisms (EC and ECE) have also been taken into consideration but the corresponding simulated curves do not match all the voltammetric features as the proposed square Scheme 3 does.] The simulation of such a mechanism leads to a reduction potential $E = -1.71$ V (vs SCE) for the ferrocenoylsilane species instead of the apparent value of -2.2 V, and to $E = -2.01$ V (vs SCE) for the silyl radical, a reasonable value on the basis of the reduction potential data available for triphenylsilyl chloride[15] and triphenylsilyl anion.[16]

The results derived from the electrochemical behaviour of **1a** and **b** do not justify the occurrence of a homogeneous outer-sphere electron transfer between the Grignard reagents (donor) and the ferrocenoylsilanes (acceptor) since the energy driving force calculated from the redox potentials of the two partners[6e,7a] would be largely unfavourable. On the other hand, in the actual chemical system the formation of a complex between ferrocenoylsilanes **1a** and **b** and the Grignard reagent can take place. Thus, an intimate interaction of some sort between the partners might render the electron transfer a thermodynamically more accessible process,[17] in a fashion akin to the inner-sphere mechanism previously evidenced in the reactions of Grignard reagents with benzophenone.[18] [Further support for the feasibility of an inner-sphere ET in the investigated reactions was gained by reacting methylmagnesium chloride with phthalonitrile and terephthalonitrile, whose reduction potentials (i.e. $E_{1/2} = -1.79$ and -1.71 V vs SCE, respectively)[19] are very close to that of **1b**. The spectrum of the radical anion of phthalonitrile was actually observed in the former case, whereas in the latter we failed to detect any ESR signal. In fact, the former species, having the two nitrile groups in *ortho* positions, would be more suitable to the formation of an inner-sphere adduct with the Grignard reagent than terephthalonitrile.] We are aware that there is a continuum of pictures between the outer-sphere and inner-sphere limiting situations and that ESR spectroscopy only gives a view of the result, yet it seems to us that once the former process has been excluded the latter remains the only alternative, its ease depending on the intimacy of the interaction between the two partners.

Although the occurrence of a SET transfer therefore seems proved, it seems unlikely that such a process lies on the reaction coordinate leading to the main isolated product, i.e. ketone **2**. Actually, although the formation of **2** might be also thought (see Scheme 4) as resulting from a combination between the ferrocenoyl radical, deriving from the radical anions **1a**$^{\cdot-}$ and **1b**$^{\cdot-}$ via loss of R_3Si^-, and a methyl radical, derived from decomposition of the radical cation of the Grignard reagent, it should be considered that, as soon as it is formed, **2** would immediately react with the excess Grignard reagent to give the higher alcohol 2-ferrocenylpropan-2-ol (not isolated from the reaction mixture).

Overall, by combining the results from products studies and ESR and electrochemical experiments, we believe that the reaction between ferrocenoylsilanes and Grignard reagents is correctly schematized as previously reported and as outlined in Scheme 1, and that SET processes also take place to some extent, triggering side reactions that may be the reason for the very low yields of the main process.

The observation of ESR signals (broad line with $g \approx 2.03$) on simple addition of lithium aluminium hydride to solutions of ferrocenoylsilanes also seems an indication of the occurrence of a SET process. Because they are featureless, it is difficult to assign these signals to any specific radical species exclusively on the basis of the values of their *g*-factor. Although several radicals containing the ferrocenyl moiety have been the subject of ESR investigations,[20] we could not find any report of the detection of signals similar to those observed in the present study. The nature of the species from which



Scheme 4

they originate therefore remains virtually unclear, although their *g*-values are indicative of a substantial interaction between the iron atom and the unpaired electron. It should be stressed that a recent computational study indicated that the ferrocenyl moiety is expected to exert a strong stabilizing action on radicals through a spin delocalization mechanism involving iron;[21] incidentally, we note that this would result in high *g*-factors such as those observed in the present study. We are not in a position to say whether the initial electron transfer leads directly to paramagnetic complexes responsible of the observed signals, or if these are due to radical species originating from their degradation. As mentioned afore, in some cases on heating the $LiAlH_4$–**1a**,**b** reaction mixture the broad line was replaced by ESR signals imputable to radical anions [$\mathbf{1a}^{\cdot -}$ and $\mathbf{1b}^{\cdot -}$]. Although not definite evidence, this allowed the possibility that the evolution of the complex proceeds via the radical anions of the starting acylsilanes, and it seems possible that also these species evolve via loss of the silyl anions. Although in principle the isolated ferrocenecarboxaldehyde might derive from hydrogen abstraction from the solvent or from $LiAlH_4$ by the ferrocenoyl radical formed in the fragmentation, the main issue remains that the newly formed aldehyde would further react with $LiAlH_4$ to afford ferrocenylmethanol.

CONCLUSIONS

Ferrocenoylsilanes exhibit an unusual reactivity towards reduction and alkylation, affording aldehydes and ketones instead of the expected secondary and tertiary alcohols. ESR experiments indicate the occurrence of electron transfer between Grignard reagents or lithium aluminium hydride and ferrocenoylsilanes. CV suggests that this is most likely due to an intimate interaction between the reactants. The nature of the final products nevertheless seems more consistent with a nucleophilic substitution than with a radical-based mechanism. The SET process and degradation of the resulting radical anions might be responsible for the very low yields of these reactions.

EXPERIMENTAL

Chemicals. Compounds **1a** and **1b** were prepared as described previously.[22] DI-*tert*-butyl peroxide (BOOB), tetrabutylammonium hexafluorophosphate (TBAH), tetrabutylammonium perchlorate (TBAP), dibenzo-18-crown-6 ether (DB18 C6), triphenylsilane, triphenylgermane, hexabutylditin, the Grignard reagents and $LiAlH_4$ were commercial products. All solvents were dried and distilled prior to use.

ESR experiments. ESR spectra were recorded on an upgraded Bruker ER200D/ESP300 X-band spectrometer equipped with a dedicated computer for data acquisition, an NMR gaussmeter for the calibration of the magnetic field and a frequency counter for the determination of *g*-factors that were corrected with respect to that of perylene radical cation in concentrated sulfuric acid ($g = 2.0025_8$).[23] The temperature of the resonant cavity was controlled through standard variable-temperature accessories and measured by means of a chromel–alumel thermocouple.

ESR spectra were recorded in the temperature range 193–298 K. In a typical experiment a Pyrex tube (i.d. 3 mm) containing a thoroughly argon-purged THF solution (200 µl) of the ferrocenoylsilane was placed inside the spectrometer cavity. When the solution had reached the desired temperature the appropriate amount of the Grignard reagent was added by means of a gas-tight

Hamilton syringe and the spectra were immediately recorded with spectrometer settings as follows: frequency $\sim$9.3 GHz (X-band), modulation amplitude 7.5×10^{-3}–1×10^{-2} mT and power level 1 mW.

Electrochemical ESR experiments could only be carried out at room temperature owing to the construction of the electrolytic apparatus that consisted of a flat cell ($5 \times 0.8 \times 0.05$ cm) equipped with a platinum gauze as working electrode (cathode) and a platinum wire as counter-electrode (anode). An AMEL 2051 potentiostat was used as power source.

Electrochemistry. TBAH from Fluka was used as received as the supporting electrolyte. Dry vacuum-distilled THF was purified using sodium anthracenide in order to remove any traces of water and oxygen,[24] according to the method of Saji *et al.*[25] The electrochemical experiments were carried out in an airtight single-compartment cell described elsewhere.[24,26] The working electrode was either a microelectrode (0.5 mm diameter platinum wire sealed in glass or 3 mm glassy carbon disc) or an ultramicroelectrode (125 or 50 μm diameter platinum disc); the counter electrode consisted of a platinum spiral and the quasi-reference electrode was a silver spiral. The drift of the quasi-reference electrode was negligible for the time required by an experiment. The cell containing the supporting electrolyte and the electroactive compound was dried under vacuum at 383–393 K for at least 60 h before each experiment. The pressure measured in the electrochemical cell prior to perform the trap-to-trap distillation of the solvent was typically (1–2) $\times 10^{-5}$ mbar.

All the $E_{1/2}$ potentials are referred to an aqueous saturated calomel electrode (SCE) and the corresponding values were determined by adding ferrocene as an internal standard,[27] measuring them with respect to the ferrocinium–ferrocene couple standard potential. Voltammograms were recorded with an AMEL Model 552 potentiostat or a custom-made fast potentiostat controlled by either an AMEL Model 568 function generator or an ELCHEMA Model FG-206F. Minimization of the uncompensated resistance effect in the voltammetric measurements was achieved by the positive-feedback circuit of the potentiostat. Data acquisition was performed with a Nicolet Model 3091 digital oscilloscope interfaced to a PC. Temperature control was accomplished within 0.1 K with a Lauda Klein-Kryomat thermostat. DigiSim 3.0 software (Bioanalytical Systems) or the Antigona software developed by Mottier and co-workers[24] was used for the simulation of the CV curves.

Acknowledgements

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