Extremely Electron-Poor Bis(diarylmethylium)-Substituted Ferrocenes and the First Peroxoferroacenophane

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Dedicated to Professor Manfred Scheer on the Occasion of his 65th Birthday

Abstract. We have prepared and studied extremely electron-poor, deeply colored dicaticonic 1,1'-bis(diarylmethylium)-substituted ferrocenes [(η⁵-C₅H₅-CAr₂)₂Fe]²⁺ with various aryl substituents as their [B[1]C₆H₄(CF₃)₂-3,5]- salts. Due to the strong acceptor substitution, the redox potential for the ferrocene-based oxidation of the anisyl- or 2-methylanisyl-substituted congeners 1b²⁺ and 1c²⁺ is close to or even surpasses that of the second oxidation of parent ferrocene, i.e. the Cp₂Fe⁷⁺²⁺ couple. The strongly Lewis-acidic character of these complexes is manifest through strong interactions with donor solvents, which lead to a significant reduction of the intensities of the charge-transfer bands in their electronic spectra and to solvatochromism. The reduced forms of the complexes tend to dimerize or oligomerize as revealed by EPR spectroscopy. Direduced 1b selectively reacts with molecular oxygen to form a peroxy-bis(diarylmethyl)[4]ferroacenophane, which was also characterized by X-ray crystallography.

Introduction

Triarylmethylium (tritylium) substituted ferrocenes constitute the most prominent examples of metal-organic tritylium dyes and were studied early on for their electronic structures. Particular focus was on the ability of the iron nucleus of the ferrocene scaffold to stabilize the positively charged, adjacent methylium center by σ- or π-interactions as expressed by the resonance forms IV and V in Scheme 1.[1] Such kind of interactions were initially inferred by the 20.7° bending of the Cp₂Fe⁺ plane toward the Fe²⁺ ion in the crystallographically determined structure of Fe-Cp₂⁺[2] (Fc = ferrocenyl, (η⁵-C₅H₅)Fe(η⁵-C₅H₅))).[3] but later refuted by the notion of a small energy barrier for rotation around the Cp–C⁺Ar₂ bond and the generally large dipole moments of ferrocenyl carbenium ions.[10]

The electron-donating ferrocenyl substituent and the strong dipolar character of such compounds usually lead to intense charge-transfer absorptions in the visible regime of the electronic spectrum (Vis), which are typical of donor-substituted tritylium dyes. Vinylogous or alkynylogous expansion of the tritylium entity to a trityl radical, which essentially removes its electron-accepting capabilities. Neutral ferrocenyl(diarylmethyl) radicals FeC⁺Ar₂ are prone to dimerize, and an authentic hexaarylethane structure was proposed for these dimers.[6]

Quite surprisingly, no 1,1'-disubstituted, dicaticonic bis(diarylmethylium)-substituted ferrocenes seem to be known to date. Only the 1,1'-bis(isopropylium)-derivative [(η⁵-C₅H₅CMe₂)₂Fe]²⁺ derivative was generated by either protonation and dehydration of the corresponding diol in FSO₃H/SbF₅ or protonation of the bis(isopropenyl) derivative with FSO₃H in liquid SO₂ and characterized by NMR spectroscopy,[8] but found to persist only at temperatures below –30 °C. Herein we present the first three representatives of such complexes, bearing aryl substituents of differing electron-donating capabilities. We have probed their electronic properties by means of electrochemistry and UV/Vis/NIR as well as EPR spectroscopic studies on the dications and their reduced and oxidized forms. We also report a unique ansa-peroxoferroacenophane, which is formed by the selective reaction of the monoreduced radical cation of the bis(anisyl) derivative with molecular oxygen.

Results and Discussion

Synthesis and Spectroscopic Characterization

The target 1,1'-bis(triarylmethylium)-substituted ferrocenes 1a²⁺ to 1c²⁺ were prepared in a two-step procedure analogous to the carbocyclic substituents to the methylium center are augmented by an additional, weaker CT band (the HOMO→LUMO transition) concomitant with the direct transfer of electron density from the Fe²⁺ ion to the methylium acceptor. In agreement with this assignment, this band is bleached on oxidation, whereby the ferrocene donor is changed into an electron-poor ferrocenium ion. The same behavior is observed on reduction of the tritylium entity to a trityl radical, which essentially removes its electron-accepting capabilities. Neutral ferrocenyl(diarylmethyl) radicals FeC⁺Ar₂ are prone to dimerize, and an authentic hexaarylethane structure was proposed for these dimers.[6]
that employed for the synthesis of their monosubstituted congeners 2a+ to 2c+ (Scheme 2). Thus, 1,1'-ferrocenedicarboxylic acid dimethyl ester[9] was reacted with ca. 4.2 equiv. of a lithiated arene to provide the corresponding 1,1'-bis(diarylmethylcarbinols) 1a-(OH)2 to 1c-(OH)2 after workup. On addition of Brookhart's acid H(OEt2)+ [B{C6H3(CF3)2-3,5}4]–,[10] an instantaneous color change to blue (1a2+), dark green (1b2+), or dark yellow (1c2+) was observed. The so-dubbed BArF24– anion, which was first reported by Kobayashi in 1984,[11] is very weakly nucleophilic and has only little ion-pairing capabilities,[6,12] which is both crucial for the stabilization of strong electrophiles such as the present ones. After solvent removal, the corresponding dicaticonic bis(tritylmethyl)ferrocenes were obtained as intensely blue, red, or vividly purple solids.

Compound 1a2+ provided well-resolved NMR spectra with the characteristic resonance signals of the monosubstituted Cp rings at δ = 5.17 and 4.99 ppm, the two resonances of an AA'BB' spin system for the para-substituted arene substituents at δ = 7.57 and 6.69 ppm, and of the N-methyl groups at δ = 3.15 ppm in addition to the proton resonances of the BArF24– anion in their correct integration ratios (see Figure S3, Supporting Information). All these resonances are shifted to lower field when compared to the bis(carbinol) precursor 1a-(OH)2.

Other characteristic assets are the resonance signal of the carbenium centers at δ = 181.1 ppm and the resonances at δ = 127.8 ppm and 84.2 ppm for the adjacent carbon atoms at the aryl and the Cp substituents (see Figures S4, Supporting Information and the Experimental Section). These signals likewise experience substantial low-field shifts with respect to the corresponding carbinol precursor. As expected, the magnitude of this shift is largest for the newly formed carbenium centers, where it amounts to more than 100 ppm. The methylium resonance signal appears nevertheless at a slightly higher field when compared to δ = 188.0 ppm for its monotritylium congener 2a+ (Scheme 2).[6] Of the remaining two bis(tritylmethyl)fer-
rocenes, 1b2+ provides rather well-resolved resonances in the 1H NMR spectrum at lower concentration levels, which become paramagnetically broadened at higher concentrations (see Figure S6, Supporting Information). This also precluded us from recording meaningful 13C NMR spectra.

In keeping with the presence of small amounts of a paramagnetic component, dicationic 1b2+ shows indeed an isotropic, unstructured EPR signal in fluid solution at a g value of 2.0086. This signal was initially of only weak intensity at room temperature, but gradually intensified on warming the solution to 60 °C (Figure 1, left) and remained at a rather constant intensity level on cooling back to room temperature. Further cooling to temperatures of –20 °C or below, however, induces a gradual decrease of the signal intensity until the initial level is reached (Figure 1, right). The entire process can be cycled several times. Such reversible intensity changes combined with a hysteretic behavior point to the existence of a thermally accessible paramagnetic state along with a substantial activation barrier connecting this state to the diamagnetic ground state.

A likely explanation for this unusual behavior is thermal equilibration between the native 1,1'-bis(diarylmethyl)ferrocene form (η5-Ar2C+-C5H4)FeII(η5-C5H4-C'Ar2) and its (η5-Ar2C+-C5H4)FeIII+(η5-C5H4-C'Ar2) valence tautomer, where the positive charge has shifted from a triarylmethylium site to the ferrocene nucleus (Scheme 3, top). This renders one of the former triarylmethylium centers a trityl-type radical. As ferrocenium ions are EPR inactive under these conditions, only the trityl component of this biradical is detected by EPR spectroscopy. This valence tautomer was computationally modeled as the triplet state of 1b2+. Our quantum chemical calculations produced indeed substantial spin densities on the ferrocene nucleus and the methyl(ium) carbon atoms (Figure 2, left). Complex 1b2+ thus complements Veciana’s ferrocenyl-perchlorotriphenylmethyl radicals, which were found to equilibrate with their zwitterionic ferrocenium-perchlorotriphenylmethane isomers.[13] These two kinds of systems are compared in Scheme 3. They mainly differ in the identity and charge state of the triarylmethyl(ium)-based acceptor units, i.e. cationic Ar2C+ in 1b2+ vs. neutral –C6Cl4–C(C6Cl5)2 in Veciana’s systems.

Figure 1. Time-dependent EPR spectra of 1b2+ in CHCl₃ on (a) warming to 60 °C, and (b) cooling the warm solution to –20 °C.

Scheme 3. Valence tautomeric forms of complex 1b2+ (top) and of perchlorotriphenyl-substituted ferrocene (bottom).
Neither meaningful NMR nor EPR spectra were, however, obtained for complex 1c2+, such that its formation was only verified by UV/Vis spectroscopy. As expected from their vivid colors, all three complexes present intense electronic transitions in their Vis spectra. Their electronic absorption spectra are compared in Figure 3. Like in the solid state, solutions of the complexes in CH₂Cl₂ are intensely blue (1a2+) or purplish red (1b,c2+). The electronic spectrum of 1a2+ is dominated by a strong band (ε = 85000 M⁻¹cm⁻¹) at 653 nm, which, in analogy to its monotritylium analog 2a+ (Scheme 2) is caused by charge-transfer (CT) from the electron-rich 4-dimethylaminophenyl substituents to the carbenium acceptor (the so-called x-band). As a token of the increased acceptor strength owing to its monotritylium analog 2a+, this band is red-shifted by 1130 cm⁻¹ (i.e. from 608 nm) when compared to the presence of two tritylium-type acceptors, this band is assigned as the combined x- and y-bands with concomitant CT character, but differing in the identity of the Fe d donor orbital (dₓ,ᵧ), is observed as a shoulder on the high-energy side of the first yM band at ca. 630 nm for 1b2+ or at ca. 690 nm for 1c2+. The main absorption feature of 1b2+ is an intense (ε = 65000 M⁻¹cm⁻¹), structured peak with a main maximum at 525 nm and separate shoulders at 485 nm and 457 nm. According to our TD-DFT calculations and in agreement with the behavior of other triarylmethylium dyes, these bands are assigned as the combined x- and y-bands with concomitant CT from the donor-substituted aryl rings or the attached Cp ligand to the methylum centers.[13] Figure 4 shows the calculated spectrum and the charge-density differences associated with the individual excitations of complex 1b2+. The Vis spectrum of 1c2+ differs from that of 1b2+ mainly in that the intensity of particularly the x,y bands at 513 nm is greatly diminished. This is a likely result of a larger torsion of the sterically more hindered 2-methyl-4-methoxyphenyl rings with respect to the plane of the methylum acceptors.

Complexes 1b2+ and 1c2+ show a remarkable solvatochromic behavior. While giving purplish red solutions in CH₂Cl₂ and nitromethane, their solutions in N- or O-donor solvents like acetone, methanol, THF, Et₂O, CH₃CN, or pyridine assume a grass-green to orange-yellow color. The observable color impressions and absorption spectra of equally concentrated solutions in various solvents are collected in Figure 5; for details to the band positions and absorptivities see Table S1 (Supporting Information). Of note are the greatly diminished absorptivities of all CT bands in any donor solvent. This indicates strong interactions between Lewis-basic solvent molecules and the Lewis-acidic methylum centers of the solute, which reduce the electron-accepting capabilities of the latter. The decrease of the band intensities consequently follows, at least on a qualitative level, the Gutmann donor number DN. The latter is defined as the negative value of ΔH° in kcal·mol⁻¹ for adduct formation between an electron pair donor with SbCl₅ in a highly diluted solution of 1,2-dichloroethane.[15] The stronger quenching of the bands in 1c2+ when compared to 1b2+ is consistent with an increased Lewis-acidity of the methylum centers in the former complex as a result of a lower...
stabilization by the more twisted aryl substituents. Complex 1a2+, where the positive charges at the methylium carbons are rather well stabilized by the strongly electron-donating Me2NCH2 substituents, shows a strongly attenuated solvatochromism, changing its color from deep blue in CH2Cl2 or nitromethane to dark green in THF or MeOH.

Figure 4. Left: TD-DFT calculated absorption spectrum of complex 1b2+; right: electron density difference plots (blue: decreasing electron density, red: increasing electron density) for the most important transitions.

Figure 5. Solvatochromism of complexes 1b2+ (top and bottom left) and 1c2+ (middle and bottom right).
Electrochemical Studies

The redox properties of the bis(diarylmethylammonium)-substituted ferrocenes were probed by cyclic and square wave voltammetry. The results of this study are shown in Figure 6; pertinent data are compiled in Table 1. All complexes show two consecutive one-electron reductions for the stepwise transformations of the cationic triarylmethylammonium to neutral triarylmethyl substituents, i.e. the CpAr₂C⁺⁺⁺ (Figure 6, left). The splitting of half-wave potentials ΔE₁/₂ amounts to 405 mV for 1a²⁺ and increases to 670 mV in 1c²⁺ and to 740 mV in 1b²⁺. In every instance, the first reduction wave appears anodic of the first reduction of the corresponding monosubstituted diarylmethylammonium ferrocenes 2a⁺ to 2c⁺ (Table 1), which is a clear token of the decreased electron density of the tritylum acceptors. The magnitude of the shift between the first reduction of complexes 1a²⁺ to 1c²⁺ and those of their corresponding counterparts 2a⁺ to 2c⁺ increases with decreasing electron-donating capabilities of the aryl substituents. It thus becomes larger the more the effect of changing an electron-donating neutral ferrocenyl entity in complexes 2a–2c to an electron-accepting, cationic (η⁵-C₅H₅)Fe(η⁵-C₅H₅-CAr₅⁺) substituent in complexes 1a–1c is felt by the methylammonium and is not compensated by the other aryl substituents. One should note here that, in 1a²⁺ and 2a⁺, the 4-Me₃NC₆H₄ substituents are stronger donors than ferrocenyl, while ferrocenyl is the strongest donor in complexes 2b⁺ and 2c⁺. Again, a larger torsion of the 2-methyl-4-methoxyphenyl substituents of 1c²⁺ as compared to the anisyl residues of 1b²⁺ is held responsible for the finding that 1c²⁺ is considerably easier to reduce than 1b²⁺ despite the nominally stronger donor properties of the aryl substituents in 1c²⁺. This effect is even amplified with respect to the corresponding monosubstituted analogs 2b⁺ and 2c⁺ (Table 1).

In the CH₂Cl₂/NBu₄BARF₂₄ electrolyte, the expected oxidation of the central ferrocene constituent can only be observed for the least electron-poor congeners 1a²⁺ as a reversible wave at E₁/₂ = 670 mV against the Cp₂Fe⁰⁺⁺⁺ couple. This process, however, lies outside the accessible potential range of this electrolyte for the other two complexes. It could nevertheless be observed as a broad square-wave peak at 1640 mV (1b²⁺) or 1870 mV (1c²⁺) in liquid SO₂, using NBu₄BARF₂₄ as the supporting electrolyte (Figure 6, right). With such positive redox potentials, 1b²⁺ and 1c²⁺ seem to be the electron-poorest ferrocenes reported to date, including other multiacceptor-substituted ferrocenes such as 1,1′-dicyanoferrocene (E₁/₂ = 865 mV), 1,1′,2,2′,4,4′- and 1,1′,2,2′,3,3′-hexakis(pentafluorophenyl)ferrocene (E₁/₂ = 940 mV and 951 mV, respectively), 1,1′,3,3′-tetra(methoxycarbonyl)ferrocene (E₁/₂ = 900 mV) and even 1,1′,2,2′-tetraformylferrocene (E₁/₂ = 1145 mV)[16]. In fact, their E₁/₂ values nearly match or even exceed the 1,1′-dicyanoferrocene value of 1640 mV.

### Table 1. Electrochemical data a) b) for all complexes.

| Complex | Reductions | Oxidation |
|---------|------------|-----------|
|         | E₁/₂ (0/+ | ΔEₚ (0/+ | E₁/₂ (+/2+) | ΔEₚ (+/2+) | E₁/₂ (2/+3+) | ΔEₚ (2/+3+) |
| 1a²⁺    | –1340      | 57        | –935        | 57        | 670        | 89         |
| 1b²⁺    | –880       | 70        | –140        | 70        | 1640 c)    | –          |
| 1c²⁺    | –690       | 70        | –20         | 100       | 1870 c)    | –          |
| 2a⁺     | –1160      | 57        | 490         | 490       | 830        | 180        |
| 2b⁺     | –780       | 57        | 870         | 870       | 224        |
| 2c⁺     | –740       | 72        |             |           |            |

a) Potentials in mV (± 3 mV) in CH₂Cl₂ at T = 293(± 3) K relative to the Cp₂Fe⁰⁺⁺⁺ couple (E₁/₂ = 0.000 V). Supporting electrolyte NBu₄⁺ [B(C₆H₄(CF₃)₂)]⁻. b) Data for complexes 2a⁺ to 2c⁺ from reference[16]. c) Potentials were determined by square wave voltammetry in liquid SO₂ at T = 253(± 3) K relative to the Cp₂Fe⁰⁺⁺⁺ couple (E₁/₂ = 0.000 V) with NBu₄⁺ [B(C₆H₄(CF₃)₂)]⁻ as the supporting electrolyte.
surpass that of 1710 mV for the second oxidation of parent ferrocene (i.e., the Cp₂Fe⁺/²⁺ couple) under similar conditions.[18]

**Spectroscopic Investigations on Some Oxidized and Reduced Forms**

The three reversible redox processes of 1a²⁺ provided us with the opportunity to probe for the spectral changes in the Vis/NIR spectra concomitant with these transformations. The results of this study are depicted in Figure 7. On one-electron oxidation, the prominent Vis band of 1a²⁺ at 653 nm is bleached and gives way to less intense bands peaking at 790 nm, 543 nm, and 450 nm. The lower-energy bands are very likely associated with CT from the C₆H₄NMe₂ donors to the methylium and ferrocenium acceptor entities. The red-shift of the 790 nm band with respect to that in 1a²⁺ is in line with an inner array of three interconnected strong electron acceptors after ferrocene oxidation.

The two consecutive one-electron reductions likewise bleach the prominent x-band of 1a²⁺ to ultimately leave two bands at 540 nm and 439 nm. By inference from their monontriarylmethylammonium-substituted congeners, for which a similar behavior was observed, these bands are assigned as a mixed transition within the ferrocene nucleus and a 1,1'-ferrocenediyl→CAR₂⁺ CT transition (λ = 540 nm) and as π→π⁺ transitions within the trityl chromophore (λ = 439 nm).[6] Of note is the absence of an electronic transition at low energy specific for any radical cation with one neutral Ar₂C• and one cationic Ar₂C⁺ substituent attached to the same ferrocene-1,1’-diyl scaffold (see also Figures S9 and S10, Supporting Information for the results of such studies on complexes 1b,c²⁺). In view of the substantial half-wave potential splitting for the individual reductions one would expect such a charge transfer absorption between differently charged pendants, may it occur through space or via the ferrocene coupling unit. Figure S11 (Supporting Information) displays a possible structure, which would allow for CT through space. Electronic transitions of this kind are well-known for π-stacked mixed-valent donor/acceptor dyads comprising of the reduced and the oxidized forms of a planar, π-conjugated electrophore (so-called pimers).[19] Only during the reduction of 1a²⁺ a suspicious feature was observed as a weak band (ε = 1000 M⁻¹·cm⁻¹). This band was, however, found to persist during the second reduction and is hence not specific to 1a⁺⁺.

The reduced forms of complexes 1a²⁺ and 1b²⁺ were also investigated by EPR spectroscopy. Singly reduced radical cations 1a⁺⁺ and 1b⁺⁺ were generated by reacting the dicationic precursors with slightly less than 1 equiv. of cobaltocene in order to avoid overreduction. EPR spectra of these samples

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**Figure 7.** Spectroscopic changes during oxidation (top) as well as the first (bottom left) and second (bottom right) reductions of complex 1a²⁺ (1,2-C₂H₄Cl₂ / NBu₄BArF₂₄ (0.02 M) at room temperature).
were measured in CH₂Cl₂ solutions in the temperature range of 20 °C to –40 °C or of 20 °C to –60 °C, respectively. As shown in Figure 8, both paramagnetic species display an isotropic signal without any resolved hyperfine splitting at g values of 2.0115 (1a⁺⁺) or 2.0301 (1b⁺⁺). Both values are slightly larger than that of ca. 2.003 expected for ordinary trityl radicals,[20] but similar to those of e.g. the triferrrocenylmethyl, phenylferroacenylmethyl, the ferrocenyl-ruthenocenylmethyl, or the ferrocenyl-diruthenocenylmethyl radicals.[21] DFT-calculated spin densities (Figure 2, middle) show indeed large contributions of the ferrocene-1,1'-diyl entity to the singly occupied molecular orbital (SOMO) of 1b⁺⁺.

During these studies we also noted an odd temperature-dependence for both radical cations. Thus the intensity of the EPR signal of 1a⁺⁺ steadily and reversibly decreases upon cooling. This is just the opposite of the normal Curie behavior as expressed by Equation (1), where g denotes the isotropic g value of the compound, μ₀ is Bohr’s magneton, B₀ the magnetic field strength and k_B is the Boltzmann’s constant. According to this equation, the population of the thermally excited state (decreasing value of ΔN) is expected to diminish with decreasing T, and this, in turn, should lead to larger signal intensities for samples with equal spin concentrations as T is lowered. Such odd behavior was already observed for reduced samples of triarylalkyl-substituted ferrocenes 2a⁺ to 2c⁺ and traced to the formation of hexaarylethane-type dimers.[6] The same obviously applies here. We however note that the reduction in signal intensity upon cooling is less pronounced for cationic 1a⁺⁺ as compared to 2a⁺, which is reasonably expected as a consequence of electrostatic repulsion between the positively charged CAr₂⁺ pendants of such a dimer. This holds to an even larger degree for radical cation 1b⁺⁺, whose signal intensity initially increases on lowering T, complying with the normal Curie-behavior, but then decreases upon cooling to even lower temperatures. We thus conclude that dimerization only commences to a noticeable degree at temperatures of or below ~20 °C. This can be seen as a token of a lesser delocalization of the positive charge at the remaining tritylium site onto the aryl substituents, which is in full agreement with our electrochemistry data.

\[ ΔN = N \left( \frac{g \mu_0 B_0}{2 k_B T} \right) \]  

(1)

Fully reduced 1a, generated by treating 1a²⁺ with an excess over 2 equiv. of cobaltocene, proved unfortunately too reactive to be reliably characterized by EPR spectroscopy. In the case of 1b, however, an indicative EPR signal was obtained and its T dependence was likewise studied. The results are shown in Figure 9. Diradical 1b produces two different isotropic signals at g values of 2.0283 and of 2.0144. The former value falls close to that of 2.0301 observed for 1b⁺⁺. On progressive cooling to lower T, this signal gradually decreases in intensity, while that of the signal at higher field first increases and then stays rather constant. We tentatively assign the signal at g = 2.0283 to the dissociated diradical and the one at g = 2.0144 to a diradical dimer or higher oligomers. We also note that, in contrast to cationic 1b⁺⁺, but in agreement with neutral 2b⁺, dimerization already sets in at or slightly below room temperature as shown by the slight intensity decrease of the low-field EPR resonance in the T interval of 20 °C to 0 °C.

![Figure 8. EPR spectra of monoreduced radical cations 1a⁺⁺ (left) and 1b⁺⁺ (right).](Image)

Figure 9. T-dependent EPR spectra of reduced 1b and proposed oligomer formation by spin pairing.

**Reactivity Studies of 1b: Formation and Characterization of a Unique Peroxo-[4]ferrocenophane**

During attempts to reduce 1b²⁺ to its radical cation on a preparative scale with Cp*₂Fe (E₁/₂ = −550 mV) as a selective reductant and without protection from the atmosphere, we observed a fading of the solution color from deep red to greenish yellow. Extraction of the solid obtained after solvent evaporation with n-hexane provided a dark yellow solution and a green, insoluble residue, which was not characterized further.
The $^1$H NMR spectrum of the product obtained from the soluble fraction after solvent removal consists of four separate AB doublets at δ = 7.86, 7.35, 6.90, and 6.52 ppm for the para-disubstituted anisyl rings, integrating as 4 protons each, 4 broad singlet resonances at δ = 5.11, 4.21, 4.03, and 3.91 ppm for the Cp protons with an integral of 2 H each, and two singlets, each accounting for 6 H, for the methoxy protons at δ = 3.33 and 3.22 ppm, along with minor impurities (Figure S12, Supporting Information). This pattern of resonance signals indicates the formation of a new 1,1′-disubstituted ferrocene derivative with $C_2$ symmetry. A pure product was obtained, when 2 equiv. of cobaltocene were added to a CH$_2$Cl$_2$ solution of 1b$^{2+}$ inside a glovebox and stirred for some min before the reaction vessel was taken out of the glove box and left stirring open to the air overnight. Workup as before gave the pure compound in quantitative yield after evaporation of the solvent. The ESI mass spectrum of this product showed the molecular ion peak at $m/z = 699.1925$, which matches with an adduct of 1b with one molecule of oxygen and one proton (Figure S14, Supporting Information). Crystallization of this compound by slow evaporation of a saturated solution in CH$_2$Cl$_2$ afforded yellow black crystals that proved suitable for X-ray structure determination. As shown in Figure 10, the newly formed product is a neutral peroxo-[4]ferrocenophane 1b-$	ext{O}_2$ (only one of the two enantiomers of the racemic pair in the crystal is shown; for details of the data collection and refinement, the cell parameters and the bond lengths and bond angles see Tables S2 to S4, Supporting Information).

In 1b-$	ext{O}_2$ the former trityl carbon centers and the O atoms of a molecule of O$_2$ have combined to form a –C–O–O–C– bridge, which interconnects the two Ar$_2$C– pendants of the upper and lower Cp decks. Within the four-atom linkage bond lengths of 1.526(2) and 1.529(2) Å for the Cp–C, 1.454(2) and 1.464(2) Å for the C–O, and 1.4789(16) Å for the O–O bonds, bond angles C–O–O of 108.1(1)° and a dihedral angle of $–134.2^\circ$ at the peroxo group are observed. The two Cp decks assume a staggered conformation with a rotation angle of 39.3° (average values C$_{Cp}$–C$_{Cp}$ centroid–C$_{Cp}$), and are tilted by a 7.8°, which indicates that the four atom C–O–O–C hinge induces an only moderate strain. The C atoms at the hinges are at a closer distance of 3.271 Å as compared to 3.438 Å or 3.540 Å at the opposite, open side of the [4]ferrocenophane structure. This is mirrored by differences in Fe–C$_{Cp}$ bond lengths, which range from 2.0229(18) to 2.0356(19) Å for the C atoms at or in the immediate vicinity of the hinge to 2.067(2) and 2.0667(19) Å at the open side.

We note a close structural similarity to the corresponding 1,1′bis(diphenyl)peroxo-[4]rhodocenophanium cation, which has a tilt angle of 5.5° between the cyclopentadienyl ligands, C$_{5}$H$_{4}$–C–O–C–O–C–O–C–O–C–C–O–C–, and O–O bond lengths of 1.531(6)/1.521(6) Å, 1.454(4)/1.458(4) Å, and 1.487(4) Å as well as a dihedral angle C–O–O–C of 144.9°.[22] The latter compound and three more derivatives from other, 4-substituted aryl substituents were obtained from the reaction of homoleptic Rh$^{1}$ complexes [(η$^5$-C$_5$H$_4$=C(C$_6$H$_4$R-4)=Rh]$^+$ (R = H, Cl, OMe, Me) bearing 6,6-diphenylfulvene ligands with air.[22–23] Besides the doubly linked (η$^5$-C$_5$H$_4$CPh(C$_6$H$_4$O-O)=CPh(η$^5$-C$_5$H$_4$)=Fe)[24] the aforementioned [4]rhodocenophanium cations seem to be the only peroxo-[4]metallocenophanes in the literature. It should be noted, though, that aerial oxidation of the trityl radical to the corresponding peroxide was noted as early as in 1903 in one of the first treatises on this compound.[25]

The tilt of 7.2° in 1b-$	ext{O}_2$ is larger than that of 0.7° to 2.8° found in [4]ferrocenophanes with butane-1,4-diy1 or 2-oxo-butyne-1,4-diyl bridges. All-carbon-bridged [4]ferrocenophanes even show the larger interplanar C–C distance at the hinge.[26] Such conformational differences result from the much smaller angle between the Fe–O–O and the Cp planes of 11.4° and 15.1° of 1b-$	ext{O}_2$ as compared to values of 49.0° to 70.6° for interplanar angles Fe–C–C/Cp in the all-carbon bridged counterparts, i.e. from more “upright” conformations of the inner –C$_2$H$_4$– or –C(O=)–CH$_2$– connectors as opposed to a rather flat-lying peroxo group. Similar or even larger tilts of up to 16.0° were observed in [4]ferrocenophanes with fluorinated all-carbon bridges,[27] or in a [4]ferrocenophane with a –CH$_2$N(Ph)–C(COOMe)$_2$CH$_2$– connector (6.5°).[28]

In further explorations of diradical 1b we also investigated its reactivity with acetylene-1,4-dicarboxylic acid dimethylester, styrene, CS$_2$, NO, water and methanol under a protective atmosphere of dinitrogen. From the product mixtures formed in these reactions, known 6,6-dianisylfulvene,[23,29] and the unsymmetrically substituted (η$^5$-C$_5$H$_4$C(C$_6$H$_4$O$_2$)OH)Fe(η$^5$-C$_5$H$_4$C(C$_6$H$_4$O$_2$)OH)$^+$ (1b-HOH, for NMR and ESI mass spectra see Figures S15 to S17, Supporting Information) as the product of water addition were identified besides various, but smaller amounts of 1b-$	ext{O}_2$. The latter is obviously formed by the trapping of 1b with adventitious oxygen. Notably, no polymer formation was observed during the reaction of 1b with styrene. The release of a 6,6-disubstituted fulvene from a 1,1′-(η$^5$-C$_5$H$_4$C(R$_2$))$_2$Fe diradical is just the opposite reaction to that observed by Tacke and co-workers in their studies on bis(ful-
vene) iron(0) derivatives of 6,6-dimethyl- and 6,6-diphenylferroocene. The latter can either undergo hydrogen atom abstraction from the solvent or, in the case of methyl substituents, C–C bond formation to a [2]ferrocenophane (Scheme 4). \(^{[30]}\)

**Summary and Conclusions**

We report on three 1,1’-bis(diarylmethyl)-substituted ferrocenes of the type \([\{\eta^5-C_5H_4C(C_6H_4R-4)\}_2Fe\}]^{2+} [R = NMe 2 \((1a^{2+})\); R = OMe \((1b^{2+})\) and \([\{\eta^5-C_5H_4C(C_6H_4(CH_3-2))(OMe-4)\}_2Fe\}]^{2+} (1c^{2+})\), which were obtained by reacting their neutral bis(carbinol) precursors with Brookhart’s acid H(OEt 2)+ \([B\{C_6H_3(CF_3)2-3,5\}]^{4-}\). \(^{[10]}\) The dicationic ferrocene derivatives \(1b^{2+}\) and \(1c^{2+}\) seem to be the most electron poor ferrocenes reported to date. Thus, the half-wave potentials of the ferrocene-based oxidation resemble or are even positive of that of the second oxidation of ferrocene itself, i.e. the CpFe+/2+ redox couple under similar conditions. \(^{[18]}\) The high Lewis acidity of these compounds becomes manifest through the bleach of the aryl→methylmethine charge-transfer band in donor solvents, which evidences the formation of Lewis acid/base pairs with the respective solvent as the Lewis base. This leads to pronounced solvatochromism. Reduction of the complexes occurs as two consecutive one-electron steps with a large redox splitting \(\Delta E_{1/2}\) of 405 to 740 mV. Nevertheless, no intercalation charge-transfer band from electron transfer from the reduced triarylmethyl to the remaining oxidized triarylmethylium entity was observed, although the ferrocene-1,1’-diyl scaffold might be expected to support through-space electronic coupling by cofacial stacking of these substituents.

Like their monotriyl-substituted counterparts \(2a^{*}-2c^{*}\) (Scheme 2), reduced \(1a-c^{*+\delta}\) tend to dimerize/oligomerize via their triarylmethyl centers with concomitant formation of C–C bonds. This tendency is attenuated for the radical cations, which is likely due to electrostatic repulsion between the remaining triarylmethylium centers. Direduced, anisyl-substituted \(1b\) was found to be reactive towards molecular oxygen and to form a novel peroxy-(bisdiarylmethyl)[4]ferrocenophane with a \(–Ar_2C–O–O–CAr_2–\) linkage between the two Cp decks. As it was shown by X-ray crystallography, the four-atom linker induces an only moderate ring strain as revealed by a 7.2° tilt between the Cp rings.

Another intriguing finding of this study is that anisyl-substituted \(1b^{2+}\) exists as a mixture of a diamagnetic and a paramagnetic form. These two isomers interconvert via a sizeable energy barrier, which gives rise to hysteresis. The paramagnetic form is obviously the result of an electron transfer from the ferrocene nucleus to one of the triarylmethylium centers. Such behavior of \(1b^{2+}\) is reminiscent of a magnetochemical switch, where, by action of an external trigger, a diamagnetic state can be altered into a diradical state with two unpaired spins. Further work in our laboratories is directed to exploring this prospect further.

**Experimental Section**

**General Methods:** All manipulations were carried out at room temperature in a nitrogen atmosphere using standard Schlenk techniques, unless stated otherwise. Solvents were dried and distilled by standard procedures and degassed by saturation with nitrogen prior to use. Ferrocene-1,1′-dicarboxylic acid was prepared according to a literature procedure \(^{[31]}\) and converted to its dimethyl ester following the procedure procured for ferrocene carboxylic acid. \(^{[32]}\) \(^1\)H NMR (400 MHz), \(^{13}\)C\(^{[1]}\)H NMR (101 MHz) and \(^{31}\)P\(^{[1]}\)H NMR (162 MHz) spectra of the compounds were measured on a Bruker Avance III 400 spectrometer at room temperature in the indicated deuterated solvent. The spectra were referenced to the signal of residual protonated solvent (\(^1\)H) or the solvent signal (\(^13\)C). UV/Vis/NIR spectra were recorded on a TIDAS fiber optic diode array spectrometer (combined MCS UV/NIR and PGS NIR instrumentation) from j&m in HELMA quartz cuvettes with 0.1 cm optical path lengths.

All electrochemical experiments were executed in a custom-built cylindrical vacuum-tight one-compartment cell. A spiral-shaped Pt wire and a Ag wire as the counter and pseudoreference electrodes were sealed into glass capillaries and fixed by Quickfit screws via standard joints. A platinum electrode was introduced as the working electrode through the top port via a Teflon screw cap with a suitable fitting. It was polished with first 1 \(\mu\)m and then 0.25 \(\mu\)m diamond paste before measurements. The cell was attached to a conventional Schlenk line via a side.
arm equipped with a Teflon screw valve, allowing experiments to be performed under an argon atmosphere with approximately 5 mL of analyte solution. NBu₄⁺[B(C₆H₄(CF₃)₂)₂]Cl⁻ (0.02 m) was used as the supporting electrolyte. Referencing was done with addition of an appropriate amount of decamethylferrocene (Cp*Fe, E₁/₂ = −550 mV with respect to Cp₂Fe) as an internal standard to the analyte solution after all data of interest had been acquired. Representative sets of scans were repeated with the added standard. Electrochemical data were acquired with a computer controlled BASi CV50 potentiostat.

The optically transparent thin-layer electrochemical (OTTLE) cell was also custom-built according to the design of Hartl et al.[33] It consists of a Pt working and counter electrode and a thin silver wire as a pseudo-reference electrode sandwiched between two CaF₂ windows of a conventional liquid IR cell. The working electrode is positioned in the center of the spectrometer beam. Electron paramagnetic resonance (EPR) studies were performed on a MiniScope MS 400 Table-top X-band spectrometer from Magnettech.

X-ray diffraction analysis was performed at 100 K on a STOE IPDS-II diffractometer equipped with a graphite-monochromated radiation source (λ = 0.71073 Å) and an image plate detection system. A yellow, blocky crystal of 1b-O₂Fe₂ obtained from slow evaporation of a solution of this complex in CH₂Cl₂ was mounted on a fine glass fiber with silicon grease. The selection, integration, and averaging procedure of the measured reflection intensities, the determination of the unit cell dimensions and a least-squares fit of the 20 values as well as data reduction, LP-correction and space group determination were performed using the X-Area software package delivered with the diffractometer. A semiautomatic absorption correction was performed.[34]

The structure was solved by the heavy-atom method. Structure solution was completed with difference Fourier syntheses and full-matrix least-squares refinements using SHELX-2017[35] and OLEX2,[36] minimizing of F² – F̃². The weighted R factor (wR²) and the goodness of the fit GOOF are based on F². All non-hydrogen atoms were refined with anisotropic displacement parameters, while hydrogen atoms were introduced in a riding model.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of this paper can be obtained free of charge on quoting the depository number CCDC-1971352 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

The ground state electronic structures of the full complexes were calculated by density functional theory (DFT) methods using the GAUSSIAN 09 program package.[37] Geometry optimizations were performed without any symmetry constraints. Open shell systems were calculated by the unrestricted Kohn–Sham approach (UKS). Geometry optimization followed by vibrational analysis was performed in solvent media. Solvent effects were described by the polarizable continuum model (PCM) with standard parameters for 1,2-dichloroethane.[38] For Fe, the ten-electron quasi-relativistic effective core potential (ECP) MDF10 was used[39] and 6-31G(d) polarized double-z basis sets[40] were employed together with the Perdew, Burke, Ernzerhof exchange and correlation functional (PBE0).[41] The GaussSum program package was used to analyze the results.[42] While the visualization of the results was performed with the Avogadro program package.[43] Graphical representations of molecular orbitals were generated with the help of GNU Parallel[44] and plotted using the vmd program package[45] in combination with POV-Ray.[46] Electronic transitions were calculated by the time-dependent DFT (TD-DFT) method.

Synthesis and Characterization of 1a(OH)₂⁺:

1.39 g (6.95 mmol, 4.2 equiv.) of 4-bromo-N,N-dimethylaniline were dissolved in 40 mL of dry degassed tetrahydrofuran. 3.9 mL (1.9 m solution in n-hexane, 7.3 mmol, 4.4 equiv.) of BuLi were added dropwise to the solution at −78 °C. After stirring for 15 min a solution of 500 mg (1.66 mmol, 1 equiv.) of dimethyl-1,1'-ferrocenedicarboxylate in 30 mL of tetrahydrofuran was added to the reaction mixture at −78 °C. After stirring overnight with slow warming to room temperature, the reaction mixture was quenched with the addition of 40 mL of water and the solvent was removed in vacuo. The residue was dissolved in Et₂O and extracted with water (3 × 50 mL). The aqueous layer was separated off and extracted with Et₂O (3 × 100 mL). The combined organic phases were washed with brine (3 × 20 mL), dried with MgSO₄, and the solvent was evaporated in vacuo. The dark green crude product was washed with 210 mL of Et₂O (1 × 150 mL, 3 × 20 mL) to yield 490 mg (0.678 mmol, 41 %) of 1a(OH)₂⁺ as a green crystalline solid.

1H NMR (CDCl₃, 400 MHz): δ = 7.12 (d, 3J_HH = 8.8 Hz, 8 H, H7), 6.62 (d, 3J_HH = 8.8 Hz, 8 H, H8), 4.15 (s, 4 H, H1), 3.96 (s, 4 H, H2), 3.84 (s, 2 H, H5), 2.91 (s, 24 H, H10) ppm. 13C NMR (CDCl₃, 101 MHz): δ = 149.4 (C9), 138.8 (C6), 128.1 (C7), 111.7 (C8), 99.0 (C3), 77.7 (C4), 69.5 (C1), 68.1 (C2), 40.8 (C10) ppm.

Synthesis and Characterization of 1a⁺²2BARF₂⁺:

1.100 g (1.01 mmol, 2.05 equiv.) of Brookhart’s acid in 40 mL of dry degassed Et₂O were added dropwise to 354 mg (0.49 mmol, 1 equiv.) of 1a(OH)₂⁺ in 40 mL of dry degassed Et₂O at room temperature. The reaction mixture turned from green to dark blue. After stirring for 30 min the blue solution was evaporated and the petrol-colored solid was dried in vacuo, yielding 1.18 g (0.489 mmol, quantitative) of 1a⁺².
Ferroocene (2.2 g, 12 mmol, 1.5 equiv.) was dissolved in 15 mL of dry THF and cooled to 0 °C. 5.5 mL of (0.1 M solution in n-hexane, 10.4 mmol, 1.3 equiv.) of BuLi were added dropwise to the solution. After stirring for 15 min, a solution of 1.94 g (8 mmol, 1 equiv.) of 4,4′-dimethoxybenzophenone in 20 mL of tetrahydrofuran was added to the reaction mixture at 0 °C. After stirring for 15 min, the ice bath was removed and the yellow solution was stirred for additional 25 min at room temperature before the reaction mixture was quenched with 30 mL of water and the solvent was removed in vacuo. The residue was dissolved in Et2O and extracted with water (3 × 50 mL). The aqueous layer was separated off and extracted with Et2O (3 × 100 mL). The combined organic phases were washed with brine (3 × 20 mL), dried with MgSO4, and the solvent was evaporated in vacuo. The residual solid was purified by column chromatography. A petroleum ether/ethyl acetate (PE/EA) 5/1 mixture eluted some monosubstituted (C5H5)2Fe(OH)2 as a red solid in quantitative yield. With pure EA as eluent, the orange band of (C5H5)2Fe(OH)2 was eluted. After solvent evaporation, (C5H5)2Fe(OH)2 was obtained in the form of dark yellow crystals. The yield was 800 mg (1.2 mmol, 30% with respect to 4,4′-dimethoxybenzophenone). 1H NMR (DMSO-d6, 400 MHz): δ = 7.07 (d, JHH = 8.0 Hz, 8 H, H8), 6.78 (d, JHH = 8.0 Hz, 8 H, H5), 6.02 (s, 2 H, H3), 3.97 (d, JHH = 2.7 Hz, 4 H, H1), 3.91 (d, JHH = 2.7 Hz, 4 H, H1), 3.71 (s, 12 H, H6) ppm. 

ESI-MS (CH3CN): calcd. for C40H38FeO6: 670.2045 [M]+; found 670.1975.

Synthesis and Characterization of 1b(OH)2:

320 mg (0.31 mmol, 2.05 equiv.) of Brookhart’s acid in 5 mL of dry degassed Et2O were added dropwise to 100 mg (0.14 mmol, 1 equiv.) of (C5H5)2Fe(OH)2 in 5 mL of dry degassed Et2O at room temperature. The reaction mixture turned from yellow to dark green. After stirring for 20 min the solvent was removed to obtain (C5H5)2Fe(OH)2 as a red solid in quantitative yield. 1H NMR (DMSO-d6, 400 MHz): δ = 7.66 (broad s, 4 H, H13), 6.58–6.63 (m, 2 H, H9, H12), 4.24 (broad s, 4 H, H13), 3.84 (s, 4 H, H2), 3.75 (s, 2 H, H5), 3.40 (s, 12 H, H8) ppm. 13C NMR (DMSO-d6, 101 MHz): δ = 158.5 (C6), 137.4 (C7), 129.9 (C1), 117.4 (C9), 109.8 (C12), 100.0 (C3), 78.1 (C4), 70.5 (C2), 55.3 (C10), 22.1 (C8).

ESI-MS (CH3CN): calcd. for C46H44FeO4 346.1306 [M]2+; found 346.1461 (measured in dichlo-
Inside a glove box 1b2+·2BArF24 (100 mg, 0.042 mmol, 1 equiv.) was dissolved in 3 mL of degassed CH2Cl2 and 16 mg (0.084 mmol, 2 equiv.) of cobaltocene were added. The mixture was stirred for 10 min, then removed from the glove box, exposed to the air and stirred at room temperature overnight. The solvent was evaporated under vacuum and the residue was extracted with n-hexane. Evaporation of the solvent gave 1b-O2 in quantitative yield. 1H NMR (400 MHz, C6D6): δ = 7.87 (d, 4 H, 3JHH = 8.85 Hz, H8), 7.35 (d, 4 H, 3JHH = 8.85 Hz, H9), 6.52 (d, 4 H, 3JHH = 8.80 Hz, H10), 4.81 (s, 1 H, H7), 4.07 (m, 2 H, H1), 4.03 (m, 2 H, H5), 3.92 (m, 2 H, H6), 3.33 (s, 6 H, CH3–11), 3.21 (s, 6 H, CH3–12), 136.4 (C7), 130.3 (C8), 128.1 (C13), 113.5 (C14), 113.4 (C9), 94.2 (C5), 89.9 (C6), 75.1 (C4), 71.7 (C1), 70.2 (C2), 67.6 (C3), 54.8 (C12), 49.9 (C7). ESI-MS (CH3CN) calcd. for C40H38FeO5: [M+] + 654.2071; found: 654.1662; [M-OH]+ 637.2077; found: 637.1668.

Supporting Information (see footnote on the first page of this article): NMR spectra of the complexes, UV/Vis/NIR spectra of the reduced forms of complexes 1b2+ and 1c2+, ESI-MS of complexes 1b-O2 and 1b-HOH, Tables with UV/Vis data in various solvents and details of the crystallographic structure determination as well as the bond lengths and bond angles.

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