Tailoring Valence Tautomerism by Using Redox Potentials: Studies on Ferrocene-Based Triarylmethylium Dyes with Electron-Poor Fluorenylium and Thioxanthenylium Acceptors

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Experimental Section

Experimental Methods and Materials. All manipulations including synthetic procedures and chemical reductions were carried out at room temperature under an atmosphere of purified nitrogen with dry, distilled, and nitrogen-saturated solvents using standard Schlenk and glovebox techniques unless stated otherwise. All reagents were purchased from commercial sources and used without further purification. Ketones 6a and 6b used for the carbinol syntheses (1a-OH, 1b-OH) were prepared by a literature procedure of Shi et al.[1] New ketone 5 was synthesized according to a procedure adapted from Kobayashi et al. (see below).[2] \(^1\)H NMR (400 MHz), \(^{19}\)F NMR (376 MHz), and \(^{13}\)C NMR (101 MHz) spectra were recorded on a Bruker Avance III 400 spectrometer in CD\(_2\)Cl\(_2\) or CDCl\(_3\) (as indicated) solutions at room temperature. The spectra are referenced to the residual protonated solvent (\(^1\)H), the solvent signal (\(^{13}\)C) or by established absolute referencing methods (\(^{19}\)F). Further characterization was carried out by ESI-MS on a Bruker micrOTOF II using dichloromethane as the solvent. NBu\(_4^+\)[B\{C\(_6\)H\(_3\)(CF\(_3\))\(_2\)-3,5\}\(_4\)]\(^-\), used as a supporting electrolyte in (spectro)electrochemical studies was synthesized in a two-step procedure starting from 3,5-bis(trifluoromethyl)bromobenzene to first yield Na\(^+\)[B\{C\(_6\)H\(_3\)(CF\(_3\))\(_2\)-3,5\}\(_4\)],[3] which was subsequently converted to the NBu\(_4^+\) salt by cation exchange.[4] Brookhart’s acid was synthesized according to an established procedure starting from the same Na\(^+\)[B\{C\(_6\)H\(_3\)(CF\(_3\))\(_2\)-3,5\}\(_4\)] precursor.[5]

Electrochemical and Spectroelectrochemical Measurements. All electrochemical experiments were conducted under argon atmosphere. Samples of the cationic complexes 1a\(^+\)-1c\(^+\), were freshly generated (in-situ) using 4 Å pore-size molecular sieves. The data were acquired with a computer-controlled BASi potentiostat. A custom-built cylindrical vacuum-tight one-compartment cell with a spiral-shaped Pt-wire as counter and an Ag wire as reference electrode were sealed into glass capillaries and fixed by Quickfit screws and used in combination with a platinum working electrode. The latter was polished with first 1 \(\mu\)m and then 0.25 \(\mu\)m diamond paste prior to measurements and consecutively introduced into the top port of the one-compartment cell that was attached to a conventional Schlenk line by a sidearm through a Teflon screw cap with a suitable fitting. NBu\(_4^+\)[B\{C\(_6\)H\(_3\)(CF\(_3\))\(_2\)-3,5\}\(_4\)]\(^-\) was used as the supporting electrolyte in dichloromethane. After data-acquisition was complete, roughly equimolar amounts
decamethylferrocene (Cp²Fe⁰⁺) or ferrocene were added as internal standards for referencing. Final referencing was done, after repetition of every measurement with the added standard, against the ferrocene/ferrocenium (Cp²Fe⁰⁺) redox couple with $E_{1/2}$(Cp²Fe⁰⁺) = -550 mV vs $E_{1/2}$(Cp²Fe⁰⁺).[6]

The simulation of cyclic voltammograms of complex 1a⁺, as shown in the Figure 3 of the manuscript and in Figure S27, was performed using the program DigiSim.[7] The simulation as depicted in Figure S27 refers to a reaction scheme with four charge transfer reactions, namely the redox couples 1a⁺/1a²⁺; 1a⁺/1a; 1a⁺/1a⁻; and 1a⁺/1a⁻/1a⁻ and the three homogeneous chemical reactions shown in Table S2. The initial parameters were set as follows: initial concentration = 0.0063 M; electrode surface area = 0.0256 cm², $T = 298 \text{ K}$, $C_{dl} = 3 \times 10^{-7} \text{ F}$, planar electrode geometry. By loading cyclic voltammograms over a range of scan rates of 200-2000 mV/s (cf. Figure S25 and Figure27), the program was free to change the chosen parameters in an interactive manner to optimally replicate the experimental CV shape. The simulation then yielded the redox potentials noted in Figure S27, the electron transfer coefficients of ca. 0.5 and electron transfer rates, the latter ranging from 0.0051 cm/s to 0.4289 cm/s, the rate constants $k_r$, $k_b$, and the equilibrium constants $k_r/k_b$ of the chemical reactions in Figure S27 and in Table S1, as well as the diffusion coefficients (range 3.34·10⁻⁷ cm²/s for 1a⁺-1a⁻ and 1.03·10⁻⁶ cm²/s for 1a²⁺.

UV/Vis/NIR spectra were recorded on a TIDAS fiber optic diode array spectrometer, which consists of a combination of MCS UV/NIR and PGS NIR instruments from J&M. For the determination of extinction coefficients, HELLMMA quartz cuvettes with 0.1 cm, 0.5 cm and 1 cm optical path lengths were used (filled under dinitrogen atmosphere inside a glovebox). According to Hartl’s design,[8] a custom-built optically transparent thin-layer electrochemical (OTTLE) cell (Pt-mesh working and counter electrodes, a thin silver wire as a pseudo reference electrode, CaF₂ windows) was used for spectroelectrochemical measurements in 1,2-C₂H₄Cl₂. Temperature-dependent UV/Vis/NIR spectra were measured inside a glovebox with the aid of a remote UV/Vis/NIR probe from Hellma Analytics. Thermostating was done in a home-built setup consisting of (i) a Cu block, which is cooled by an outer cryostat loop, (ii) a connected Al block as a “cold reservoir”, and (iii) a Cu cell holder, which is cooled by four computer-controlled Peltier elements. The setup comprises two vials made from thermally conducting Al-oxide, one of which serves as the sample and the other one as the reference. Alternation between sample and
reference is done completely automatically by moving the vials. The setup allows for measurements down to -75 °C, and the temperature is measured directly at the cell vials.

**EPR Spectroscopy.** Electron paramagnetic resonance (EPR) spectroscopy was performed on the X-band benchtop spectrometer MiniScope MS5000 by Magnettech GmbH using the program ESR Studio 1.63.0 in the temperature range from 20 °C to -150 °C. The thermostat makes use of the temperature control unit HO3 and liquid nitrogen as a cooling agent. All EPR samples (glass tubes: 3 mm outer, 2 mm inner diameter, filling height of exactly 60 mm) were prepared inside of a glovebox and sealed under nitrogen atmosphere. The following parameters were kept constant at all times and for all measurements: B = 3300 G-3450 G, Sweep Time = 60 s, modulation = 3 G, power = 6.3096 mW. Simulation of the measured spectra was performed using the MATLAB Easyspin program ‘garlic’.\(^9\) The DPPH\(^•\) radical standard was used as a calibrating agent. Its purity was checked by titration with hydroquinone using a UV/Vis/NIR probe prior to measurements.\(^{10}\) Further details on the employed method, calibration and error calculations are given in the EPR-Section of this Supporting Information. X-band EPR spectra at 10 K were recorded on an ELEXSYS E580 spectrometer equipped with a super-high-Q probe head (both from Bruker BioSpin). Temperature control was realized with an ESR900 cryostat in combination with an intelligent temperature controller ITC503 (both from Oxford Instruments). Liquid helium was used as a cooling agent. Experimental setting were adjusted to avoid any overmodulation and saturation effects: microwave frequency of 9.4 GHz, microwave attenuation of 36 dB (corresponds to 0.05 mW of microwave power), modulation amplitude of 3 G, sweep width of 6000 G, and number of points of 8192. Data were baseline-corrected by substraction of a first-order polynomial. A background signal originating from the solvent was used for further corrections.

**Mößbauer Spectroscopy.** Mößbauer samples were freshly prepared under inert gas atmosphere. An alternating constant acceleration Wissel Mößbauer spectrometer with a \(^{57}\)Co source in a Rh matrix and a Janis closed-cycle helium cryostat were operated in the transmission mode to record the spectra. Simulation of the recorded data was done with the Mfit program using Lorentzian line doublets.\(^{11}\) The isomer shifts are given relative to iron metal at ambient temperature.

**Quantum Chemical Calculations.** The ground, excited and triplet state electronic structures were calculated by density functional theory (DFT) making use of the Gaussian
16 program package. Geometry optimization without any symmetry constraints followed by vibrational analysis was performed in 1,2-dichloroethane as solvent including the polarizable continuum model (PCM).[12] Open-shell systems were calculated by the unrestricted Kohn-Sham approach (UKS). At these optimized geometries, electronic spectra were calculated by the time-dependent TD-DFT method. For Fe, the WACHTER basis set[13] was used, and 6-316(d)[14] olarized double-ζ basis sets were employed for all other atoms with PBEO[15] as correlation functional. The GaussSum[16] program package was used to analyze the results. The visualization of the results, data processing and graphical representation was performed by a combination of Avogadro, GNU Parallel and vmd program packages as well as POV-Ray.[17] GaussSum was used to process MULLIKEN spin densities with contributions of the hydrogen artoms summed into heavy atoms to which they are bonded

**Synthesis and Characterization.** All carbinol precursors 1a-OH-1c-OH were synthesized by the General Synthesis of Carbinols (vide infra) and all cationic complexes 1a⁺-1c⁺ were synthesized by the General Synthesis of Cationic Dyes (vide infra).

*General Synthesis of Carbinols.* tert-Butyllithium (2.2 eq, 1.9 M in hexanes) was added dropwise at -78°C (inert gas atmosphere!) to a 10 mL THF-solution of 4-bromophenylferrocene (1.0 eq). The deep orange reaction mixture was stirred for 1 h at -78°C. A solution of the respective ketone electrophile (1.0 eq) in THF was prepared and added dropwise to the reaction mixture. After complete addition, the mixture was allowed to warm to r.t. and stirred for 12h at ambient temperature. Then, the reaction mixture was heated to 60°C for 4h and consecutively quenched by the addition of 3 mL of water. The aqueous phase was extracted with diethyl ether (3 x 40 mL), the combined organic phases were washed with brine (30 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The orange residue was purified by gradient column chromatography (n-pentane/ethyl acetate 1:0-20:1) to yield the respective carbinols 1a-OH-1c-OH as pure orange solids.

**1a-OH.** 3,6-Dimethoxy-9H-fluoren-9-one (6a) was prepared according to a literature procedure and then used as electrophile.[1] For a batch size of 0.96 mmol, a yield of 230 mg (0.46 mmol, 48%) of the orange, crystalline complex 1a-OH was obtained. **1H-NMR** (CD₂Cl₂, 400 MHz) δ [ppm] = 7.38 (d, 3JHH = 8.31 Hz, 2H, H-6), 7.27 (d, 3JHH = 8.31 Hz, 2H, H-7), 7.23 (d, 3JHH = 8.31 Hz, 2H, H-11), 7.20 (d, 4JHH = 2.34 Hz, 2H,
H-14), 6.81 (dd, $^3J_{HH} = 8.31$ Hz, $^4J_{HH} = 2.34$ Hz, 2H, H-12), 4.59 (vt, $^3J_{HH} = 1.8$ Hz, 2H, H-2), 4.28 (vt, $^3J_{HH} = 1.8$ Hz, 2H, H-3), 4.01 (s, 5H, H-1), 3.87 (s, 6H, H-16), 2.49 (s, 1H, OH). $^{13}$C($^1$H)-NMR (CD$_2$Cl$_2$, 101 MHz) δ [ppm] = 161.4 (C-15), 144.2 (C-10), 142.2 (C-8), 141.5 (C-13), 138.7 (C-5), 126.5 (C-7), 125.9 (C-6), 114.6 (C-12), 114.5 (C-11), 106.1 (C-14), 85.8 (C-4), 83.2 (C-9), 70.2 (C-3), 70.0 (C-1), 67.1 (C-2), 56.1 (C-16). ESI-MS calcd. for C$_{31}$H$_{25}$FeO$_3$ (1a-OH); C$_{31}$H$_{25}$FeO$_3$ (1a-OH-H) m/z = 502.123 (1a-OH); 501.115 (1a-OH-H); found 502.135 (1a-OH); 501.125 (1a-OH-H) (measured in CH$_2$Cl$_2$, calibrated). Elemental analysis (CHN only) calcd (%) for C$_{31}$H$_{25}$FeO$_3$ (502.39 g mol$^{-1}$): C 74.11, H 5.22; found: C 73.70, H 5.55.

1b-OH. 3,6-Dimethyl-9H-fluoren-9-one (6b) was prepared according to a literature procedure.$^{[1]}$ For a batch size of 0.96 mmol, a yield of 334 mg (0.71 mmol, 74%) was obtained. $^1$H-NMR (CDCl$_3$, 400 MHz) δ [ppm] = 7.47 (s, 2H, H-14), 7.35 (d, $^3J_{HH} = 8.29$ Hz, 2H, H-6), 7.30 (d, $^3J_{HH} = 8.29$ Hz, 2H, H-7), 7.25 (d, $^3J_{HH} = 7.45$ Hz, 2H, H-11), 7.07 (d, $^3J_{HH} = 7.45$ Hz, 2H, H-12), 4.57 (br s, 2H, H-2), 4.27 (br s, 2H, H-3), 4.01 (s, 5H, H-1), 2.43 (s, 6H, H-16), 2.41 (s, 1H, OH). $^{13}$C($^1$H)-NMR (CDCl$_3$, 101 MHz) δ [ppm] = 148.2 (C-15), 141.3 (C-8), 139.9 (C-10), 139.0 (C-13), 138.1 (C-5), 129.2 (C-12), 126.1 (C-6), 125.5 (C-7), 124.6 (C-11), 120.8 (C-14), 83.3 (C-9), 85.5 (C-4), 69.7 (C-1), 68.9 (C-3), 66.6 (C-2), 21.6 (C-16). ESI-MS calcd. for C$_{31}$H$_{25}$FeO$_3$ (1b-OH-H) m/z = 469.125 (1b-OH-H); found 469.141 (measured in CH$_2$Cl$_2$, calibrated). Elemental analysis (CHN only) calcd (%) for C$_{31}$H$_{25}$FeO$_3$ (470.39 g mol$^{-1}$): C 79.16, H 5.57; found: C 77.84, H 5.68.

1c-OH. 3,6-Bis(trifluoromethyl)-9H-thioxanthen-9-one (5) was prepared according to a four-step procedure as described below that was adapted from a literature procedure$^{[2]}$ and then used as the electrophile. For a batch size of 0.72 mmol, a yield of 290 mg (0.48 mmol, 66%) was obtained. $^1$H-NMR (CD$_2$Cl$_2$, 400 MHz) δ [ppm] = 8.27 (d, $^3J_{HH} = 8.26$ Hz, 2H, H-11), 7.76 (d, $^4J_{HH} = 1.19$ Hz, 2H, H-14), 7.74 (dd, $^3J_{HH} = 8.26$ Hz, $^4J_{HH} = 1.19$ Hz, 2H, H-12), 7.28 (d, $^3J_{HH} = 8.45$ Hz, 2H, H-6), 6.77 (d, $^3J_{HH} = 8.45$ Hz, 2H, H-7), 4.56 (vt, $^3J_{HH} = 1.7$ Hz, 2H, H-2), 4.29 (vt, $^3J_{HH} = 1.7$ Hz, 2H, H-3), 3.98 (s, 5H, H-1), 3.13 (s, 1H, OH). $^{13}$C($^1$H)-NMR (CD$_2$Cl$_2$, 101 MHz) δ [ppm] = 143.9 (C-15), 140.5 (C-5), 139.2 (C-10), 132.8 (C-9), 130.0 (t, $^2J_{CF} = 33$ Hz, C-13), 127.4 (C-11), 127.2 (C-7), 126.4 (C-6), 124.3 (d, $^1J_{CF} = 237$ Hz, C-16), 124.3 (q, $^3J_{CF} = 3.5$ Hz, C-14), 124.1 (q, $^3J_{CF} = 3.5$ Hz, C-12), 84.5 (C-3), 77.6 (C-8), 70.0 (C-1), 67.0 (C-2), 69.7 (C-3). $^{19}$F($^1$H)-
NMR (CD$_2$Cl$_2$, 376 MHz) $\delta$ [ppm] = -62.8 (s, -CF$_3$). ESI-MS calcd. for C$_{31}$H$_{20}$F$_6$FeOS (1c-OH) m/z = 610.049 (1c-OH); found 610.044 (measured in CH$_2$Cl$_2$, calibrated). Elemental analysis (CHN only) calcd (%) for C$_{31}$H$_{20}$F$_6$FeOS (610.40 g mol$^{-1}$): C 61.00, H 3.30; found: C 61.42, H 3.96.

**General Synthesis of the Cationic Dyes.** Brookhart’s acid ([H(OEt)$_2$]$^+$ [BARF$_{24}$]$^-$, 1.0 eq) was added as a white crystalline solid to a dry, degassed dichloromethane solution of the respective carbinol precursor 1a-OH-1c-OH in the presence of molecular sieves (4 Å), causing an immediate, intense colorization of the solution (for colors, vide infra). Removal of the solvent quantitatively afforded the [B{C$_6$H$_5$(CF$_3$)$_2$-3,5}$_4$]$^+$ = [BARF$_{24}$]$^-$ salts of the cationic dyes as intensely colored, amorphous solids 1a$^+$-1c$^+$. The respective complex was purified by washing with dry, degassed n-pentane (3×10 mL) and dried under vacuum for 1-2 h. Due to gradual decomposition in solution and in the solid stored at r.t, the complexes were freshly synthesized before every measurement in order to obtain reproducible results. The cationic complexes can be stored with only minor degradation inside a glovebox in a fridge.

$^1$H-, $^{13}$C- and $^{19}$F-NMR resonances of the [B{C$_6$H$_5$(CF$_3$)$_2$-3,5}$_4$]$^+$ ([BARF$_{24}$]$^-$) anion in CD$_2$Cl$_2$ were essentially invariant for all cations.$^{[18]}$ The spectroscopic data for the anion are provided below and are not further mentioned in the NMR characterization of the complexes. $^1$H-NMR (CD$_2$Cl$_2$, 400 MHz) $\delta$ [ppm] = 7.73 (br s, 8H, H$_{ortho}$), 7.55 (s, 4H, H$_{para}$). $^{13}$C($^1$H)-NMR (CD$_2$Cl$_2$, 101 MHz) $\delta$ [ppm] = 161.9 (q, $^1$J$_{CB}$ = 49.8 Hz, C$_{ipso}$), 135.1 (s, C$_{ortho}$), 129.3 (q, $^2$J$_{CF}$ = 31.4 Hz, C$_{meta}$), 124.7 (q, $^1$J$_{CF}$ = 272.6 Hz, CF$_3$), 117.9 (s, C$_{para}$). $^{19}$F($^1$H)-NMR (CD$_2$Cl$_2$, 376 MHz) $\delta$ [ppm] = -62.9 (s, CF$_3$). Resonance signals from diethyl ether associated with Brookhart’s acid are also present in the spectra due to the *in-situ* preparation for NMR experiments: $^1$H-NMR (CD$_2$Cl$_2$, 400 MHz) $\delta$ [ppm] = 3.43 (q, $^3$J$_{HH}$ = 7.0 Hz, CH$_2$), 1.15 (t, $^3$J$_{HH}$ = 7.0 Hz, CH$_3$). $^{13}$C($^1$H)-NMR (CD$_2$Cl$_2$, 101 MHz) $\delta$ [ppm] = 66.11 (s, CH$_2$), 15.44 (s, CH$_3$).

1a$^+$. The product was obtained as an eggplant-colored solid in quantitative yield. $^1$H-NMR (CD$_2$Cl$_2$, 400 MHz) $\delta$ [ppm] = 7.14 (d, $^4$J$_{HH}$ = 2.17 Hz, 2H, H-14), 7.10 (d, $^3$J$_{HH}$ = 8.31 Hz, 2H, H-11), 7.05 (br d, $^3$J$_{HH}$ = 5.78 Hz, 2H, H-6), 6.90 (br, 2H, H-7), 6.76 (dd, $^3$J$_{HH}$ = 8.31 Hz, $^4$J$_{HH}$ = 2.17 Hz, 2H, H-12), 6.50 (br s, possibly +1a-1a$^+$), 5.87 (br s, 2H, H-2), 5.52 (br s, 2H, H-3), 5.15 (br s, possibly +1a-1a$^+$), 5.11 (br s, 1H, possibly +1a-1a$^+$), 4.99 (br s, 5H, H-1), 4.24 (s, possibly +1a-1a$^+$), 3.85 (s, 6H, H-16). $^{13}$C($^1$H)-NMR...
(CD$_2$Cl$_2$, 101 MHz) $\delta$ [ppm] = 129.3 (C$_{1a}$), 126.0 (C$_{1a}$), 123.3 (C$_{1a}$), 77.1 (C-2), 73.8 (C-1), 66.6 (C-3), 57.9 (C-16). **ESI-MS calcd.** for C$_{31}$H$_{25}$FeO$_2$ $^+$ (1a$^+$): C$_{31}$H$_{26}$FeO$_2$ $^+$ (1a$^+$+H); C$_{62}$H$_{50}$Fe$_2$O$_4$ $^{2+}$ (*1a-1a$^+$); C$_{31}$H$_{25}$FeO$_3$ (1a-OH); C$_{31}$H$_{25}$FeO$_3$ (1a-OH-H) m/z = 485.120 (1a$^+$); 486.128 (1a$^+$+H); 485.120 (*1a-1a$^+$); 502.123 (1a-OH); 501.115 (1a-OH-H); found 485.134 (1a$^+$); 486.142 (1a$^+$+H); 485.134 (*1a-1a$^+$); 502.135 (1a-OH); 501.125 (1a-OH-H) (measured in CH$_2$Cl$_2$, calibrated). **Elemental analysis** (CHN only) calcd (%) for C$_{63}$H$_{37}$BF$_{24}$FeO$_2$ (1348.6 g mol$^{-1}$): C 56.11, H 2.77; found: C 56.31, H 4.05.

1b$. The product was obtained as a turquoise-colored solid in quantitative yield. **$^1$H-NMR** (CD$_2$Cl$_2$, 400 MHz) $\delta$ [ppm] = 6.05 (br s, 2H, H-2), 5.58 (br s, 2H, H-3), 4.54 (br s, 5H, H-1). **$^{13}$C$[^1]$H-$NMR$** (CD$_2$Cl$_2$, 101 MHz) $\delta$ [ppm] = 67.1 (br s, C-1/C-2/C-3). **ESI-MS calcd.** for C$_{31}$H$_{25}$Fe $^+$ (1b$^+$); C$_{31}$H$_{26}$Fe $^+$ (1b$^+$+H); C$_{31}$H$_{25}$FeO (1b-OH-H); C$_{62}$H$_{50}$Fe$_2$O$_2$ $^{2+}$ (*1b-1b$^+$) m/z = 453.130 (1b$^+$); 454.138 (1b$^+$+H); 469.125 (1b-OH-H); 453.130 (*1b-1b$^+$); found 453.147 (1b$^+$); 454.148 (1b$^+$+H); 469.141 (1b-OH-H); 453.147 (*1b-1b$^+$) (measured in CH$_2$Cl$_2$, calibrated). **Elemental analysis** (CHN only) calcd (%) for C$_{63}$H$_{37}$BF$_{24}$Fe (1316.61 g mol$^{-1}$): C 57.47, H 2.83; found: C 59.10, H 3.71.

1c$. The product was obtained as a royal blue solid in quantitative yield. **$^1$H-NMR** (CD$_2$Cl$_2$, 400 MHz) $\delta$ [ppm] = 8.21 (br s, 1H, H-11), 8.10 (br s, 1H, H-14), 7.91 (d, 1H, $^3$J$_{HH} = 8.27$ Hz, H-12), 7.81 (br s, 2H, H-6/H-7), 7.58 (br s, possibly *1c-1c$^+$), 6.03 (br s, possibly *1c-1c$^+$), 5.06 (br s, 2H, H-2), 4.91 (br s, 2H, H-3), 4.34 (s, 5H, H-1). **$^{13}$C$[^1]$H-$NMR$** (CD$_2$Cl$_2$, 101 MHz) $\delta$ [ppm] = 134.9 (C$_{1c}$), 133.5 (C$_{1c}$), 125.7 (C$_{1c}$), 123.2 (C$_{1c}$), 122.7 (C$_{1c}$), 74.1 (C-3), 72.8 (C-2), 66.2 (C-1). **$^{19}$F$[^1]$H-$NMR$** (CD$_2$Cl$_2$, 376 MHz) $\delta$ [ppm] = -63.35 (CF$_3$). **ESI-MS calcd.** for C$_{31}$H$_{19}$F$_6$FeS $^+$ (1c$^+$); C$_{31}$H$_{20}$F$_6$FeOS (1c-OH); C$_{31}$H$_{20}$F$_6$FeO$^-$ (1c-O$^-$) m/z = 593.046 (1c$^+$); 610.049 (1c-OH); 609.042 (1c-O$^-$); found 593.044; 610.044; 609.025 (measured in CH$_2$Cl$_2$, calibrated). **Elemental analysis** (CHN only) calcd (%) for C$_{63}$H$_{31}$BF$_{30}$FeS (1456.61 g mol$^{-1}$): C 51.95, H 2.15; found: C 54.08, H 3.10.

2-Bromo-2' -fluoro-4,4' -di(trifluoromethyl)benzhydrol (3). 1.50 g of 1-bromo-2-fluoro-4-(trifluoromethyl)benzene (6.17 mmol, 1.0 eq) were dissolved in 20 mL of dry, degassed diethyl ether and cooled to -78°C. 4.26 mL of $^n$BuLi (1.6 M solution in hexanes, 6.79 mmol, 1.1 eq) were added dropwise and the mixture was stirred for 5 minutes. A solution of 1.56 g of 2-bromo-4-(trifluoromethyl)benzaldehyde (6.17 mmol, 1.0 eq) in 5 mL dry, degassed diethyl ether was added dropwise, the solution turned yellow and the mixture was stirred at -78°C for 15 minutes (Cautionary Note: do not stir longer, danger.
of aryne formation!). The reaction was quenched in the cold by adding 40 mL of saturated aqueous NH₄Cl and was then warmed to r.t. After the addition of 15 mL of water, the phases were separated, and the aqueous phase was extracted with ethyl acetate (3 x 60 mL). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residual solid was purified by gradient column chromatography (n-pentane/ethyl acetate 10:1 - 5:1) to yield 0.91 g (2.18 mmol, 35%) of compound 3 as a dark orange oil. 

**1H-NMR** (CDCl₃, 400 MHz) δ [ppm] = 7.82 (s, 1H, H-12), 7.69 (d, ³JHH = 6.79 Hz, 1H, H-10), 7.62 (d, ³JHH = 8.05 Hz, 1H, H-4), 7.43 - 7.30 (m, 3H, H-3, H-6, H-9), 6.49 - 6.37 (m, 1H, H-1), 3.54 (br s, 1H, OH). 

**13C{¹H}-NMR** (CD₂Cl₂, 101 MHz) δ [ppm] = 161.4 (C-7), 158.9 (C-2), 144.5 (C-13), 133.1-131.2 (m, C-11/C-5), 130.1 (q, ³JCF = 3.5 Hz, C-3), 129.4 (d, ³JCF = 3.5 Hz, C-12), 128.9 (d, ³JCF = 3.5 Hz, C-10), 124.8-124.6 (m, C-4), 123.3 (d, ¹JC = 271 Hz, C-8), 123.1 (d, ¹JC = 273 Hz, C-15), 122.8 (C-14), 121.5-121.3 (m, C-9), 113.3 (d, ²JC = 24.7 Hz, C-6), 68.6 (C-1). 

**¹⁹F{¹H}-NMR** (CDCl₃, 376 MHz) δ [ppm] = -114.7 (s, 1F, -F), -63.0 (s, 6F, -CF₃).

**2-Bromo-2'-fluoro-4,4'-di(trifluoromethyl)benzophenone (4).** This reaction was carried out open to the air. 0.91 g of compound 3 (2.18 mmol, 1.0 eq) were dissolved in dried CH₂Cl₂ and Celite 545 (2.5 g) was added. 0.99 g of pyridinium chlorochromate (4.58 mmol, 2.10 eq) were added in portions over a period of 15 minutes and the mixture was stirred for 2 h at r.t. The mixture was then filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by gradient column chromatography (n-pentane/ethyl acetate 1:0 - 5:1) to yield 0.72 g (1.73 mmol, 80%) of compound 4 as a yellow solid. 

**1H-NMR** (CDCl₃, 400 MHz) δ [ppm] = 7.96 (vt, ³JHH = 7.44 Hz, ⁴JHF, 1H, H-3), 7.90 (d, ⁴JHH = 0.74 Hz, 1H, H-12), 7.71 (dd, ³JHH = 7.90 Hz, ⁴JHH = 0.74 Hz, 1H, H-10), 7.57 (d, ³JHH = 7.44 Hz, 1H, H-4), 7.54 (d, ³JHH = 7.90 Hz, 1H, H-9), 7.39 (d, ³JHF = 10.25 Hz, 1H, H-6). 

**13C{¹H}-NMR** (CD₂Cl₂, 101 MHz) δ [ppm] = 190.7 (C-1), 162.6 (C-2), 160.0 (C-7), 144.3 (C-14), 137.2 (dq, ³JCF = 8.4 Hz, ²JCF = 33.5 Hz, C-5), 134.1 (q, ²JCF = 33.5 Hz, C-13), 132.3 (d, ³JCF = 1.5 Hz, C-3), 130.5 (q, ³JCF = 3.8 Hz, C-12), 129.7 (d, ³JCF = 1.5 Hz, C-9), 124.8 (d, ³JCF = 3.8 Hz, C-10), 122.8 (d, ¹JC = 273 Hz, C-15), 122.7 (d, ¹JC = 273 Hz, C-8), 121.8 (quint, ³JCF = 3.8 Hz, C-4), 119.7 (d, ³JCF = 2.2 Hz, C-11), 114.6 (dq, ³JCF = 3.8 Hz, ²JCF = 25.6 Hz, C-6). 

**¹⁹F{¹H}-NMR** (CDCl₃, 376 MHz) δ [ppm] = -107.5 (s, 1F, -F), -63.5 (s, 3F, -CF₃-8) -63.2 (s, 3F, -CF₃-15).
**3,6-Bis(trifluoromethyl)-9H-thioxanthen-9-one (5).** This reaction was carried out under ambient atmosphere. 0.72 g of compound 4 (1.73 mmol, 1.0 eq) and 2.68 g of Na₂S · 9 H₂O (11.16 mmol, 6.45 eq) were suspended in 20 mL of DMF, yielding a turquoise suspension. The mixture was heated to 85°C and stirred for 5 days until TLC control showed complete consumption of the starting material. After cooling to r.t., 60 mL of water were added, causing a yellow solid to precipitate. The solid was filtered off and re-dissolved in CH₂Cl₂. The orange aqueous phase was washed with CH₂Cl₂ (4 x 60 mL) and the combined organic phases were washed with 150 mL of brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residual, pale yellow solid was purified by gradient column chromatography (n-pentane/ethyl acetate 1:0 - 5:1) to yield 0.49 mg (1.41 mmol, 81%) of ketone 5 as a bright yellow solid. ¹H-NMR (CD₂Cl₂, 400 MHz) δ [ppm] = 8.68 (d, ³JHH = 8.42 Hz, 2H, H-3), 7.91 (br s, 2H, H-6), 7.73 (dd, ³JHH = 8.42 Hz, ⁴JHH = 1.21 Hz, 2H, H-4). ¹³C{¹H}-NMR (CD₂Cl₂, 101 MHz) δ [ppm] = 178.6 (C-1), 137.9 (C-7), 134.4 (q, ²JCF = 33.0 Hz, C-5), 131.7 (C-2), 131.1 (C-3), 123.7 (d, ¹JCF = 273 Hz, C-8), 124.1 (q, ³JCF = 3.5 Hz, C-4), 123.5 (q, ³JCF = 3.5 Hz, C-6). ¹⁹F{¹H}-NMR (CD₂Cl₂, 376 MHz) δ [ppm] = -63.7 (s, -CF₃-8).
NMR Spectra (Part I)

Figure S1: General overview of all carbinol precursors 1a-OH to 1c-OH (cf. Figures S3-S9) and cationic dyes 1a* to 1c* (cf. Figures S14-S22).

Figure S2: Proton (left) and carbon (right) atom assignments in the NMR characterization in the Experimental Section and in Figures S14-S22.
Figure S3: $^1$H-NMR spectrum of complex 1a-OH in CD$_2$Cl$_2$.

Figure S4: $^{13}$C($^1$H)-NMR spectrum of complex 1a-OH in CD$_2$Cl$_2$. 
Figure S5: $^1$H-NMR spectrum of complex 1b-OH in CDCl$_3$.

Figure S6: $^{13}$C-$^1$H-NMR spectrum of complex 1b-OH in CDCl$_3$. 
Figure S7: $^1$H-NMR spectrum of complex 1c-OH in CD$_2$Cl$_2$. 
Figure S8: $^{13}$C($^1$H)-NMR spectrum of complex 1c-OH in CD$_2$Cl$_2$.

Figure S9: $^{19}$F($^1$H)-NMR spectrum of complex 1c-OH in CD$_2$Cl$_2$. 
Figure S10: ESI-MS spectrum and simulations of complex 1a*.

Figure S11: ESI-MS spectrum and simulations of complex 1b*.
Figure S12: ESI-MS spectrum and simulations of complex 1c+.
Figure S13: $^1$H-NMR spectrum of complex 1a$^*$ in CD$_2$Cl$_2$. 
Figure S14: $^{13}$C($^1$H)-NMR spectrum of complex 1a* in CD$_2$Cl$_2$.

Figure S15: $^{19}$F($^1$H)-NMR spectrum measured in CD$_2$Cl$_2$ of complex 1a*.
Figure S16: $^1$H-NMR spectrum of complex 1b$^*$ in CD$_2$Cl$_2$. 
Figure S17: $^{13}$C-$^1$H-NMR spectrum of complex 1b$^+$ in CD$_2$Cl$_2$.

Figure S18: $^{19}$F-$^1$H-NMR spectrum of complex 1b$^+$ in CD$_2$Cl$_2$. 
Figure S19: $^1$H-NMR spectrum of complex 1c$^+$ in CD$_2$Cl$_2$. 
Figure S20: $^{13}$C{[^1]H}-NMR spectrum of complex 1c* in CD$_2$Cl$_2$.

Figure S21: $^{19}$F{[^1]H}-NMR spectrum of complex 1c* in CD$_2$Cl$_2$. 
Electrochemical Data – Cyclic Voltammetry

Figure S22: Cyclic voltammograms of carbinol precursors 1a-OH – 1c-OH and 1d-OH in CH₂Cl₂ / 0.1 M NBu₄⁺[BArF₂₄]⁻ at r. t. and ν = 100 mV/s.

Figure S23: Cyclic voltammogram of complex 1c* in CH₂Cl₂ / 0.1 M NBu₄⁺[BArF₂₄]⁻ at r. t. and ν = 100 mV/s with decamethylferrocene (marked by an asterisk) as a standard, also showing the second reduction wave.
Figure S24: Cyclic voltammograms of 1a⁺ (CH₂Cl₂ / 0.1 M NBu₄⁺ [BArF₂₄⁻] at r. t.) at various sweep rates v from 25 mV/s to 2000 mV/s.

Figure S25: Cyclic voltammograms of 1b⁺ (CH₂Cl₂ / 0.1 M NBu₄⁺ [BArF₂₄⁻] at r. t.) at various sweep rates v from 25 mV/s to 2000 mV/s.

Figure S26: Cyclic voltammograms of 1c⁺ (CH₂Cl₂ / 0.1 M NBu₄⁺ [BArF₂₄⁻] at r. t.) at various sweep rates v from 25 mV/s to 2000 mV/s.
Table S1: Data from CV simulations on complex 1a⁺.

| Homogeneous reactions       | $K_{eq}$ in mol L$^{-1}$ | $k_0$  | $k_r$  |
|-----------------------------|--------------------------|--------|--------|
| [1] $1a^+ + 1a^+ \rightarrow 1a-1a^+$ | 0.0002                   | 16.09  | 0.0033 |
| [2] $1a^+ + 1a^+ \rightarrow 1a-1a$  | 25.76                    | 67.52  | 1739   |
| [3] $1a^+ + 1a^+ \rightarrow 1a-1a$  | 2.1E+5                   | 1.261  | 2.65E+5|

Figure S27: Scheme of redox and chemical reactions employed for the simulations of cyclic voltammograms of 1a⁺ (voltammogram shown for $\nu = 400$ mV/s; experimental CV: black line, simulated: blue dots).
UV/Vis/NIR Data & TD-DFT Data

Figure S28: Molecular orbital contributions to major transitions calculated of complex 1a+ via TD-DFT, with EDDMs (electron density difference maps, blue: electron loss, red: electron gain). The experimental spectrum and data are given in black, the TD-DFT calculated spectrum and data are given in blue, transitions shown schematically at the bottom-left.

Figure S29: Molecular orbital contributions to major transitions calculated of complex 1c+ via TD-DFT, with EDDMs (electron density difference maps, blue: electron loss, red: electron gain). The experimental spectrum and data are given in black, the TD-DFT calculated spectrum and data are given in blue, transitions shown schematically at the bottom-left.
Figure S30: Experimental UV/Vis/NIR spectra (black line) and TD-DFT calculated spectra for the singlet $1^+$ (blue line) and triplet states $1^+$ (blue dotted line) in wavenumbers of $1a$-$1c$. 
UV/Vis/NIR Spectroelectrochemistry

Figure S31: Spectroelectrochemistry (1,2-C$_2$H$_4$Cl$_2$, 0.1 M NBu$_4^+$ [BArF$_{24}$]$^-$, r. t.) of complex 1b$: Right: Spectroscopic changes upon oxidation of 1b$^+$ (blue) to 1b$^{2+}$ (red); and upon reduction from 1b$^+$ (blue) to 1b (green).

Figure S32: Spectroelectrochemistry (1,2-C$_2$H$_4$Cl$_2$, 0.1 M NBu$_4^+$ [BArF$_{24}$]$^-$, r. t.) of complex 1c$: Right: Spectroscopic changes upon oxidation of 1c$^+$ (blue) to 1c$^{2+}$ (red); and upon reduction from 1c$^+$ (blue) to 1c (green).
$T$-dependent UV/Vis/NIR Spectroscopy

Figure S33: $T$-dependent UV/Vis/NIR spectra in CH$_2$Cl$_2$ of complex 1a$^*$.  

Figure S34: $T$-dependent UV/Vis/NIR spectra in CH$_2$Cl$_2$ of complex 1c$^*$.  

| Temperature | λ in nm |
|-------------|---------|
| 20°C        | 500 1000 1500 2000 |
| 10°C        | 500 1000 1500 2000 |
| 0°C         | 500 1000 1500 2000 |
| -10°C       | 500 1000 1500 2000 |
| -20°C       | 500 1000 1500 2000 |
| -30°C       | 500 1000 1500 2000 |
| -40°C       | 500 1000 1500 2000 |
| -50°C       | 500 1000 1500 2000 |
| -60°C       | 500 1000 1500 2000 |
| -70°C       | 500 1000 1500 2000 |
EPR Data (Part I)

Figure S35: EPR spectra of 1a−1c (right) and 1a**−1c** (left) recorded at 20 °C and -100 °C (marked) in CH₂Cl₂ (scaling of y-axis normalized).

Table S2: EPR spectroscopic data obtained via simulations.

| Complex | T (°C) | g-value | A (¹H) in G | A (¹H) in G | A (¹H) in G | A (¹H) in G |
|---------|-------|---------|-------------|-------------|-------------|-------------|
| 1a*     | -100  | 2.0032  | n.a.        | 7.8 (2)     | 2.9 (2)     | 2.7 (2)     |
| 1a**    | -100  | 2.0032  | 10.0 (2)    | 7.8 (2)     | 2.9 (2)     | 2.7 (2)     |
| 1b*     | -100  | 2.0041  | 11.7 (2)    | 8.1 (2)     | 7.5 (2)     | 4.9 (2)     |
| 1b**    | 20    | 2.0041  | 11.7 (2)    | 8.1 (2)     | 7.5 (2)     | 4.9 (2)     |
| 1c*     | -100  | 2.0044  | 16.5 (2)    | 12.0 (2)    | 10.0 (2)    | 9.5 (2)     |
| 1c**    | 20    | 2.0044  | 16.5 (2)    | 11.0 (2)    | 10.0 (2)    | 9.5 (2)     |

a) 1* refers to the chemically reduced species (2.2 eq. of decamethylferrocene as reducing agent), 1** refers to the diradical VT content in the cationic species. b) Number of equivalent protons in parantheses.
Figure S36: DFT-calculated LUMOs of 1a·-1c·, spin densities for the radicals 1a·-1c· and the triplet forms 1a··-1c··. Geometry-optimized, calculated structures of neutral and dicationic dimers 1a-1a to 1c-1c.
Figure S37: T-dependent EPR spectra of 1a-1c recorded in CH₂Cl₂.

Quantification method via EPR

A quantification of the dimerization in the reduced species 1⁺ was done as described by Casper et al. A brief description is also provided here, followed by the quantification of the valence tautomerism at 20°C.

Quantification of the Dimerization

According to Eaton et al., the double integral (DI) of an isotropic EPR spectrum depends on many parameters such as a setup constant, the microwave power, the modulation amplitude, the resonator’s quality factor, the total electron spin (here: ½) as well as the spatial distribution of microwave and modulation field in the sample. All these factors are kept stable in this study according to the measurement conditions described in the Experimental Section (vide supra). The DI is likewise proportional to the Boltzmann factor for temperature dependence (only the same temperatures can be compared, here 20°C, vide infra for thermodynamic data analysis at different temperatures) and number of spins in the sample (spin count, spin concentration c_{spin}).

To properly retract the double integrals (DI) from the measurements, the spectrum is background corrected using a control sample containing pure CH₂Cl₂. In a second step, a zero-offset correction is done. Then, the signal is integrated once, baseline corrected again and consecutively integrated a second time to obtain the second integral, whose value then amounts to the double integral (DI). The resulting calibration curve for eight different DPPH concentrations is given in Figure S38. The rearrangement of the linear equation of the regression yields Equation S1 for the spin concentration c_{spin}. In the next step, the spin concentrations
calculated by Equation S1 were compared to the actual concentrations \( c_{\text{real}} \) (calculated by Equation S2 using the relation between molecular weight \( M \), mass of the sample \( m \) and the volume of solvent \( V \)), yielding the ratio \( c_{\text{spin}} / c_{\text{real}} \) that corresponds to the amount of monomer in the sample at 20°C. Table S3 (1'-values only) summarizes the obtained data including the double integrals (DI), the derived spin concentrations \( c_{\text{spin}} \) and the real concentrations \( c_{\text{real}} \) of the complexes, as well as the amount of monomer and dimerization (100%-[amount of monomer]) for all investigated complexes 1a-1c. The data were obtained at 20°C and is partially also occurring in Table 6 (full paper). The uncertainties were calculated following the GAUSSIAN Equations S3-5 for the propagation of uncertainties starting from the following defined, initial uncertainties \( u_m = 0.05 \) mg for the weight-in masses, \( u_V = 50 \) µL for the measured volumes, \( u_b = 5.32*10^{-4} \) for the slope of the regression line, \( u_{\text{DI}} = 10 \) % of the value of DI for the determined double integral values). Not included in these calculations is the error due to evaporation of solvent during sample preparation.

Figure S38: Calibration curve for quantitative EPR evaluation (here exemplarily for 293.15 K): double integral in arbitrary units for 8 different concentrations of the calibrating agent DPPH in mM, 95% confidence and prediction band are shown for the linear fit; lower right corner: zoom into the low concentration region.

\[
\frac{b(\text{slope})}{c_{\text{spin}}} \Rightarrow c_{\text{spin}} = \frac{D I}{b} = \frac{D I}{0.003415} \text{ mM}
\]

\[
c_{\text{real}} = \frac{m}{M \cdot V}
\]

\[
u_{c_{\text{spin}}} = \sqrt{\left(\frac{\partial c_{\text{spin}}}{\partial b} \cdot u_b\right)^2 + \left(\frac{\partial c_{\text{spin}}}{\partial DI} \cdot u_{\text{DI}}\right)^2} = \sqrt{\left(-\frac{D I}{b^2} \cdot u_b\right)^2 + \left(\frac{1}{b} \cdot u_{\text{DI}}\right)^2}
\]

\[
u_{c_{\text{real}}} = \sqrt{\left(\frac{\partial c_{\text{real}}}{\partial m} \cdot u_m\right)^2 + \left(\frac{\partial c_{\text{real}}}{\partial V} \cdot u_V\right)^2} = \sqrt{\left(-\frac{1}{M \cdot V} \cdot u_m\right)^2 + \left(-\frac{m}{M \cdot V^2} \cdot u_V\right)^2}
\]

\[
u_{c_{\text{spin}}/c_{\text{real}}} = u_{\text{ratio}} = \sqrt{\left(\frac{\partial \text{ratio}}{\partial c_{\text{spin}}} \cdot u_{c_{\text{spin}}}\right)^2 + \left(\frac{\partial \text{ratio}}{\partial c_{\text{real}}} \cdot u_{c_{\text{real}}}\right)^2} \cdot 100
\]

\[
= \sqrt{\left(\frac{1}{c_{\text{real}}} \cdot u_{c_{\text{spin}}}\right)^2 + \left(-\frac{c_{\text{spin}}}{c_{\text{real}}^2} \cdot u_{c_{\text{real}}}\right)^2} \cdot 100 \text{ in } [%]
\]
Quantification of the Valence Tautomerism (VT)

The quantification of VT also included in Table S3 was obtained by the use of the calculated (method as described above) data from the non-reduced, cationic species 1\('\)\(+\) (cf. Table S3, 1\(+\)\(\)\(-\)values) of the same nominal concentration (exact same measurement conditions to ensure comparability). As the cationic complexes do not have an unpaired spin in their ground state, they can only produce an EPR signal in their organic radical ferrocenium Fe(III) radical valence tautomeric form 1\(+\)\(\)\(•\)\(•\). The mere existence of EPR signals at organic \(g_{iso}\) values equal to those of the reduced species in the cationic complexes hints at the presence of the suggested valence tautomer. By comparing the double integrals (DI, cf. Table S3) and therefore also the spin concentrations \(c_{\text{spin}}\) of the cationic complexes 1\(+\)\(••\) to those of the reduced complexes 1\(•\), an upper limit of the amount of radical valence tautomer in the sample is deduced by the use of the ratio \(D_{\text{cat}}/D_{\text{red}}\). The results are presented in Figure 9 and 10 (full paper), Table 6 (full paper) and Table S3.

Table S3: Quantitative EPR data for reduced complexes; spin concentration \(c_{\text{spin}}\) determined from double integral \(D_{\text{red}}\) compared with real concentration \(c_{\text{real}}\).

| complex | reducing agent | Double integral DI [a.u.] | \(c_{\text{spin}}\) [mM] | \(c_{\text{real}}\) [mM] | \(c_{\text{spin}}/c_{\text{real}}\) [%] | amount VT \(D_{\text{cat}}/D_{\text{red}}\) [%] |
|---------|----------------|-----------------------------|-------------------------|-------------------------|-----------------------------------|-----------------------------|
| 1a\(+\) | Cp\(2\)Fe      | 2.69·10\(^{-4}\)±2.7·10\(^{-5}\) | 7.9·10\(^{-3}\)±8.0·10\(^{-4}\) | 25.0±3.1 | 0.032±0.005 | n.a.                         |
| 1a\(+••\) | n.a.           | 2.15·10\(^{-5}\)±2.2·10\(^{-6}\) | 6.3·10\(^{-4}\)±6.4·10\(^{-5}\) | 25.0±3.1 | n.a.       | 7.97±1.13                   |
| 1b\(\) | Cp\(2\)Fe      | 1.18·10\(^{4}\)±1.2·10\(^{-5}\) | 3.5·10\(^{-3}\)±3.5·10\(^{-4}\) | 25.0±3.1 | 0.014±0.001 | n.a.                         |
| 1b\(+••\) | n.a.           | 1.14·10\(^{-5}\)±1.1·10\(^{-6}\) | 3.3·10\(^{-4}\)±3.4·10\(^{-5}\) | 25.0±3.1 | n.a.       | 9.65±0.99                   |
| 1c\(\) | Cp\(2\)Fe      | 7.02·10\(^{-1}\)±7.0·10\(^{-2}\) | 2.1·10\(^{-1}\)±2.1 | 50.0±5.0 | 41.1±5.8 | n.a.                         |
| 1c\(+••\) | n.a.           | 4.96·10\(^{-2}\)±5.0·10\(^{-3}\) | 1.5·1·10\(^{-1}\)±1.5·10\(^{-1}\) | 50.0±5.0 | n.a.       | 7.07±1.37                   |
| 2\(\) | Cp2Co         | 6.64·10\(^{-2}\)±6.6·10\(^{-3}\) | 1.94±0.20 | 60.0 | 3.250±0.460 | n.a.                         |
| 2\(+••\) | n.a.           | 4.01·10\(^{-5}\)±4.0·10\(^{-6}\) | 1.17·10\(^{3}\)±1.19·10\(^{4}\) | 60.0±6.0 | n.a.       | 0.06±8.5·10\(^{-3}\)     |
Figure S39: EPR spectra of 1a••-1c•• recorded at 10 K in CH₂Cl₂.
Mößbauer Spectroscopy

Figure S40: Mößbauer spectra of 1a*: blue dots: experimentally recorded, black, grey and blue curves: simulations.

Figure S41: Mößbauer spectra of 1b*: blue dots: experimentally recorded, black, grey and blue curves: simulations.

Figure S42: Mößbauer spectra of 1c*: blue dots: experimentally recorded, black, grey and blue curves: simulations.
Figure S43: $^1$H-NMR spectrum of compound 3 in CDCl$_3$.

Figure S44: $^{19}$F($^1$H)-NMR spectrum of compound 3 in CDCl$_3$. 
Figure S45: $^{13}$C\text{[}$^1$H$\text{]}$-NMR spectrum of compound 3 in CDCl$_3$.

Figure S46: $^1$H-NMR spectrum of compound 4 in CDCl$_3$. 

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Figure S47: $^{19}$F\text{[H]}-NMR spectrum of compound 4 in CDCl$_3$.

Figure S48: $^{13}$C\text{[H]}-NMR spectrum of compound 4 in CDCl$_3$. 
Figure S49: $^1$H-NMR spectrum of compound 5 in CDCl$_3$. 
Figure S50: $^{13}$C{H}-NMR spectrum of compound 5 in CD$_2$Cl$_2$.

Figure S51: $^{19}$F{H}-NMR spectrum of compound 5 in CD$_2$Cl$_2$. 
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