



Zeitschrift für anorganische und allgemeine Chemie

Accepted Article

Title: Extremely Electron-Poor Bis(diarylmethylium)-Substituted Ferrocenes and the First Peroxoferrocenophane

Authors: Rainer Friedrich Winter, Larissa A. Casper, Steffen Oßwald, Patrick Anders, and Lisa-Catherine Rosenbaum

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Z. anorg. allg. Chem. 10.1002/zaac.201900347

Link to VoR: http://dx.doi.org/10.1002/zaac.201900347

WILEY-VCH

www.zaac.wiley-vch.de

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

Larissa A. Casper, Steffen Oßwald, Patrick Anders, Lisa-Catherine Rosenbaum, and Rainer F. Winter*

Fachbereich Chemie, Universität Konstanz, Universitätsstraße 10, D-78453 Konstanz, Germany

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

Abstract

We have prepared and studied extremely electron-poor, deeply coloured dicationic 1,1'bis(diarylmethylium)-substituted ferrocenes $[(\eta^5-C_5H_4-CAr_2)_2Fe]^{2+}$ with various aryl substituents as their $[B\{C_6H_3(CF_3)_2-3,5\}_4]^-$ salts. Due to the strong acceptor substitution, the redox potential for the ferrocene-based oxidation of the anisyl- or 2-methylanisyl-substituted congeners $1b^{2+}$ and $1c^{2+}$ is close to or even surpasses that of the second oxidation of parent ferrocene, i. e. the Cp₂Fe^{+/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 peroxobis(diarylmethyl)[4]ferrocenophane, 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 CPh₂⁺ plane toward the Fe²⁺ ion in the crystallographically determined structure of Fc–CPh₂^{+[2]} (Fc = ferrocenyl, (η^5 -C₅H₅)Fe(η^5 -C₅H₄)) and by quantum chemical calculations,^[3] but later refuted by the notion of a small energy barrier for rotation around the Cp–C⁺Ar₂ bond^[4] and the generally large dipole moments of ferrocenyl carbenium ions.^[1f]



Scheme 1. Resonance formulas of ferrocenyl-substituted methylium cations.

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 ferrocenyl arm of such dyes shifts the corresponding charge transfer band further red and increases its oscillator strength.^[5] In ferrocenyl-tritylium dyes Fc- C^+Ar_2 , the CT transitions from the carbocyclic substituents to the methylium center are augmented by an additional, weaker CT band (the HOMO \rightarrow 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 behaviour is observed on reduction of the tritylium entity to a trityl radical, which essentially removes its electron-accepting capabilities. Neutral ferrocenyl(diaryl)methyl radicals FcC•Ar₂ are prone to dimerize, and an authentic hexaarylethane structure was proposed for such dimers.^[6]

Quite surprisingly, no 1,1'-disubstituted, dicationic bis(diarylmethylium)-substituted ferrocenes seem to be known to date. Only the 1,1'-bis(isopropylium)-derivative $[(\eta^5 - C_5H_4CMe_2)_2Fe]^{2+}$ derivative was generated, either by protonation and dehydration of the corresponding diol in FSO₃H/SbF₅^[7] or by protonation of the bis(isopropenyl) derivative with FSO₃H in liquid SO₂^[8] and characterized by NMR spectroscopy, but found to persist only at temperatures of -30 °C or lower. Here 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*-peroxoferrocenophane, which is formed by the selective reaction of the monoreduced radical cation of the bis(anisyl) derivative with molecular oxygen.

Accepted Manuscript

Results and Discussion

Synthesis and spectroscopic characterization

The target 1,1'-bis(triarylmethylium)-substituted ferrocenes $1a^{2+}$ to $1c^{2+}$ were prepared in a two-step procedure analogous to 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 colour change to blue ($1a^{2+}$), dark green ($1b^{2+}$), or dark yellow ($1c^{2+}$) was observed. The so-dubbed BAr_{F24}⁻ anion, which was first reported by Kobayshi 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 dicationic bis(triarylmethylium)-substituted ferrocenes were obtained as intensely blue, red, or vividly purple solids.

Compound $1a^{2+}$ provided well-resolved NMR spectra with the characteristic resonance signals of the monosubstituted Cp rings at $\delta = 5.17$ and 4.99 ppm, the two resonances of an AA'BB' spin system for the para-substituted arene substituents at 7.57 and 6.69 ppm, and of the Nmethyl groups at 3.15 ppm in addition to the proton resonances of the $BArF_{24}$ anion in their correct integration ratios (see Figure S3 of the 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 181.1 ppm and the resonances at 127.8 ppm and 84.2 ppm for the adjacent carbon atoms at the aryl and the Cp substituents (see Figures S4 of the 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 $\delta = 188.0$ ppm for its monotritylium congener $2a^+$ (Scheme 2).^[6] Of the remaining two bis(tritylium) ferrocenes, $1b^{2+}$ provides rather well-resolved resonances in the ¹H NMR spectrum at lower concentration levels, which become paramagnetically broadened at higher concentrations (see Figure S6 of the Supporting Information). This also precluded us from recording meaningful ¹³C NMR spectra.



Scheme 2. Synthesis of the 1,1'-bis(triarylmethylium)-substituted ferrocenes $1a^{2+}-1c^{2+}$ and their monotritylium congeners $2a^+-2c^+$.

In keeping with the presence of small amounts of a paramagnetic component, dicationic $1b^{2+}$ shows an isotropic, unstructured EPR signal in fluid solution at a *g* value of 2.0086. This signal was initially of only weak intensity at r. t., 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 r. t. Further cooling to temperatures of -20 °C or below, however, induces a gradual decrease of the signal intensity until the initial stage is reached (Figure 1, right). The entire process can be cycled several times. Such reversible intensity changes combined with a hysteretic behaviour point to the existence of a thermally accessible paramagnetic state along with a substantial activation barrier connecting this state to the diamagnetic ground state.



Figure 1. Time-dependent EPR spectra of $1b^{2+}$ in CHCl₃ on a) warming to 60 °C, and b) cooling the warm solution to -20 °C.

A likely explanation for this unusual behaviour is thermal equilibration between the native 1,1'- $Ar_2C^+-(\eta^5-C_5H_4)Fe^{II}(\eta^5-C_5H_4)-C^+Ar_2$ bis(diarylmethylium)ferrocene form and its $Ar_2C^+-(\eta^5-C_5H_4)Fe^{III+}(\eta^5-C_5H_4)-C^{\bullet}Ar_2$ 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 $1b^{2+}$. Our quantum chemical calculations produced indeed substantial spin densities on the ferrocene nucleus and the methyl(ium) carbon atoms (Figure 2, left). Complex $1b^{2+}$ thus complements Veciana's ferrocenyl-perchlorotriphenylmethyl radicals (PCT[•]), which were found to equilibrate with their zwitterionic ferrocenium-perchlorotriphenylmethanide 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 Ar_2C^+ in $1b^{2+}$ versus neutral $-C_6Cl_4-C(C_6Cl_5)_2$ in Veciana's systems.



Scheme 3. Valence tautomeric forms of complex $1b^{2+}$ (top) and of perchlorotriphenyl-substituted ferrocene (bottom).



Figure 2. DFT-calculated spin densities for $1b^{2+}$ in its triplet state (left), monoreduced $1b^{++}$ (middle) and neutral 1b (right).

Neither meaningful NMR nor EPR spectra were, however, obtained for complex $1c^{2+}$, such that its formation was only verified by UV/Vis spectroscopy. As expected from their vivid colours, all three complexes present intense electronic transitions in their Vis spectra. Their electronic absorption spectra in CH₂Cl₂ are compared in Figure 3. Like in the solid state, solutions of the complexes in CH₂Cl₂ are intensely blue ($1a^{2+}$) or purplish red ($1b,c^{2+}$). The electronic spectrum of $1a^{2+}$ is dominated by a strong band ($\varepsilon = 85000 \text{ M}^{-1} \text{ cm}^{-1}$) 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 the presence of two tritylium-type acceptors, this band is red-shifted by 1130 cm⁻¹ (i. e. from 608 nm) when compared to the monotrityliumsubstituted counterpart $2a^+$. The expected CT transition originating from the substituted Cp ring as the donor (y-band) is presumably associated with the weaker feature at 530 nm, which is present in the spectra of all three complexes. No Fe \rightarrow tritylium CT band (the so-called y_M-band) is, however, observed; it is likely hidden underneath the intense main band of $1a^{2+}$.

In contrast, Vis spectra of complexes $1b_{c}c^{2+}$ with anisyl or 2-methyl-4-methoxyphenyl substituents at the tritylium centre, show a y_M band at 799 nm ($\varepsilon = 9500 \text{ M}^{-1} \text{ cm}^{-1}$) or at 765 nm ($\epsilon = 9900 \text{ M}^{-1} \text{ cm}^{-1}$, Figure 3). According to our TD-DFT calculations, this absorption is associated with charge-transfer from mainly the Fe $d_x^2 v^2$ orbital to the empty p-orbitals at the methylium carbon atoms. A second feature with a similar character, but differing in the identity of the Fe d donor orbital (d_z^2) , is observed as a shoulder at ca. 630 nm for $1b^{2+}$ or at ca. 690 nm for in $1c^{2+}$, i. e. on the high-energy side of the other y_M band. The main absorption feature of $1b^{2+}$ is an intense ($\varepsilon = 65000 \text{ M}^{-1} \text{ cm}^{-1}$), structured peak with a main maximum 525 nm and separate shoulders at 485 nm and 457 nm. According to our TD-DFT calculations and in agreement with the behaviour 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 methylium centres.^[14] Figure 4 shows the calculated spectrum and the charge-density differences associated with the individual excitations of complex $1b^{2+}$. The Vis spectrum of $1c^{2+}$ differs from that of $1b^{2+}$ 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 methylium acceptors.



Figure 3. UV/Vis spectra of the bis(triarylmethylium)-substituted ferrocenes in CH₂Cl₂.



Figure 4. Left: TD-DFT calculated absorption spectrum of complex $1b^{2+}$; right: electron density difference plots (blue: decreasing electron density, red: increasing electron density) for the most important transitions.

Complexes $1b^{2+}$ and $1c^{2+}$ show a remarkable solvatochromic behaviour. 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 colour. The observable colour impressions and absorption spectra of equally concentrated solutions in various solvents are collected in Figure 5; details to the band positions and absorptivities can be obtained from Table S1 of the 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 methylium centres 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 $1c^{2+}$ when compared to $1b^{2+}$ is consistent with an increased Lewisacidity of the methylium centres in the former complex as a result of a lower stabilization by the more twisted any substituents. Complex $1a^{2+}$, where the positive charges at the methylium carbons are rather well stabilized by the strongly electron-donating Me₂NC₆H₄ substituents, shows a strongly attenuated solvatochromism, changing its colour from deep blue in CH₂Cl₂ or nitromethane to dark green in THF or MeOH.



Figure 5. Solvatochromism of complexes $1b^{2+}$ and $1c^{2+}$.

Electrochemical studies

The redox properties of the bis(diarylmethylium)-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 triarylmethylium to neutral triarylmethyl substituents, i. e. the CpAr₂C^{+/•} couples (Figure 6, left). The splitting of half-wave potentials $\Delta E_{1/2}$ amounts to 405 mV for **1a**²⁺ and increases to 670 mV in **1c**²⁺ and to 740 mV in **1b**²⁺. In every instance, the first reduction wave appears anodic of the first reduction of the corresponding monosubstituted diarylmethylium ferrocenes **2a**⁺ to **2c**⁺ (Table 1), which is a clear token of the decreased electron density of the tritylium acceptors. The magnitude of the shift between the first reduction of complexes **1a**²⁺ to **1c**²⁺ 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-c** to an electron-accepting, cationic (η^5 -C₅H₄)Fe(η^5 -C₄H₄-CAr₂⁺) substituent in complexes **1a-c** is felt by the methylium acceptors and is not compensated by the other aryl substituents. One should note here that, in **1a**²⁺ and **2a**⁺, the 4-Me₂NC₆H₄ 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 **1c**²⁺ as compared to the anisyl residues of **1b**²⁺ is held responsible for the finding that **1c**²⁺ is considerably easier to reduce than **1b**²⁺ despite the nominally stronger donor properties of the aryl substituents in **1c**²⁺. This effect is even amplified with respect to the corresponding monosubstituted analogs **2b**⁺ and **2c**⁺ (Table 1).



Figure 6. Left: Cyclic voltammograms of complexes $1a^{2+}$ to $1c^{2+}$ in CH₂Cl₂/NBu₄BAR_{F24} (0.02 mM) at r. t. at a scan rate v = 100 mV/s. Right: Square wave voltammograms of complexes $1b^{2+}$ and $1c^{2+}$ in SO_{2(l)} at -20 °C with NBu₄BAR_{F24} (0.02 mM). The peak at 0 mV is due to the internal Cp₂Fe^{0/+} redox standard.

In the CH₂Cl₂/NBu₄BAr_{F24} electrolyte, the expected oxidation of the central ferrocene constituent can only be observed for the least electron-poor congener $1a^{2+}$ as a reversible wave at $E_{1/2} = 670$ mV against the Cp₂Fe^{0/+} 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 ($1b^{2+}$) or 1870 mV ($1c^{2+}$) in liquid SO₂, using NBu₄BAr_{F24} as the supporting electrolyte (Figure 6, right). With such positive redox potentials, $1b^{2+}$ and $1c^{2+}$ seem to be the electron-poorest ferrocenes reported to date, including other multiacceptor-substituted ferrocenes such as 1,1'-dicyanoferrocene ($E_{1/2} = 865$ mV), 1,1',2,2',4,4'- and 1,1',2,2',3,3'-hexakis(pentafluorophenylferrocene) ($E_{1/2} = 940$ mV and

951 mV, respectively), 1,1',3,3'-tetra(methoxycarbonyl)ferrocene $(E_{1/2} = 900 \text{ mV})^{[16]}$ and even 1,1',2,2'-tetraformylferrocene $(E_{1/2}^{0/+} = 1145 \text{ mV})$.^[17] In fact, their $E_{1/2}$ values nearly match or even surpass that of 1710 mV for the *second* oxidation of parent ferrocene (i. e. the Cp₂Fe^{+/2+} couple) under similar conditions.^[18]

	reductions				oxidation	
complex –	$E_{1/2}$	$\Delta E_{\rm p}$	$E_{1/2}$	$\Delta E_{\rm p}$	$E_{1/2}$	$\Delta E_{ m p}$
	(0/+)	(0/+)	(+/2+)	(+/2+)	(2+/3+)	(2+/3+)
1a ²⁺	-1340	57	-935	57	670	89
1b ²⁺	-880	70	-140	70	1640 ^{c)}	-
1c ²⁺	-690	70	-20	100	1870 ^{c)}	-
	(0/+)	(0/+)			(+/2+)	(+/2+)
2a ⁺	-1160	57			490	91
$2b^+$	-780	57			830	180
2c ⁺	-740	72			870	224

Table 1. Electrochemical data^{a),b)} for all complexes.

^{a)} Potentials in mV (\pm 3 mV) in CH₂Cl₂ at $T = 293(\pm 3)$ K relative to the Cp₂Fe^{0/+} couple ($E_{1/2} = 0.000$ V). Supporting electrolyte NBu₄⁺B{C₆H₃(CF₃)₂}⁴. ^{b)} Data for complexes **2a**⁺ to **2c**⁺ from ref. [6] ^{c)} Potentials were determined by square wave voltammetry in liquid SO₂ at $T = 253(\pm 3)$ K relative to the Cp₂Fe^{0/+} couple ($E_{1/2} = 0.000$ V) with NBu₄⁺B{C₆H₃(CF₃)₂}⁴ as the supporting electrolyte.

Spectroscopic Investigations on some oxidized and reduced forms

The three reversible redox processes of $1a^{2+}$ 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 $1a^{2+}$ 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 $1a^{2+}$ 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 $1a^{2+}$ to ultimately leave two bands at 540 nm and 439 nm. By inference from their mono-

triarylmethylium-substituted congeners, for which a similar behaviour was observed, these bands are assigned as a mixed transition within the ferrocene nucleus and a 1,1'ferrocenediyl— CAr_2^{\bullet} CT transition ($\lambda = 540$ nm) and as $\pi \rightarrow \pi^*$ transitions within the trityl chromophore ($\lambda = 439$ nm).^[6] Of note is the absence of a specific electronic transition at low energy for any radical cation with one neutral Ar_2C^{\bullet} and one cationic Ar_2C^+ substituent attached to the same ferrocene-1,1'-diyl scaffold (see also Figures S9 and S10 of the Supporting Information for the results of such studies on complexes **1b**,**c**²⁺). In view of the substantial halfwave potential splittings 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 of the 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 **1a**²⁺ a suspicious feature was observed as a weak band ($\varepsilon \approx 1000$ M⁻¹ cm⁻¹). This band was, however, found to persist during the second reduction and is hence not specific to **1a**⁺⁺.



Figure 7. Spectroscopic changes during oxidation (top) as well as the first (bottom left) and second (bottom right) reductions of complex $1a^{2+}$ (1,2-C₂H₄Cl₂ / NBu₄BAr_{F24} (0.02 M) at r. t.). The reduced forms of complexes $1a^{2+}$ and $1b^{2+}$ were also investigated by EPR spectroscopy. Singly reduced radical cations $1a^{\bullet+}$ and $1b^{\bullet+}$ were generated by reacting the dicationic

Accepted Manuscript

precursors with slightly less than 1 equiv. of cobaltocene in order to avoid overreduction. EPR spectra of these samples 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 ($1a^{\bullet+}$) or 2.0301 ($1b^{\bullet+}$). 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 triferrocenylmethyl, phenyldiferrocenylmethyl, 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 $1b^{\bullet+}$.

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 behaviour as expressed by equation 1, where gdenotes the isotropic g value of the compound, $\mu_{\rm B}$ is Bohr's magneton, B_0 the magnetic field strength and k_B is Boltzmann's constant. According to this equation, the population of the thermally excited state 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 behaviour was already observed for reduced samples of triarylmethylium-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 $2a^{\bullet+}$ as compared to $1a^{\bullet}$, which is a reasonable 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-behaviour, 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 agrees with our electrochemistry data.

$$\Delta N \approx N \cdot \frac{g \cdot \mu_B}{2 \cdot k_B} \frac{B_0}{T} \qquad (\text{eq. 1})$$



Figure 8. EPR spectra of monoreduced radical cations 1a^{•+} (left) and 1b^{•+} (right).

Fully reduced **1a**, generated by treating $1a^{2+}$ 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 2.0031 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 r. t. as shown by the slight intensity decrease of the low-field EPR resonance in the *T* interval of 20 °C to 0 °C.



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 $1b^{2+}$ to its radical cation on a preparative scale with Cp*₂Fe ($E_{1/2} = -$ 550 mV) as a selective reductant and without protection from the atmosphere, we observed a fading of the solution colour 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 ¹H NMR spectrum of the product obtained from the soluble fraction after solvent removal consists of four separate AB doublets at $\delta =$ 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 $\delta = 5.11$, 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 of the Supporting Information). This pattern of resonance signals indicates the formation of a chiral 1,1'-disubstituted ferrocene derivative with C_2 symmetry. A pure product was obtained, when 2 equiv. of cobaltocene were added to a CH₂Cl₂ solution of $1b^{2+}$ inside a glovebox and stirred for some minutes 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 of the Supporting Information). Crystallization of this compound by slow evaporation of a saturated solution in CH₂Cl₂ afforded yellow blocky 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-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 of the Supporting Information).

In **1b-O**₂ the former trityl carbon centers and the O atoms of a molecule of O₂ have combined to form a -C-O-O-C- bridge, which interconnects the two Ar₂C- 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 C_{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 107.0(1)°, and a dihedral angle of -134.2° 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}-Cp_{centroid}-Cp_{centroid}-C_{Cp}) and are tilted by a 7.2°, 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.



Figure 10. Molecule structure of one enantiomer of **1b-O**₂ as determined by X-ray crystallography. H-atoms are removed for reasons of clarity. Ellipsoids are displayed at a 50% probability level.

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_{Cp}–C-, C–O-, 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 with other, 4-substituted aryl substituents were obtained from the reaction of homoleptic Rh(I) complexes $[(\eta^4-C_5H_4=C(C_6H_4R-4)_2Rh]^+$ (R = H, Cl, OMe, Me) bearing differently substituted 6,6-diphenylfulvene ligands with air.^[22-23] Besides the doubly linked $(\eta^5-C_5H_4CPh\{(C_2H_4)(O-O)\}CPh(\eta^5-C_5H_4)Fe,^{[24]}$ 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 bistrityl 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-O**₂ is larger than that of 0.7° to 2.8° found in [4]ferrocenophanes with butane-1,4-diyl or 2-oxo-butane-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-O₂** 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 $-C_2H_4-$ or $-C(O=)-CH_2-$ connectors as opposed to a rather flat-lying peroxo group. Similar or even smaller tilts were, however, observed in [4]ferrocenophanes with fluorinated all-carbon bridges (up to 16.0°),^[27] or in a [4]ferrocenophane with a $-CH_2N(Ph)-C(COOMe)_2CH_2-$ connector (6.5°).^[28]

In further explorations of direduced **1b** we also investigated its reactivity with acetylene-1,4dicarboxylic acid dimethylester, styrene, CS₂, NO, water and methanol under a protective atmosphere of dinitrogen. From the product mixtures formed in these reactions, known 6,6dianisylfulvene^[23, 29] and the unsymmetrically substituted (η^5 -C₅H₄C(C₆H₄OMe)₂OH)Fe(η^5 -C₅H₄C(C₆H₄OMe)₂H (**1b-HOH**, for NMR and ESI mass spectra see Figures S15 to S17 of the Supporting Information) as the product of water addition were identified besides various, but smaller amounts of **1b-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 -C₅H₄C(*****R₂)₂Fe diradical is just the opposite reaction to that observed by Tacke and coworkers in their studies on bis(fulvene) iron(0) derivatives. The latter can either undergo H atom abstraction from the solvent (**R** = Ph, Me) or, in the case of methyl substituents, alternative C-C bond formation to a [2]ferrocenophane (Scheme 4).^[30]



Scheme 4. Formation and reactions of bisfulvene iron(0) complexes.^[30]

Summary and Conclusions

We here report on three 1,1-bis(diarylmethylium)-substituted ferrocenes of the type [$\{\eta^5$ - $C_5H_4C(C_6H_4R-4)$ ₂Fe]²⁺ (R = NMe₂: **1a**²⁺; R = OMe: **1b**²⁺ and [{ η^5 -C₅H₄C(C₆H₃(CH₃- $2)(OMe-4))_{2}Fe^{2+}$ (1c²⁺), 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 $Cp_2Fe^{+/2+}$ redox couple under similar conditions.^[18] The high Lewis acidity of these compounds becomes manifest through the bleach of the aryl→methylium 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 oneelectron steps with a large redox splitting $\Delta E_{1/2}$ of 405 to 740 mV. Nevertheless, no intervalence charge-transfer band for 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 monotritylium-substituted counterparts $2a^{\circ}-2c^{\circ}$ (Scheme 2), reduced $1a-c^{\circ+/0}$ 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 peroxo-(bisdiarylmethyl)[4]ferrocenophane with a -Ar₂C-O-O-CAr₂- linkage between the two Cp decks. As revealed 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 sizable 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 centres. Such behaviour 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 under 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] ¹H NMR (400 MHz), ¹³C{¹H} NMR (101 MHz) and ³¹P{¹H} 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 (¹H) or the solvent signal (¹³C). 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 HELLMA quartz cuvettes with 0.1 cm optical path lengths.

All electrochemical experiments were executed in a custom-built cylindrical vacuum-tight onecompartment 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 µm and then 0.25 µm 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{C₆H₃(CF₃)₂}^{4⁻} (0.1 mM) was used as the supporting electrolyte. Referencing was done with addition of an appropriate amount of decamethylferrocene (Cp*₂Fe, E₁₇₂ = -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 pseudoreference electrode sandwiched between two CaF₂ windows of a conventional liquid IR cell. The working electrode is positioned in the centre 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 ($\lambda = 0.71073$ Å) and an image plate detection system. A yellow, blocky crystal of **1b-O**₂ 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 2 θ values as well as data reduction, LPcorrection and space group determination were performed using the X-Area software package delivered with the diffractometer. A semiempirical 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 last-squares refinements using SHELX-2017^[35] and OLEX2^[36], minimizing $\omega(Fo^2 - Fc^2)^2$. The weighted *R* factor (w*R*²) and the goodness of the fit GOOF are based on *F*². 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 of **1b-O**₂ have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-197352 (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 quasirelativistic effective core potential (ECP) MDF10 was used,^[39] and 6-31G(d) polarized double- ξ 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 time-dependent DFT (TD-DFT) method.

Synthesis and characterization data

1a(OH)2



1.39 g (6.95 mmol, 4.2 eq.) of 4-bromo-N,Ndimethylaniline were dissolved in 40 mL of dry degassed tetrahydrofuran. 3.9 mL (1.9 M solution in n-hexane, 7.3 mmol, 4.4 eq.) of ^{*t*}BuLi were added dropwise to the solution at -78 °C. After stirring for 15 minutes a solution of 500 mg (1.66 mmol, 1 eq.) 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 r. t., 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 x 50 mL). The aqueous layer was separated off and extracted with Et₂O (3 x 100 mL). The combined organic phases were washed with brine (3 x 20 mL), dried over MgSO₄, and the solvent was evaporated *in vacuo*. The dark green crude product was washed with 210 mL of Et₂O (1 x 150 mL, 3 x 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_{H-H} = 8.8 Hz, 8H, H7), 6.62 (d, ³J_{H-H} = 8.8 Hz, 8H, H8), 4.15 (s, 4H, H1), 3.96 (s, 4H, H2), 3.84 (s, 2H, H5), 2.91 (s, 24H, 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.





1.100 g (1.01 mmol, 2.05 eq.) of Brookhart's acid in 40 mL of dry degassed Et_2O were added dropwise to 354 mg (0.49 mmol, 1 eq.) of **1a(OH)**₂ in 40 mL of dry degassed Et_2O at room temperature. The reaction mixture turned from green to dark blue. After stirring for 30 minutes the blue solution was evaporated and the petrol-coloured solid was dried

in vacuo, yielding 1.18 g (0.489 mmol, quantitative) of $1a^{2+}$. ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.72 (s, 16H, BAr _{F24}-CF₃CHCF₃), 7.57 (d, ³*J*_{H-H} = 9.4 Hz, 8H, H6), 7.55 (s, 8H, BAr _{F24}-CF₃CHCBCHR'), 6.69 (d, ³*J*_{H-H} = 9.4 Hz, 8H, H7), 5.17 (s, 4H, H1), 4.99 (s, 4H, H2), 3.15 (s, 24H, H9). ¹³C NMR (CD₂Cl₂, 101 MHz): δ 181.1 (C4), 161.79 (BAr_{F24}), 156.8 (C8), 139.3 (C6), 134.8 (BAr _{F24}), 127.8 (C5), 117.5 (BAr _{F24}), 112.6 (C7), 84.2 (C3), 79.2 (C2), 77.9 (C1),

40.5 (C9) ppm. MS (ESI): calcd. for $C_{44}H_{48}FeN_4$: 344.1607 [M]²⁺; found 344.1478. CHN-analysis: calcd. for $C_{108}H_{72}B_2F_{48}FeN_4$: C, 53.71 %; H, 3.00 %; N, 2.32 % N. Found: C, 52.79 %; H, 2.29 %; N, 2.36 %.

1b(OH)2



Ferrocene (2.2 g, 12 mmol, 1.5 eq.) was dissolved in 15 mL of dry THF and cooled to 0 °C. 5.5 mL (1.9 M solution in *n*-hexane, 10.4 mmol, 1.3 eq.) of ^{*t*}BuLi were added dropwise to the solution. After stirring for 15 minutes, a solution of 1.94 g (8 mmol, 1 eq.) of 4,4'-dimethoxybenzophenone in 20 mL of tetrahydrofuran was added to the reaction mixture at 0 °C.

After stirring for 15 minutes, the ice bath was removed and the yellow solution was stirred for additional 25 minutes at r. t. 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 x 50 mL). The aqueous layer was separated off and extracted with Et₂O (3 x 100 mL). The combined organic phases were washed with brine (3 x 20 mL), dried over MgSO₄, and the solvent was evaporated *in vacuo*. The residual solid was purified by column chromatography. A petroleum ether/ethylacetate (PE/EA) 5/1 mixture eluted some monosubstituted (η^5 -C₅H₅)Fe(η^5 -C₅H₄C(C₆H₄OMe-4)₂OH (**2aOH**) and unreacted 4,4'-dimethoxybenzophenone). With pure EA as eluent, the orange band of **1b(OH)**₂ was eluted. After solvent evaporation, **1b(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, ³J_{H-H} = 8.0 Hz, 8H, H4), 6.78 (d, ³J_{H-H} = 8.0 Hz, 8H, H5), 6.02 (s, 2H, H3), 3.97 (d, ³J_{H-H} = 2.7 Hz, 4H, H1), 3.71 (s, 12H, H6) ppm. ESI-MS (CH₃CN): calcd. for C₄₀H₃₈FeO₆: 670.2045 [M] ⁺; found 670.1975.

$1b^{2+} \cdot 2 BAr_{F24}$



320 mg (0.31 mmol, 2.05 eq.) of Brookhart's acid in 5 mL of dry degassed Et_2O were added dropwise to 100 mg (0.14 mmol, 1 eq.) of **1b(OH)**₂ in 5 mL of dry degassed Et_2O at r. t. The reaction mixture turned from yellow to dark green. After stirring for 20 minutes the solvent was removed to obtain **1b**²⁺ as a red solid in quantitative yield. ¹H NMR (CDCl₈,

400 MHz): δ 7.66 (s, 16H, BArF-CF₃CHCF₃), 7.55 (d, ³*J*_{H-H} = 8.9 Hz, 8H, H3), 7.47 (s, 8H,

22

BArF-CF₃C*H*CBC*H*R'), 6.96 (d, ${}^{3}J_{H-H}$ = 8.9 Hz, 8H, H4), 5.45 (t, ${}^{3}J_{H-H}$ = 2.1 Hz, 4H, H1), 5.10 (t, ${}^{3}J_{H-H}$ = 2.1 Hz, 4H, H2), 3.92 (s, 12H, H5).

1c(OH)2



2.10 g (1.5 mL, 10.4 mmol, 4.2 eq.) of 1-bromo-4methoxy-1-methyl-benzene were dissolved in 200 mL of dry degassed absolute ether (Et₂O). 3.9 mL of a 1.9 M solution of ^{*t*}BuLi in *n*-hexane (7.3 mmol, 4.4 eq.) were added dropwise to the solution at -78 °C. After stirring for 15 minutes, a solution of 7.5 g (2.48 mmol, 1 eq.) of dimethyl-1,1'ferrocenedicarboxylate in 200 mL of Et₂O was added

to the reaction mixture at -78 °C. After stirring overnight, the reaction mixture was quenched with 100 mL of water. The residue was dissolved in Et₂O and extracted with water (3 x 50 mL). The aqueous layer was separated off and extracted with Et₂O (3 x 100 mL). The combined organic phases were washed with brine (3 x 20 mL), dried over MgSO₄, and the solvent was evaporated *in vacuo*. The orange crude product was purified by recrystallization from Et₂O to yield 1.12 g (1.54 mmol, 62 %) of **1c(OH)**₂ as a yellow crystalline solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.48 (broad s, 4H, H13), 6.65-6.72 (m, 4H, H12), 6.55-6.59 (m, 4H, H9), 4.18 (broad s, 4H, H1), 4.00 (s, 4H, H2), 3.99 (s, 2H, H5), 3.78 (s, 12H, H10), 1.74 (s, 12H, H8) ppm. ¹H-NMR (toluene-d₈, 400 MHz): δ 7.65 (broad s, 4H, H13), 6.58-6.63 (m, 8H, H9, H12), 4.24 (broad s, 4H, H1), 3.84 (s, 4H, H2), 3.75 (s, 2H, H5), 3.40 (s, 12H, H10), 1.89 (s, 12H, H8) ppm. ¹³C NMR (CDCl₃, 101 MHz): δ 158.5 (C6), 137.4 (C7), 129.9 (C13), 117.4 (C9), 109.8 (C12), 100.0 (C3), 78.1 (C4), 70.5 (C1), 68.5 (C2), 55.3 (C10), 22.1 (C8).

 $1c^{2+} \cdot 2 BAr_{F24}$



550 mg (0.51 mmol, 2.05 eq.) of Brookhart's acid in 40 mL of dry degassed Et₂O were added dropwise to 179.4 mg (0.25 mmol, 1 eq.) of $1c(OH)_2$ in 40 mL of dry degassed Et₂O at r. t. The colour of the reaction mixture changed from yellow to dark yellow. After stirring for 30 minutes the solvent was stripped off the ochre solution. The resulting purple solid was dried *in vacuo*, yielding 590 mg

(0.246 mmol, quantitative) of $1c^{2+}$. Due to paramagnetic broadening it was not possible to obtain meaningful NMR spectra. MS (ESI): calcd. for C₄₄H₄₄FeO₄ 346.1306 [M]²⁺; found

23

346.1461 (measured in dichloromethane, non-calibrated). CH-analysis: calcd. for $C_{108}H_{68}B_2F_{48}FeO_4$: 53.62 % C, 2.83 % H; found: 52.71 % C, 3.42 % H.

1b-O₂



Inside a glove box $1b^{2+} \cdot 2 \text{ BArF24}^{-}$ (100 mg, 0.042 mmol, 1 eq.) was dissolved in 3 mL of degassed CH₂Cl₂ and 16 mg (0.084 mmol, 2 eq.) of cobaltocene were added. The mixture was stirred for 10 min, then removed from the glove box, exposed to the air and stirred at r. t. 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, 4H, ³*J*_{HH} = 8.85 Hz, H8), 7.35 (d, 4H, ³*J*_{HH} = 8.85 Hz, H13), 6.90 (d, 4H, ³*J*_{HH} = 8.85 Hz, H9), 6.52 (d, 4H, ³*J*_{HH} = 8.85 Hz, H14), 5.11 (m, 2H, H1), 4.21 (m, 2H, H2), 4.03 (m, 2H, H4), 3.91 (m, 2H, H3), 3.33 (s, 6H, CH₃-11), 3.21 (s, 6H, CH₃-16). ¹³C NMR (C₆D₆, 101 MHz): δ 159.3 (C10), 158.9 (C15), 136.9 (C12), 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 (C11), 54.7 (C16). ESI-MS (CH₃CN) calcd. for C₄₀H₃₆FeO₆+H⁺ [MH] ⁺ 669.1915; found 669.1925.

1b-HOH

Inside a glove box $1b^{2+} \cdot 2 BAr_{F24}$ (100 mg, 0.042 mmol, 1 eq.) was dissolved in 3 mL of degassed



CH₂Cl₂. 16 mg (0.084 mmol, 2 eq.) of cobaltocene and $0.76 \,\mu$ L of water were added and the mixture was allowed to stir at r. t. for 2 h. During this time the solution turned green. The solvents were removed under reduced pressure and the green solid was extracted with n-hexane. Solvent was stripped off the filtered extract and the solid

residue was purified by solvent chromatography (silica, PE/EA 5/1). The first fraction contained small quantities of 6,6-diansiylfluorene. The second, orange band provided complex **1b-HOH** after solvent evaporation and washing with cold *n*-pentane.

¹H-NMR (400 MHz, C₆D₆): δ 7.41 (d, 4H, ³*J*_{HH} = 8.80 Hz, H15), 7.04 (d, 4H, ³*J*_{HH} = 8.85 Hz, H9), 6.76 (d, 4H, ³*J*_{HH} = 8.80 Hz, H16), 6.74 (d, 4 H, ³*J*_{HH} = 8.85 Hz, H10), 4.81 (s, 1H, H7),

4.07 (m, 2H, H2), 4.03 (m, 2H, H1), 4.02 (m, 2H, H5), 3.92 (m, 2H, H6), 3.32 (s, 12H, H12, H18), 3.01 (s, 1H, OH). ¹³C-NMR (100.61 MHz, C₆D₆) δ 158.6 (C17), 158.2 (C11), 140.4 (C14), 137.6 (C8), 129.6 (C9), 128.5 (C15), 113.5 (C10), 112.8 (C16), 100.2 (C4), 93.2 (C3), 76.9 (C13), 69.5 (C2), 69.4 (C5), 68.9 (C6), 68.2 (C1), 54.4 (C12, C18), 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 $1b^{2+}$ and $1c^{2+}$, ESI-MS of complexes **1b-O**₂ 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.

Keywords: ferrocene, tritylium, electrochemistry, spectroelectrochemistry, ferrocenophane, peroxo compound, EPR spectroscopy, solvatochromism

Acknowlegements

We gratefully acknowledge financial support of this work by the Deutsche Forschungsgemeinschaft (DFG, grant no. Wi1262/9-2). Larissa A. Casper thanks the Studienstiftung des Deutschen Volkes for a PhD grant. We are also grateful to the DFG and the State of Baden-Württemberg for providing us with access to the computational facilities of the JUSTUS HPC facilities as a part of the bw_FOR network at the University of Ulm (grant no. INST 40/467-1 FUGG). We also thank Eva Schiebel for the synthesis of compound **1b**-(**OH**)₂ as a part of an internship.

References

- [1] a) J. H. Richards, E. A. Hill, J. Am. Chem. Soc. 1959, 81, 3484-3485; b) E. A. Hill, R. Wiesner, J. Am. Chem. Soc. 1969, 91, 509-510; c) E. A. Hill, J. H. Richards, J. Am. Chem. Soc. 1961, 83, 4216-4221; d) E. A. Hill, J. H. Richards, J. Am. Chem. Soc. 1961, 83, 3840-3846; e) M. Cais, Organomet. Chem. Rev. 1966, 1, 435-454; f) W. E. Watts, J. Organomet. Chem 1981, 220, 165-172.
- [2] U. Behrens, J. Organomet. Chem 1979, 182, 89-98.
- [3] R. Gleiter, R. Seeger, *Helv. Chim. Acta* **1971**, *54*, 1217-1220.
- [4] T. D. Turbitt, W. E. Watts, J. Chem. Soc., Perkin Trans. 2 1974, 177-184.
- [5] a) T. D. Turbitt, W. E. Watts, *J. Chem. Soc., Perkin Trans.* 2 1974, 185-189; b) D.
 Hellwinkel, H. Fritsch, *Chem. Ber.* 1989, *122*, 2351-2359; c) C. Arbez-Gindre, B. R.
 Steele, G. A. Heropoulos, C. G. Screttas, J.-E. Communal, W. J. Blau, I. Ledoux-Rak, *J. Organomet. Chem.* 2005, *690*, 1620-1626; d) C. Villalonga-Barber, B. R. Steele, V.

Kovač, M. Micha-Screttas, C. G. Screttas, *J. Organomet. Chem.* **2006**, *691*, 2785-2792; e) C. Villalonga-Barber, K. Vallianatou, S. Georgakopoulos, B. R. Steele, M. Micha-Screttas, E. Levin, N. Gabriel Lemcoff, *Tetrahedron* **2013**, *69*, 3885-3895.

- [6] S. Oßwald, L. A. Casper, P. Anders, E. Schiebel, S. Demeshko, R. F. Winter, *Chem. Eur. J.* 2018, 24, 12524-12538.
- [7] C. U. Pittman, *Tet. Lett.* **1967**, *8*, 3619-3623.
- [8] C. R. Jablonski, J. Organomet. Chem. 1979, 174, C3-C10.
- [9] K. Gonsalves, L. Zhan-Ru, M. D. Rausch, J. Am. Chem. Soc. 1984, 106, 3862-3863.
- [10] M. Brookhart, B. Grant, A. F. Volpe, *Organometallics* **1992**, *11*, 3920–3922.
- [11] H. Nishida, N. Takada, M. Yoshimura, T. Sonoda, H. Kobayashi, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600-2604.
- [12] a) R. J. LeSuer, C. Buttolph, W. E. Geiger, *Anal. Chem.* 2004, 76, 6395-6401; b) F. Barrière, W. E. Geiger, *J. Am. Chem. Soc.* 2006, *128*, 3980-3989; c) A. Hildebrandt, H. Lang, *Organometallics* 2013, *32*, 5640-5653.
- [13] a) I. Ratera, D. Ruiz-Molina, F. Renz, J. Ensling, K. Wurst, C. Rovira, P. Guetlich, J. Veciana, J. Am. Chem. Soc. 2003, 125, 1462-1463; b) I. Ratera, C. Sporer, D. Ruiz-Molina, N. Ventosa, J. Baggerman, A. M. Brouwer, C. Rovira, J. Veciana, J. Am. Chem. Soc. 2007, 129, 6117-6129; c) G. D'Avino, L. Grisanti, J. Guasch, I. Ratera, J. Veciana, A. Painelli, J. Am. Chem. Soc. 2008, 130, 12064-12072; d) J. Guasch, L. Grisanti, S. Jung, D. Morales, G. D'Avino, M. Souto, X. Fontrodona, A. Painelli, F. Renz, I. Ratera, J. Veciana, Chem. Mater. 2013, 25, 808-814; e) M. Souto, D. C. Morales, J. Guasch, I. Ratera, C. Rovira, A. Painelli, J. Veciana, A. Painelli, J. Attera, C. Rovira, A. Painelli, J. Veciana, J. Phys. Org. Chem. 2014, 27, 465-469.
- [14] a) A. S. Ferguson, G. Hallas, J. Soc. Dyers Colour. 1973, 89, 22-24; b) G. Hallas, K. N. Paskins, D. R. Waring, J. R. Humpston, A. M. Jones, J. Chem. Soc., Perkin Trans. 2 1977, 450-456; c) D. F. Duxbury, Chem. Rev. 1993, 93, 381-433.
- [15] V. Gutmann, Coord. Chem. Rev. 1976, 18, 225-255.
- [16] S. D. Waniek, J. Klett, C. Foerster, K. Heinze, *Beilstein J. Org. Chem.* 2018, 14, 1004-1015.
- [17] A. Hildebrandt, K. Al Khalyfeh, D. Schaarschmidt, M. Korb, *J. Organomet. Chem.* **2016**, *804*, 87-94.
- [18] P. R. Sharp, A. J. Bard, *Inorg. Chem.* **1983**, *22*, 2689-2693.
- [19] a) J.-M. Lü, S. V. Rosokha, J. K. Kochi, J. Am. Chem. Soc. 2003, 125, 12161-12171;
 b) J.-M. Lü, S. V. Rosokha, I. S. Neretin, J. K. Kochi, J. Am. Chem. Soc. 2006, 128, 16708-16719; c) S. V. Rosokha, J. K. Kochi, J. Am. Chem. Soc. 2007, 129, 3683-3697; d) S. V. Rosokha, I. S. Neretin, D. Sun, J. K. Kochi, J. Am. Chem. Soc. 2006, 128, 9394-9407; e) A. C. Benniston, G. Copley, A. Harriman, D. Howgego, R. W. Harrington, W. Clegg, J. Org. Chem. 2010, 75, 2018-2027; f) T. Nishinaga, Y. Kanzaki, D. Shiomi, K. Matsuda, S. Suzuki, K. Okada, Chem. Eur. J. 2018, 24, 11717-11728.
- [20] a) W. J. van der Hart, *Mol. Phys.* 1970, *19*, 75-84; b) K. Ishizu, K. Mukai, A. Shibayama, K. Kondo, *Bull. Chem. Soc. Japan* 1977, *50*, 2269-2271; c) N. I. Tzerpos, A. K. Zarkadis, R. P. Kreher, L. Repas, M. Lehnig, *J. Chem. Soc. Perkin Trans.* 2 1995, 755-761.
- [21] S. P. Solodovnikov, A. Z. Kreindlin, L. S. Shilovtseva, M. I. Rybinskaya, *Organomet. Chem. USSR* **1991**, *4*, 142-145.
- [22] J. Jeffery, R. J. Mawby, M. B. Hursthouse, N. P. C. Walker, J. Chem. Soc., Chem. Commun. **1982**, 1411-1412.
- [23] J. Jeffery, E. J. Probitts, R. J. Mawby, J. Chem. Soc., Dalton Trans. 1984, 2423-2427.
- [24] M. Hisatome, S. Minagawa, K. Yamakawa, J. Organomet. Chem 1973, 55, c82-c84.
- [25] M. Gomberg, J. Am. Chem. Soc. 1903, 25, 1274-1277.

- [26] a) M. Görmen, P. Pigeon, E. A. Hillard, A. Vessières, M. Huché, M.-A. Richard, M. J. McGlinchey, S. Top, G. Jaouen, *Organometallics* 2012, *31*, 5856-5866; b) M. Hisatome, K. Nakanishi, K. Yamakawa, K. Kozawa, T. Ucnida, *Bull. Chem. Soc. Jpn.* 1992, *65*, 3275-3281; c) K.-L. Gibis, G. Helmchen, G. Huttner, L. Zsolnai, *J. Organomet. Chem* 1993, *445*, 181-186; dR. M. Gleixner, K. M. Joly, M. Tremayne, B. M. Kariuki, L. Male, D. M. Coe, L. R. Cox, *Chem. Eur. J.* 2010, *16*, 5769-5777.
- [27] M. Roemer, D. Heinrich, Y. K. Kang, Y. K. Chung, D. Lentz, *Organometallics* **2012**, *31*, 1500-1510.
- [28] S. Harthong, R. Bach, C. Besnard, L. Guénée, J. Lacour, Synthesis 2013, 45, 2070-2078.
- [29] F. Edelmann, B. Lubke, U. Behrens, *Chem. Ber.* 1982, 115, 1325-1331.
- [30] aS. Fox, John P. Dunne, M. Tacke, D. Schmitz, R. Dronskowski, *Eur. J. Inorg. Chem.* 2002, 2002, 3039-3046; bR. Teuber, R. Köppe, G. Linti, M. Tacke, *J. Organomet. Chem.* 1997, 545-546, 105-110.
- [31] H. S. Sørensen, J. Larsen, B. S. Rasmussen, B. Laursen, S. G. Hansen, T. Skrydstrup, C. Amatore, A. Jutand, *Organometallics* 2002, 21, 5243-5253.
- [32] P. Witte, T. K. Lal, R. M. Waymouth, Organometallics 1999, 18, 4147-4155.
- [33] M. Krejcik, M. Danek, F. Hartl, J. Electroanal. Chem. 1991, 317, 179-187.
- [34] W. Herrendorf, W. Bärnighausen, Version 1.06 ed., Fa. Stoe, Darmstadt, Karlsruhe, Gießen, **1999**.
- [35] G. M. Sheldrick, *Acta Cryst. A* **2015**, *71*, 3-8.
- [36] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. *Appl. Cryst.* **2009**, *42*, 339-341.
- [37] M. J. Frisch, G. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, M. Caricato, A. Marenich, J. Blonio, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Vol. 2016*, Gaussian, Inc., Wallingford CT, **2016**.
- [38] M. Cossi, N. Rega, G. Scalmani, V. Barone, J. Comput. Chem. 2003, 24, 669-681.
- [39] M. Dolg, U. Wedig, H. Stoll, H. Preuss, J. Chem. Phys. 1987, 86, 866-872.
- [40] P. H. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213-222.
- [41] aJ. P. Perdew, K. Burke, M. Enzerhof, *Phys. Rev. Lett.* **1996**, 77, 3865-3868; bC. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158-6170.
- [42] N. M. O'Boyle, A. L. Tenderholt, K. M. Langner, J. Comput. Chem. 2008, 29, 839-845.
- [43] a) M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek, G. R. Hutchinson, J. Cheminf. 2012, 4, 17; b) in <u>http://avogadro.cc/</u>.
- [44] O. Tange, USENIX Magazine **2011**, *36*, 42-47.
- [45] W. Humphrey, A. Dalke, K. Schulten, J. Mol. Graph. 1996, 14, 33-38.
- [46] <u>http://www.povray.org/download/</u>, 2004.