Iron(0)-Mediated Stereoselective (3+2)-Cycloaddition of Thiochalcones via a Diradical Intermediate

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1 Experimental procedures

1.1 General information

Thiochalcones 1a-e were synthesized by treatment of corresponding chalcones with Lawesson’s reagent in accordance with established literature procedures starting from the corresponding ketones and aldehydes.\[1\] Triiron dodecarbonyl was prepared from iron pentacarbonyl following a known protocol.\[2\] Syntheses of complexes 2a-e, 3a-e and 4 were performed under N$_2$ atmosphere by using standard Schlenk technique. Tetrahydrofuran used in all reactions was dried and deoxygenated over Na metal. Solvents used for column chromatography were distilled before the usage. All other solvents as well as commercially available compounds were purchased (Sigma-Aldrich, Acros, TCI, Alfa Aesar, abc) and used as received without further purification. Geduran Si 60 (0.063-0.200 mm) was used as the stationary phase for column chromatography; TLC monitoring was performed on TLC Silica gel 60 F254.

Decomposition points were determined with APOTEC apparatus and are uncorrected. NMR spectra were recorded with Bruker 600 MHz and 400 MHz spectrometers (Avance III) using dried and deoxygenated CDCl$_3$ as solvent. IR spectra were measured with a Tensor 27 FT-IR spectrometer. DIP-EI mass spectrometry (70 eV) was performed with a Finnigan MAT SSQ 710. Elemental analysis was performed using an Euro Vector EA3000 element analyser. For single crystal X-Ray diffraction a Nonius KappaCCD diffractometer was used.

Cyclic voltammetry for complexes 3a-e was accomplished with a three-electrode setup (working electrode: glassy carbon (d = 1.6 mm); reference electrode: Ag/Ag$^+$ in acetonitrile; counter electrode: Pt (wire)) using a Reference 600 Potentiostat/Galvanostat/ZRA from Gamry Instruments. The measurements were conducted in deoxygenated CH$_2$Cl$_2$-[n-Bu$_4$N][BF$_4$] (0.1 M) solutions with a complex concentration of 1 mM. After each measurement the glassy carbon electrode was polished with alumina. To ensure oxygen-free conditions, solution and headspace were purged with N$_2$ while opening the system, during the runs only the headspace was purged. The cyclic voltammograms were referenced against the ferrocenium/ferrocene (Fc$^+$/Fc) couple.
1.2 Synthesis and isolation of the iron complexes

Scheme S1. Thiochalcones 1a-e reactions with Fe$_3$(CO)$_{12}$ resulting in mono and cyclic dinuclear iron complexes 2a-e and 3a-e, respectively, as well as in thiopyran complex 4 (isolated for substituents $\text{Ar}^1 = \text{Ar}^2 = 2$-Th$^b$, only). $^a$Unexpectedly, a second experiment with another sample of 1b resulted in a better yield of 4. $^b2$-Th = thien-2-yl. $^c$Fc = ferrocenyl. $^d$Calculated for the reactions of 1a-e with Fe$_3$(CO)$_{12}$ in 1:1 ratio (in the case of 3:1 ratio 2a was obtained in 22 % yield and 3a in 6 % yield).
General procedure for the synthesis and purification of mono (2a-e) (Scheme S1) and cyclic dinuclear iron complexes (3a-e), exemplarily shown for 2a and 3a:

1-(Thien-2-yl)-3-phenylprop-2-enethione 1a (51 mg, 0.22 mmol, 1 eq) and Fe₃(CO)₁₂ (110 mg, 0.22 mmol, 1 eq) were placed in a three-necked Schlenk flask equipped with a condenser and dissolved in a portion of THF (15 mL). The green solution was slowly heated to reflux for 1.5 h (until no more Fe₃(CO)₁₂ was observed by TLC). Next, the solvent was removed in a nitrogen flow and the dark brown residue was purified by column chromatography (n-hexane:CH₂Cl₂ = 3:1) affording 2a (5.7 mg, 0.015 mmol, 7%) and 3a (25.7 mg, 0.035 mmol, 32%) as red solids. Single crystals suitable for X-Ray diffraction were obtained by slow evaporation of concentrated n-hexane solutions of 2a and 3a.

Procedure for the synthesis and isolation of thiopyran complex 4:
The general procedure as shown above using 1b as thiochalcone yielded 4 only in traces. According to the same procedure, a second experiment performed with another sample of 1b resulted in an enhanced yield of 4 (26%). This result can be explained by the presence of a variable ratio of dimers A and B (Scheme S1) as major components of the "thiochalcone fractions" obtained after column chromatography.

1.3 Characterization of the iron complexes
General comment: NMR signal assignment for complexes 2 is based on reported literature.[3]

Compound 2a

Yield: 6 mg (7%) of red solid after drying in vacuo;
Rf = 0.49 (n-hexane:CH₂Cl₂ 3:1);
Decomposition point: > 107 °C (slow decomposition);
¹H NMR (400 MHz, CDCl₃): δ = 7.75 (dd, J₁H₂ = 3.80 Hz, 1H, Ar-H₁), 7.24-7.45 (m, 6H, Ar-H and CDCl₃ residual signal), 7.05-7.10 (m, 1H, Ar-H), 6.91 (d, J₂H₁ = 9.35 Hz, 1H, H₂), 3.34 ppm (d, J₁H₁ = 9.65 Hz, 1H, H₁);
¹³C NMR (101 MHz, CDCl₃): δ = 71.1 (C3), 85.9 (C₂), 109.6, 125.9, 126.7, 127.0, 127.7, 127.9, 129.1, 137.8, 145.7 ppm;
IR: ν = 1971 (vs), 1992 (s), 2003 (s), 2049 (vs) cm⁻¹ (CO);
MS (El, 70 eV): m/z (%) = 370 (10) [M]+, 342 (20) [M-CO]+, 314 (24) [M-2 CO]+, 286 (100) [M-3 CO]+;
EA: calcld (%) for C₁₆H₁₀FeO₃S₂: C 51.91, H 2.72, S 17.32; found C 52.29, H 2.71, S 17.59.
Compound 2b

Yield: 33 mg (20 %) of red solid after drying in vacuo; 
$R_f = 0.49 \text{ (n-hexane:CH}_2\text{Cl}_2\text{ 3:1)}$; 
Decomposition point: $> 108 \degree \text{C (slow decomposition)}$; 
$^1\text{H NMR (400 MHz, CDCl}_3\text{:)}$ δ $= 7.72$ (dd, $J_{H,H} = 3.51$, 0.88 Hz, 1H, Ar-H), 7.37 (dd, $J_{H,H} = 5.26$, 0.88 Hz, 1H, Ar-H), 7.24 (d, $J_{H,H} = 4.97$ Hz, 1H, Ar-H), 7.15 (d, $J_{H,H} = 3.15$ Hz, 1H, Ar-H), 7.07 (dd, $J_{H,H} = 4.97$, 3.80 Hz, 1H, Ar-H), 6.97 (dd, $J_{H,H} = 4.97$, 3.80 Hz, 1H, Ar-H), 6.74 (d, $^3J_{H,H} = 9.35$ Hz, 1H, H2), 3.63 ppm (d, $^3J_{H,H} = 9.06$ Hz, 1H, H3); 
$^{13}\text{C NMR (151 MHz, CDCl}_3\text{:)}$ δ $= 66.4$ (C3), 88.3 (C2), 108.7, 124.9, 125.7, 125.9, 127.1, 128.0, 128.1, 143.0, 145.3 ppm; 
IR: $\tilde{\nu} = 1981$ (vs), 2055 (s) cm$^{-1}$ (CO); 
MS (EI, 70 eV): $m/z\% =$ 376 (8) [M$^+$], 348 (20) [M-CO]$^+$, 320 (36) [M-2 CO]$^+$, 292 (100) [M-3 CO]$^+$; 
EA: calcd (%) for C$_{14}$H$_8$FeO$_3$S$_3$: C 44.69, H 2.14, S 25.56; found C 44.40, H 2.11, S 25.34.

Compound 2c

Yield: 38 mg (21 %) of red solid after drying in vacuo; 
$R_f = 0.49 \text{ (n-hexane:CH}_2\text{Cl}_2\text{ 3:1)}$; 
Decomposition point: $> 110 \degree \text{C (slow decomposition)}$; 
$^1\text{H NMR (600 MHz, CDCl}_3\text{:)}$ δ $= 7.98$-8.04 (m, 2H, Ar-H), 7.39-7.49 (m, 5H, Ar-H), 7.31-7.37 (m, 2H, Ar-H), 7.27-7.30 (m, 1H, Ar-H), 6.94 (d, $^3J_{H,H} = 9.35$ Hz, 1H, H2), 3.34 ppm (d, $^3J_{H,H} = 9.54$ Hz, 1H, H3); 
$^{13}\text{C NMR (151 MHz, CDCl}_3\text{:)}$ δ $= 72.3$ (C3), 87.6 (C2), 115.8, 126.8, 127.5, 127.7, 128.7, 129.1, 129.7, 138.0, 139.6 ppm; 
IR: $\tilde{\nu} = 1935$ (vs), 1956 (vs), 1963 (vs), 1982 (s), 1996 (vs), 2012 (s), 2054 (vs) cm$^{-1}$ (CO); 
MS (EI, 70 eV): $m/z\% =$ 364 (8) [M$^+$], 336 (12) [M-CO]$^+$, 308 (20) [M-2 CO]$^+$, 280 (100) [M-3 CO]$^+$; 
EA: calcd (%) for C$_{18}$H$_{12}$FeO$_3$S$_2$: C 59.36, H 2.14, S 25.56; found C 59.52, H 3.23, S 8.89.
Compound 2d

Yield: 48 mg (33 %) of red solid after drying in vacuo;

$R_f = 0.38$ (n-hexane:CH$_2$Cl$_2$ 3:1);

Decomposition point: > 125 °C (slow decomposition);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.37-7.42$ (m, 2H, Ar-$H$), 7.30-7.36 (m, 2H, Ar-$H$), 7.23-7.27 (m, 1H, Ar-$H$), 6.56 (d, $^3J_{CH} = 9.35$ Hz, 1H, H2), 4.91-4.98 (m, 2H, Cp-$H$), 4.44-4.52 (m, 2H, Cp-$H$), 4.21 (s, 5H, Cp-$H$), 3.37 ppm (d, $^3J_{CH} = 9.35$ Hz, 1H, H3);

$^{13}$C NMR (400 MHz, CDCl$_3$): $\delta = 65.6, 69.2, 70.2, 70.4, 70.4, 84.7, 85.2, 118.1$ (C2), 126.7, 127.4, 129.0, 138.4 ppm.

IR: $\tilde{\nu} = 1970$ (s), 1984 (m), 2005 (s), 2043 (m), 2052 (s) cm$^{-1}$ (CO);

MS (EI, 70 eV): $m/z$ (%) = 472 (8) $[M]^+$, 416 (24) $[M-2 CO]^+$, 388 (100) $[M-3 CO]^+$;

EA: calcd (%) for C$_{22}$H$_{16}$Fe$_2$O$_3$S: C 55.97, H 3.42, S 6.79; found C 56.35, H 3.36, S 6.41.

Compound 2e

Yield: 34 mg (24 %) of red solid after drying in vacuo;

$R_f = 0.38$ (n-hexane:CH$_2$Cl$_2$ 3:1);

Decomposition point: > 135 °C (slow decomposition);

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.21$ (d, $^3J_{CH} = 5.26$ Hz, 1H, Ar-$H$), 7.12 (d, $^3J_{CH} = 3.51$ Hz, 1H, Ar-$H$), 6.96 (dd, $^3J_{CH} = 4.97$, 3.80 Hz, 1H, Ar-$H$), 6.39 (d, $^3J_{CH} = 9.06$ Hz, 1H, H2), 4.88-4.95 (m, 2H, Cp-$H$), 4.47 (dd, $^3J_{CH} = 12.13$, 1.32 Hz, 2H, Cp-$H$), 4.21 (s, 5H, Cp-$H$), 3.66 ppm (d, $^3J_{CH} = 9.35$ Hz, 1H, H3);

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 65.6, 65.6$ (C3, Cp-C), 69.2, 70.2, 70.4, 70.4 (Cp-C), 84.8, 85.2 (C2), 117.3, 124.5, 125.3, 128.0, 143.7 ppm.

IR: $\tilde{\nu} = 1976$ (vs), 2049 (s) cm$^{-1}$ (CO);

MS (EI, 70 eV): $m/z$ (%) = 478 (24) $[M]^+$, 422 (28) $[M-2 CO]^+$, 394 (100) $[M-3 CO]^+$;

EA: calcd (%) for C$_{20}$H$_{14}$Fe$_2$O$_3$S$_2$: C 50.24, H 2.95, S 13.41; found C 50.58, H 3.04, S 13.49.
Compound 3a

Yield: 26 mg (32%) of red solid after drying in vacuo; 
\( R_f = 0.33 \) (n-hexane:CH\(_2\)Cl\(_2\) 3:1);
Decomposition point: > 160 °C (slow decomposition);
\(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 7.38-7.45 \) (m, 2H, Ar-\( H \)), 7.09-7.20 (m, 4H, Ar-\( H \)), 6.86-7.02 (m, 8H, Ar-\( H \)), 6.78 (dd, \( J_{\text{HH}} = 7.60, 1.46 \) Hz, 2H, Ar-\( H \)), 5.98 (d, \( J_{\text{HH}} = 2.05 \) Hz, 1H, H4), 4.08 (dd, \( J_{\text{HH}} = 8.18, 2.05 \) Hz, 1H, H2);
\(^13\)C NMR (CDCl\(_3\), 101 MHz): \( \delta = 43.6 \) (C1), 51.0 (C3), 59.2 (C6), 65.4 (C2), 125.5, 125.9, 126.0, 126.6, 126.9, 127.0, 127.3, 127.7, 127.8, 127.9, 128.0, 128.7, 136.1 (C4), 136.2, 140.2, 142.0, 142.5, 148.3, 207.3 ppm (C0);
IR: \( \tilde{\nu} = 1967 \) (vs), 2027 (vs), 2070 (vs) cm\(^{-1}\) (CO);
MS (EI, 70 eV): \( m/z \) (%) = 684 (1) [M-2 CO]\(^+\), 656 (6) [M-3 CO]\(^+\), 628 (2) [M-4 CO]\(^+\), 600 (5) [M-5 CO]\(^+\), 572 (36) [M-6 CO]\(^+\);
EA: calcld (%) for C\(_{32}\)H\(_{20}\)Fe\(_2\)O\(_6\)S\(_4\): C 51.91, H 2.72, S 17.32; found C 51.87, H 2.64, S 17.37.

Compound 3b

Yield: 24 mg (15%) of red solid after drying in vacuo; 
\( R_f = 0.30 \) (n-hexane:CH\(_2\)Cl\(_2\) 3:1);
Decomposition point: > 160 °C (slow decomposition);
\(^1\)H NMR (CDCl\(_3\), 600 MHz): \( \delta = 7.39 \) (dd, \( J_{\text{HH}} = 5.14, 1.10 \) Hz, 1H, Ar-\( H \)), 7.34 (dd, \( J_{\text{HH}} = 3.58, 1.19 \) Hz, 1H, Ar-\( H \)), 7.19 (dd, \( J_{\text{HH}} = 5.04, 1.01 \) Hz, 1H, Ar-\( H \)), 7.09 (dd, \( J_{\text{HH}} = 5.14, 3.67 \) Hz, 1H, Ar-\( H \)), 7.01 (dd, \( J_{\text{HH}} = 5.14, 1.10 \) Hz, 1H, Ar-\( H \)), 6.98 (d, \( J_{\text{HH}} = 4.77 \) Hz, 1H, Ar-\( H \)), 6.91 (dd, \( J_{\text{HH}} = 5.04, 3.76 \) Hz, 1H, Ar-\( H \)), 6.83-6.87 (m, 2H, Ar-\( H \)), 6.70 (dd, \( J_{\text{HH}} = 5.05, 3.58 \) Hz, 1H, Ar-\( H \)), 6.61 (dd, \( J_{\text{HH}} = 5.14, 3.48 \) Hz, 1H, Ar-\( H \)), 6.28 (dd, \( J_{\text{HH}} = 3.48, 0.73 \) Hz, 1H, Ar-\( H \)), 6.07 (d, \( J_{\text{HH}} = 2.20 \) Hz, 1H, H4), 4.36
(dd, $J_{HH} = 7.98$, 2.11 Hz, 1H, $H3$), 4.04 (d, $J_{HH} = 4.58$ Hz, 1H, $H1$), 3.58 ppm (dd, $J_{HH} = 7.98$, 4.68 Hz, 1H, $H2$); $^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 39.2$ (C1), 46.4 (C3), 58.7 (C6), 67.7 (C2), 123.6, 124.4, 125.0, 125.8, 125.8, 126.3, 126.6, 126.8, 127.0 (2 C atoms), 128.4, 134.9, 135.9, 142.3, 144.5, 147.4, 148.1, 207.0 ppm (CO); IR: $\tilde{\nu} = 1969$ (vs), 2028 (vs), 2072 (vs) cm$^{-1}$ (CO); MS (EI, 70 eV): $m/z$ (%) = 752 (<1) $[M]^+$, 696 (2) $[M-2 \text{ CO}]^+$, 668 (8) $[M-3 \text{ CO}]^+$, 640 (1) $[M-4 \text{ CO}]^+$, 612 (8) $[M-5 \text{ CO}]^+$, 584 (100) $[M-6 \text{ CO}]^+$; EA: calcd (%) for C$_{28}$H$_{16}$Fe$_2$O$_6$S$_6$: C 44.69, H 2.14, S 25.56; found C 45.76, H 2.38, S 25.75.

Compound 3c

Yield: 56 mg (31 %) of red solid after drying in vacuo; $R_f = 0.34$ ($n$-hexane:CH$_2$Cl$_2$ 3:1);

Decomposition point: 180-185 °C (rapid decomposition);

$^1$H NMR (CDCl$_3$, 600 MHz): $\delta = 7.82$ (d, $J_{HH} = 7.70$ Hz, 2H, Ar-H), 7.43 (t, $J_{HH} = 7.70$ Hz, 2H, Ar-H), 7.32-7.37 (m, 1H, Ar-H), 7.23-7.27 (m, 2H, Ar-H), 7.13-7.21 (m, 3H, Ar-H), 7.07 (d, $J_{HH} = 7.52$ Hz, 2H, Ar-H), 6.87-6.99 (m, 6H, Ar-H), 6.84 (d, $J_{HH} = 7.15$ Hz, 2H, Ar-H), 6.17 (d, $J_{HH} = 2.02$ Hz, 1H, H4), 4.23 (dd, $J_{HH} = 8.25$, 1.83 Hz, 1H, H3), 3.72 (d, $J_{HH} = 4.03$ Hz, 1H, H1), 3.42 ppm (dd, $J_{HH} = 8.25$, 4.22 Hz, 1H, H2); $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 44.3$ (C1), 51.2 (C3), 62.5 (C6), 63.9 (C2), 125.9, 127.2, 127.5, 127.6, 127.7, 127.9, 127.9, 127.9, 128.1, 128.4, 128.5, 134.0 (Ar-C), 137.3 (C4), 140.4, 142.8, 144.1, 147.1 (Ar-C), 207.5 ppm (CO); IR: $\tilde{\nu} = 1974$ (vs), 1981 (vs), 1994 (vs), 2013 (s), 2033 (s), 2073 (s) cm$^{-1}$ (CO); MS (EI, 70 eV): $m/z$ (%) = 728 (1) $[M]^+$, 672 (2) $[M-2 \text{ CO}]^+$, 644 (8) $[M-3 \text{ CO}]^+$, 616 (12) $[M-4 \text{ CO}]^+$, 588 (14) $[M-5 \text{ CO}]^+$, 560 (100) $[M-6 \text{ CO}]^+$; EA: calcd (%) for C$_{36}$H$_{24}$Fe$_2$O$_6$S$_2$: C 59.36, H 3.32, S 8.80; found C 59.44, H 3.34, S 8.55.
Compound 3d

Yield: 24 mg (17%) of red solid after drying in vacuo;
$R_f = 0.28$ (n-hexane:CH$_2$Cl$_2$ 3:1);
Decomposition point: 185 °C (rapid decomposition);
$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.25$ (m, 1H), 6.87-7.12 (m, 6H), 6.78 (d, $\text{J}_{\text{H,H}} = 5.26$ Hz, 2H), 6.09 (m, 1H, H4), 5.38 (m, 1H), 4.46 (m, 1H), 4.14-4.41 (m, 12H), 4.06-4.12 (m, 1H), 4.01-4.05 (m, 1H), 3.98 (s, 5H, Cp-H), 3.50-3.61 ppm (m, 1H, H2);
$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 44.0$ (C1), 50.5 (C3), 57.0 (C6), 59.1 (C2), 65.7, 67.0, 67.2, 67.9, 68.8, 69.2, 69.7, 73.9, 82.7, 92.7, 125.6, 127.3, 127.4, 127.9, 127.9, 128.1, 136.2, 141.1, 143.1, 146.2, 208.1 ppm (C0);
IR: $\tilde{\nu} = 1973$ (vs), 1980 (s), 1986 (s), 2024 (m), 2067 (m) cm$^{-1}$ (CO);
MS (EI, 70 eV): $m/z$ (%) = 944 (<1) [M]$^+$, 776 (1) [M-6 CO]$^+$, 510 (100) [C$_{31}$H$_{26}$Fe$_2$]$^+$;
EA: calcd (%) for C$_{44}$H$_{32}$Fe$_4$O$_6$S$_2$: C 58.70, H 4.70, S 6.12; found C 58.86, H 4.46, S 6.05.

Compound 3e

Yield: 20 mg (14%) of red solid after drying in vacuo;
$R_f = 0.30$ (n-hexane:CH$_2$Cl$_2$ 3:1);
Decomposition point: > 180 °C (slow decomposition);
$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 6.99-7.05$ (m, 3H, Ar-H), 6.75 (dd, $\text{J}_{\text{H,H}} = 4.97$, 3.80 Hz, 1H, Ar-H), 6.65 (dd, $\text{J}_{\text{H,H}} = 4.97$, 3.51 Hz, 1H, Ar-H), 6.28 (dd, $\text{J}_{\text{H,H}} = 3.51$, 0.88 Hz, 1H, Ar-H), 6.17 (d, $^3\text{J}_{\text{H,H}} = 2.05$ Hz, 1H, H4), 5.26-5.30 (m, 1H, Cp-H), 4.45-4.50 (m, 1H, Cp-H), 4.38-4.43 (m, 1H, H3), 4.34-4.38 (m, 1H, Cp-H), 4.30-4.33 (m, 1H, Cp-H), 4.25-4.30 (m, 7H, H1 and Cp-H), 4.19-4.21 (m, 2H, Cp-H), 4.03-4.06 (m, 5H, Cp-H), 4.01-4.03 (m, 1H, Cp-H), 3.55 ppm (dd, $^3\text{J}_{\text{H,H}} = 8.18$, 4.97 Hz, 1H, H2);
SUPPORTING INFORMATION

$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta = 40.1$ (C1), 46.3 (C3), 59.0 (C6), 60.6 (C2), 65.6, 67.1, 67.3, 68.0, 68.9, 69.4, 69.5, 69.6, 73.8, 82.3, 92.5 (Cp-C), 123.3, 124.7, 124.8, 125.7, 126.4, 126.5, 135.1 (C4), 145.1, 147.0, 147.9, 207.8 ppm (CO); 

IR: $\tilde{\nu} = 1974$ (s), 1981 (m), 1995 (m), 2017 (m), 2028 (m), 2071 (m) cm$^{-1}$ (CO); 

MS (El, 70 eV): $m$/z (%) = 612 (8) [C$_{34}$H$_{28}$Fe$_2$S$_2$]$^+$, 516 (100) [C$_{29}$H$_{24}$Fe$_2$S]$^+$; 

EA: calcd (%) for C$_{40}$H$_{28}$Fe$_4$O$_6$S$_4$: C 52.49, H 3.85, S 12.51; found C 52.38, H 3.51, S 12.49.

Compound 4

Yield: 126 mg (26 %, experiment with the better yield) of red solid after drying in vacuo; 

$R_f = 0.26$ (n-hexane:CH$_2$Cl$_2$ 3:1); 

Decomposition point: > 150 °C (slow decomposition); 

$^1$H NMR (600 MHz, CDCl$_3$): $\delta =$ 7.49 (d, $\mathcal{J}_{\mathcal{H},\mathcal{H}} =$ 4.95 Hz, 1H, Ar-$\mathcal{H}$), 7.37 (d, $\mathcal{J}_{\mathcal{H},\mathcal{H}} =$ 4.95 Hz, 1H, Ar-$\mathcal{H}$), 7.29 (d, $\mathcal{J}_{\mathcal{H},\mathcal{H}} =$ 3.12 Hz, 1H, Ar-$\mathcal{H}$), 7.22-7.26 (m, 1H, Ar-$\mathcal{H}$), 7.19 (d, $\mathcal{J}_{\mathcal{H},\mathcal{H}} =$ 2.93 Hz, 1H, Ar-$\mathcal{H}$), 7.06 (dd, $\mathcal{J}_{\mathcal{H},\mathcal{H}} =$ 4.58, 3.85 Hz, 1H, Ar-$\mathcal{H}$), 6.84 (d, $\mathcal{J}_{\mathcal{H},\mathcal{H}} =$ 4.95 Hz, 1H, Ar-$\mathcal{H}$), 6.70 (d, $\mathcal{J}_{\mathcal{H},\mathcal{H}} =$ 4.95 Hz, 1H, Ar-$\mathcal{H}$), 6.57 (d, $\mathcal{J}_{\mathcal{H},\mathcal{H}} =$ 2.38 Hz, 1H, Ar-$\mathcal{H}$), 6.42-6.47 (m, 1H, Ar-$\mathcal{H}$), 6.38-6.42 (m, 1H, Ar-$\mathcal{H}$), 6.34 (d, $\mathcal{J}_{\mathcal{H},\mathcal{H}} =$ 5.50 Hz, 1H, H4), 6.06 (d, $\mathcal{J}_{\mathcal{H},\mathcal{H}} =$ 12.29 Hz, 1H), 5.99 (d, $\mathcal{J}_{\mathcal{H},\mathcal{H}} =$ 3.30 Hz, 1H, Ar-$\mathcal{H}$), 4.01 (d, $\mathcal{J}_{\mathcal{H},\mathcal{H}} =$ 12.29 Hz, 1H), 3.56 ppm (d, $\mathcal{J}_{\mathcal{H},\mathcal{H}} =$ 5.87 Hz, 1H, H3); 

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta =$ 37.9 (C3), 47.5 (C1), 52.6, 55.0, 119.7, 121.1, 123.3, 125.4, 125.5, 126.4, 126.5, 126.6, 126.9, 127.3, 128.2, 128.6, 129.5 (Ar-C), 130.0 (C4), 137.3, 143.7, 144.7, 157.4 (Ar-C), 207.3, 210.8, 211.2 (CO) ppm; 

IR: $\tilde{\nu} = 1956$ (vs), 1984 (vs), 2022 (vs), 2063 (vs) cm$^{-1}$ (CO); 

MS (El, 70 eV): $m$/z (%) = 753 (2) [M]$^+$, 724 (8) [M-CO]$^+$, 696 (12) [M-2 CO]$^+$, 668 (66) [M-3 CO]$^+$, 640 (6) [M-4 CO]$^+$, 612 (20) [M-5 CO]$^+$, 584 (100) [M-6 CO]$^+$; 

EA: calcd (%) for C$_{26}$H$_{16}$Fe$_2$O$_6$S$_6$: C 44.69, H 2.14, S 25.56; found C 44.39, H 2.16, S 25.30.
1.4 Computational details

In order to elucidate the reaction mechanism underlying the selective formation of the cycloadduct (3a), shown in Scheme 2 and Scheme S1, a suite of quantum chemical methods has been utilized. Initially, two rotamers of 1a the E (EA and EB) and the Z (ZA and ZB) isomers of the free thiochalcones (Ar1 = thiophenyl, Ar2 = phenyl, see Figure S1) were fully optimized at the DF-HF+DF-MP2\[4]/cc-pVTZ\[5](cc-pVTZ/JKFIT+cc-pVTZ/C) level of theory using PSI4 1.2.1,\[6] followed by a vibrational analysis to confirm that a minimum on the 3N-6 dimensional potential energy (hyper-)surface (PES) was obtained. Subsequently, the energy of EA, EB,ZA and ZB was recalculated within these optimized structures by LNO-CCSD(T)\[7] and using the cc-pVQZ\[5] basis set as implemented in the program MRCC.\[8]

Figure S1. Relative Gibbs energies of 1a (ΔG in kJ mol\(^{-1}\)), i.e., two rotamers of E (EA and EB) and Z (ZA and ZB) isomers within the fully optimized equilibrium structures, obtained at the DF-MP2/cc-pVTZ level of theory. The electronic energy contribution was subsequently obtained at the LNO-CCSD(T)/cc-pVQZ level of theory.

In the following, two molecules of thiochalcone are coordinated to the [Fe\(_2\)(CO)\(_6\)] fragment forming the respective adduct (A), while all combinations of EA, EB, ZA and ZB were considered, see Table S1 (left) exemplarily for A(EAEB). In addition to the ten possible combinations of the four isomers, coordination in a parallel as well as in an antiparallel fashion is conceivable. However, in the present study, we focused exclusively on adducts obtained by parallel coordination as the following reaction is highly unlikely to proceed starting from the antiparallel adducts, due to an unfavorable stereochemistry, i.e. regarding the required carbon-carbon bond formation (C2-C3') among the two thioketones. All ten (parallel coordinated) adducts were optimized using the TPSSh\[9] hybrid functional and the def2-TZVPP\[10] basis set as implemented in ORCA 4.1.1 and 4.2.1,\[11] while the resolution of identity approach was applied, using the respective def2/J auxiliary basis and the RIJCOSX\[12] approximation for the Coulomb and exchange integrals, to reduce the computational demand. Furthermore, D3 dispersion correction with Becke-Johnson damping (D3BJ)\[13] was added to account for (attractive) long-range interactions among the coordinated thioketones. A subsequent frequency analysis confirmed the presence of minima on the PES. For the adduct A(EAEB), resulting from coordination of the most stable isolated thioketone (EA, Figure S1), the structural and electronic properties were additionally calculated within the equilibrated triplet ground state structure.

Table S1. Relative Gibbs energies of the adducts (ΔG in kJ mol\(^{-1}\), A), formed upon coordination of the [Fe\(_2\)(CO)\(_6\)] fragment by two molecules of 1a (EA, EB, ZA and ZB), respectively, and of the resulting products (P). All values are obtained for the closed-shell singlet ground state, triplet energies in
parenthesis, and given with respect to $A(E_AE_A)$ and $P(E_AE_A)$, respectively. Selectively formed stereocenters (1, 2, 3 and 6) of the possible products are labeled; incorrectly formed centers are highlighted in red.

| Adduct ($A$) | Product ($P$) |
|--------------|--------------|
| (OC)$_3$FeS(OC)$_3$ | (OC)$_3$FeS(OC)$_3$ |
| $E_A$ | 0.00 (66.93) |
| $E_B$ | -5.96 |
| $Z_A$ | 26.34 |
| $Z_B$ | 35.86 |
| $E_A$ | $E_B$ | $Z_A$ | $Z_B$ |
| 1236 | 1236 | 1236 | 1236 |
| 1236 | 1236 | 1234 | 1234 |
| 1236 | 1236 | 1236 | 1236 |

$\Delta G$ / kJ mol$^{-1}$

Originating from these ten adducts, 16 products ($P$) are conceivable. These products are not symmetric – with one thiolketone contributing three and the other thiolketone contributing two carbon atoms to the formed cyclopentene moiety. Thus, the products are denoted accordingly: Firstly, the thiolketone contributing three carbon atoms; secondly, the thiolketone contributing two carbon atoms, e.g. $P(E_AZ_A)$ vs. $P(Z_AE_A)$. The structural and electronic properties of these product structures, resulting from a formal (3+2) cycloaddition, were obtained at the same level of theory as described previously for the adducts. However, three of the constructed products, namely $P(E_AZ_A)$, $P(Z_AE_A)$ and $P(Z_AZ_A)$, relax in already covered product states, thus a total number of 13 products is obtained. From these 13 products, merely two species – $P(E_AE_A)$ and $P(Z_AE_A)$ – feature the correct stereochemistry of all four chiral carbon atoms as observed experimentally, see Table S1 (right). These two products only differ with respect to the torsion of the thiophenyl (Ar$^1$) and the phenyl (Ar$^2$) groups. Furthermore, $P(E_AE_A)$, as obtained from the adduct $A(E_AE_A)$ resulting from coordination of the most stable 1a isomer ($E_A$, Figure S1), was optimized within triplet multiplicity, followed by a vibrational analysis. These computational results clearly show that both $A(E_AE_A)$ and $P(E_AE_A)$ are closed-shell singlet species.

In order to determine the reaction mechanism leading to the (3+2)-cycloproduct, the minimum energy path (MEP) along the reaction coordinate from the adduct to the respective product was approximated by the climbing image nudge elastic band (CI-NEB) method.$^{[14]}$ Based on the previously calculated thermodynamic properties of the free thiochalcones, their adducts and their respective products, the most plausible reaction coordinate connects $E_A$, via the adduct $A(E_AE_A)$ to the final product $P(E_AE_A)$. Thus, the MEP, connecting $A(E_AE_A)$ and $P(E_AE_A)$, was obtained at the TPSSH/def2-SVP$^{[10]}$ level of theory within singlet multiplicity (closed-shell); subsequently, open-shell singlet (images 6 to 9) and triplet single point calculations (TPSSH/def2-SVP) were obtained within all CI-NEB images (Figure S2 A).
In order to estimate the influence of solvent stabilization along the closed-shell singlet reaction coordinate, single point calculations (closed-shell singlet) including the tetrahydrofuran solvent by the SMD continuum model \(^{[15]}\) were performed (Figure S2 B). The energy of all images is stabilized by an almost constant value of approximately 70 kJ mol\(^{-1}\). However, an explicit description of solvent molecules might reduce the activation barrier further, as the homolytic carbon sulfur bond cleavage yields a highly reactive biradical intermediate. Furthermore, a triplet reaction path was optimized connecting the closed-shell adduct and product, \(A(E_AE_A)\) and \(P(E_AE_A)\), respectively, see Figure S2 C. In addition, open-shell singlet energies were calculated along the triplet pathway. However, the resulting activation energy along the triplet coordinate is with roughly 310 kJ mol\(^{-1}\) (for both: open-shell singlet as well as triplet wavefunction) – more than 100 kJ mol\(^{-1}\) higher than the most favorable open-shell singlet solution along the singlet pathway (recall Figure 2 A and Figure S2 A).

**Figure S2:** Reaction profiles, connecting singlet equilibria of \(A(E_AE_A)\) and \(P(E_AE_A)\), A, along the closed-shell singlet minimum energy pathway, B, including solvent stabilization, and, C, along the triplet minimum energy pathway. Singlet energies are given in black (circles: closed-shell, dots: open-shell); solvent-stabilized closed-shell singlet energies are given in gray (B); triplet energies (open-shell: dots) are illustrated in red. All energies are calculated at the TPSSh/def2-SVP level of theory.
Furthermore, reaction profiles were simulated for the formation of all 13 possible products from the respective adducts at a reduced level of theory. Therefore, MEPs within the singlet multiplicity (closed-shell) were obtained by a locally developed program package\(^{[16]}\) using the CI-NEB method and Grimme’s semi-empirical GFN-xTB package.\(^{[17]}\) The resulting PESs reveal that for the formation of \(\text{P}(E_A E_A)\) (Figure 3 A) the barrier is slightly lowered upon reduction of the level of theory (recall Figure 2 A). Both conceivable reaction pathways with correctly formed stereocenters – originating from \(\text{A}(E_A E_A)\) and \(\text{A}(E_A Z_B)\) – feature with approximately 170 kJ mol\(^{-1}\) almost identical activation energies, see Figure 3 A and Figure 3 D.

Figure S3. A – M Reaction profiles, connecting the respective adduct and product states (3a) originating from the two rotamers of 1a, \(E\) (E\(_A\) and E\(_B\)) and \(Z\) (Z\(_A\) and Z\(_B\)). Closed-shell singlet ground state minimum energy pathways were obtained by CI-NEB and GFN-xTB. Relative Gibbs energies (\(\Delta G\) in kJ mol\(^{-1}\)) and activation energies (\(E_A\) in kJ mol\(^{-1}\)) are indicated.
1.5 Structure Determinations

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-Kα radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.\textsuperscript{[18]}

The structures were solved by direct methods (SHELXS\textsuperscript{[19]}) and refined by full-matrix least squares techniques against SHELXL-2018.\textsuperscript{[20]} All hydrogen atoms of the compound 2d and the hydrogen atoms bonded to the carbon atoms C1 to C4 of 1c, 3a, 4 and C3 of 2e were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters.

The crystal of 3d, and 3e contains large voids, filled with disordered solvent molecules. The size of the voids are (475, and 292) Å\textsuperscript{3}/unit cell, respectively. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON\textsuperscript{[21]} resulting in (215, and 80) electrons/unit cell, respectively. All non-hydrogen atoms were refined anisotropically.\textsuperscript{[21]}
SUPPORTING INFORMATION

2 Molecular structures

Crystallographic data as well as structure solution and refinement details are summarized in Table S2. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1986392 for 1c, CCDC-1986188 for 2c, CCDC-1986189 for 2d, CCDC-1986190 for 2e, CCDC-1986191 for 3a, CCDC-1986377 for 3d, CCDC-1986192 for 3e, and CCDC-1986193 for 4. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.cam.ac.uk].

Figure S4. Molecular structure and atom labeling scheme of dimer B derived from 1c. The ellipsoids represent a probability of 30 %, H atoms are shown with arbitrary radii. Selected bond lengths (Å): S(2)-C(18) 1.634(4).
Figure S5. Molecular structure and atom labeling scheme of 2a. The ellipsoids represent a probability of 30 %, H atoms are shown with arbitrary radii. Selected bond lengths (Å): S(1A)-C(1A) 1.741(3), C(1A)-C(2A) 1.421(4), C(2A)-C(3A) 1.420(4).

Figure S6. Molecular structure and atom labeling scheme of 2c. The ellipsoids represent a probability of 30 %, H atoms are shown with arbitrary radii. Selected bond lengths (Å): S(1A)-C(7A) 1.745(2), C(7A)-C(8A) 1.418(3), C(8A)-C(9A) 1.427(3).
Figure S7. Molecular structure and atom labeling scheme of 2d. The ellipsoids represent a probability of 30 %, H atoms are shown with arbitrary radii. Selected bond lengths (Å): S(1)-C(1) 1.7439(17), C(1)-C(2) 1.426(2), C(2)-C(3) 1.417(2).

Figure S8. Molecular structure and atom labeling scheme of 2e. The ellipsoids represent a probability of 30 %, H atoms are shown with arbitrary radii. Selected bond lengths (Å): S(1)-C(1) 1.739(4), C(1)-C(2) 1.416(5), C(2)-C(3) 1.412(5).
Figure S9. Molecular structure and atom labeling scheme of 3d. The ellipsoids represent a probability of 30%, H atoms are shown with arbitrary radii. Selected bond lengths (Å): Fe(1)-Fe(2) 2.5079(4), Fe(1)-S(1) 2.2495(6), Fe(1)-S(2) 2.2530(6), Fe(2)-S(1) 2.2727(6), Fe(2)-S(2) 2.2407(6), C(4)-C(5) 1.338(3); angles (°): S(1)-Fe(1)-S(2) 83.58(2), S(1)-Fe(1)-Fe(2) 56.761(17), S(2)-Fe(1)-Fe(2) 55.843(16), Fe(1)-S(1)-Fe(2) 67.439(15), Fe(2)-S(2)-Fe(1) 67.848(18).
Figure S10. Molecular structure and atom labeling scheme of 3e. The ellipsoids represent a probability of 30 %, H atoms are shown with arbitrary radii. Selected bond lengths (Å): Fe(1)-Fe(2) 2.5146(6), Fe(1)-S(1) 2.2495(9), Fe(1)-S(2) 2.2518(9), Fe(2)-S(1) 2.2485(9), Fe(2)-S(2) 2.2319(9), C(4)-C(5) 1.332(4); angles (°): S(1)-Fe(1)-S(2) 83.08(3), S(1)-Fe(1)-Fe(2) 55.99(2), S(2)-Fe(1)-Fe(2) 55.51(2), Fe(2)-S(1)-Fe(1) 67.98(3), Fe(2)-S(2)-Fe(1) 68.22(3).
Figure S11. Molecular structure and atom labeling scheme of 4. The ellipsoids represent a probability of 30%, H atoms are shown with arbitrary radii. Selected bond lengths (Å): Fe(1)-Fe(2) 2.6365(6), Fe(1)-S(1) 2.2143(9), Fe(1)-C(6) 2.131(3), Fe(2)-S(1) 2.2430(9), Fe(2)-S(2) 2.2635(9), S(2)-C(5) 1.788(3); angles (°): C(6)-Fe(1)-S(1) 83.59(8), C(6)-Fe(1)-Fe(2) 82.67(8), S(1)-Fe(1)-Fe(2) 54.24(2), Fe(1)-S(1)-Fe(2) 72.52(3), S(1)-Fe(2)-S(2) 91.82(3), S(1)-Fe(2)-Fe(1) 53.23(2), S(2)-Fe(2)-Fe(1) 71.11(2).
**Supporting Information**

**Table S2**: Crystal data and refinement details for the X-ray structure determinations.

| Compound | 1c | 2a | 2c | 2d | 2e | 3a | 3d | 3e | 4  |
|----------|----|----|----|----|----|----|----|----|----|
| formula  | C_{10}H_{12}FeO_{2}S_{2} | C_{10}H_{12}FeO_{2}S_{2} | C_{10}H_{12}FeO_{2}S_{2} | C_{10}H_{12}FeO_{2}S_{2} | C_{10}H_{12}FeO_{2}S_{2} | C_{10}H_{12}FeO_{2}S_{2} | C_{10}H_{12}FeO_{2}S_{2} | C_{10}H_{12}FeO_{2}S_{2} | C_{10}H_{12}FeO_{2}S_{2} |
| fw (g·mol⁻¹) | 448.61 | 370.21 | 364.19 | 472.11 | 478.13 | 740.42 | 944.21 | 956.26 | 752.47 |
| T/°C | -140(2) | -140(2) | -140(2) | -140(2) | -140(2) | -140(2) | -140(2) | -140(2) | -140(2) |
| Crystal system | monoclinic | orthorhombic | monoclinic | orthorhombic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | P 2₁/c | P 2₁/c | P 2₁/c | P 2₁/c | P 2₁/c | P 2₁/c | P 2₁/c | P 2₁/c | P n n a |
| a/Å | 17.4715(8) | 7.36270(10) | 9.2326(2) | 7.5337(1) | 7.2300(2) | 12.4609(2) | 11.7313(3) | 9.2923(3) | 21.4814(4) |
| b/Å | 13.2987(6) | 10.5736(2) | 11.1911(2) | 11.2202(3) | 19.2587(5) | 17.2330(2) | 12.0885(3) | 11.6337(3) | 17.7378(3) |
| c/Å | 10.2512(3) | 38.7371(8) | 16.5850(4) | 11.2731(3) | 7.4499(2) | 14.8589(2) | 18.1949(4) | 19.5942(6) | 16.0989(3) |
| a° | 90 | 90 | 70.469(1) | 90 | 90 | 90 | 90 | 90 | 90 |
| β° | 99.875(2) | 90 | 89.609(1) | 97.348(1) | 117.110(1) | 105.669(1) | 95.573(2) | 96.186(2) | 90 |
| γ° | 90 | 90 | 78.848(1) | 90 | 90 | 90 | 90 | 90 | 90 |
| Va/Å³ | 2339.31(17) | 3015.69(9) | 1581.41(6) | 945.09(4) | 923.36(4) | 3072.21(7) | 2263.15(10) | 2041.10(11) | 6134.21(19) |
| Z | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| r (g·cm⁻³) | 1.274 | 1.631 | 1.530 | 1.659 | 1.720 | 1.801 | 1.386 | 1.556 | 1.630 |
| µ (cm⁻¹) | 2.43 | 12.84 | 10.96 | 16.66 | 18.15 | 12.61 | 13.91 | 16.42 | 13.95 |
| measured data | 25813 | 37045 | 12153 | 13468 | 11466 | 24271 | 30753 | 25005 | 43926 |
| data with I > 2σ(I) | 4415 | 6607 | 4627 | 3905 | 6286 | 9156 | 7335 | 5575 |
| unique data (Rint) | 5348/0.0825 | 6761/0.0377 | 7129/0.0259 | 4305/0.0207 | 4170/0.0340 | 7045/0.0325 | 10314/0.0261 | 9235/0.0343 | 7027/0.0973 |
| wR2 | 0.1689 | 0.1058 | 0.0773 | 0.0422 | 0.0755 | 0.0639 | 0.0876 | 0.0928 | 0.1000 |
| R1 (I > 2σ(I)) | 0.0843 | 0.0377 | 0.0357 | 0.0181 | 0.0352 | 0.0294 | 0.0333 | 0.0450 | 0.0498 |
| S | 1.238 | 1.163 | 1.043 | 1.058 | 1.136 | 1.062 | 1.058 | 1.071 | 1.106 |
| Res/dens./e Å⁻³ | 0.894-0.323 | 0.808-0.684 | 0.498-0.528 | 0.285-0.230 | 0.316-0.326 | 0.351-0.225 | 0.423-0.347 | 0.592-0.473 | 0.730-0.373 |
| Flack-parameter | - | -0.399(18) | - | -0.001(5) | -0.021(13) | multi-scan | multi-scan | multi-scan | multi-scan |
| absorpt corr T_max/| 0.6710/0.7456 | 0.6600/0.7457 | 0.7027/0.7456 | 0.6883/0.7456 | 0.6908/0.7456 | 0.6908/0.7456 | 1986191 | 1986377 | 1986192 |
| CCDC No. | 1986392 | 1986187 | 1986188 | 1986189 | 1986190 | 3a | 3d | 3e | 4 |

[*] derived parameters do not contain the contribution of the disordered solvent.

a) Definition of the R indices: R1 = (Σ ||Fo|| - |F||) / Σ |Fo|; 

wR2 = [Σ (w(F0²- Fc²)²)/Σ (w(F0²))²]¹/² with w = σ²(Fc)² + (aP²)² + bP; P = [2F₀² + Max|Fc|²]/3;

b) S = [Σ (w(F0²- Fc²)²)/(Nc-Np)]¹/².
3 Cyclic voltammetry

Figure S12 shows the cyclic voltammetry of complexes 3a-e in CH₂Cl₂-[n-Bu₄N][BF₄] solutions at a scan rate of 0.2 V s⁻¹.

![Cyclic voltammetry plots](image)

**Figure S12.** Cyclic voltammetry of 1.0 mM complexes 3a-c (left) and complexes 3d-e (right) in CH₂Cl₂-[n-Bu₄N][BF₄] (0.1 M) solutions at 0.2 V s⁻¹ scan rate. The arrows indicate the scan direction. The potentials E are given in V and referenced to the Fc⁺/Fc couple.

The cyclic voltammetry of complexes 3a-e at a scan rate of 0.2 V s⁻¹ exhibit quasi-reversible peaks at \(E_{pc} = (-1.64, -1.60, -1.67, -1.74 \text{ and } -1.69)\) V, respectively, in their cathodic region, which are all ascribed to the reduction process of Fe²⁺Fe²⁺ to Fe⁺Fe⁰ similar to their reported analogue complexes.²² It can be noticed from Figure S12 that complex 3d shows a more negative reduction potential in comparison to complexes 3a-c and 3e. This indicates that the electron density of the iron core of 3d is higher than those of 3a-c and 3e, as consistent with the IR data. On initiating the electrochemical scan in the anodic direction of complexes 3d and 3e, two quasi-reversible anodic events at \(E_{1/2} = 0.07\) V and 0.22 V for complex 3d and at \(E_{1/2} = 0.08\) V and 0.23 V for complex 3e were observed. These oxidation peaks are corresponding to one-electron transfer of the ferrocene ligands.

The electrocatalytic ability of complexes 3a-e toward hydrogen production were investigated in the presence of various concentrations of acetic acid (AcOH). However, their electrocatalytic behaviors are almost identical. Therefore, complex 3d is illustrated in Figure S13 exemplarily. The addition of different equivalents of AcOH to a solution of complex 3d causes a small shift of its primary reduction peak to less negative potential together with the disappearance of its anodic peak in the reverse scan (Figure 13), which is a typical observation when protonation of a reduced species takes place.²³ At more reducing potentials, in the vicinity of -2.00 V to -2.30 V, the voltammetric profile of complex 3d shows a reduction peak with a current that increases in response to the systematic increase in the acid concentration, indicating a catalytic proton reduction.
Figure S13. Cyclic voltammetry of 1.0 mM of complex 3d in CH$_2$Cl$_2$-[n-Bu$_4$N][BF$_4$] (0.1 M) solutions at 0.2 V s$^{-1}$ in the presence of various concentrations of AcOH. The arrows indicate the scan directions. The potentials $E$ are given in V and referenced to the Fc$^{\bullet\bullet}$/Fc couple.
**SUPPORTING INFORMATION**

4 NMR spectra

$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 2a.

$^{13}$C NMR spectrum (CDCl$_3$, 101 MHz) of 2a.
**SUPPORTING INFORMATION**

1H NMR spectra (CDCl₃, 400 MHz) of 2b.

13C NMR spectra (CDCl₃, 151 MHz) of 2b.
**SUPPORTING INFORMATION**

1H NMR spectra (CDCl₃, 600 MHz) of 2c.

13C NMR spectra (CDCl₃, 151 MHz) of 2c.
$^1$H NMR spectra (CDCl$_3$, 400 MHz) of 2d.

$^{13}$C NMR spectra (CDCl$_3$, 101 MHz) of 2d.
$^1$H NMR spectra (CDCl$_3$, 600 MHz) of 2e.

$^{13}$C NMR spectra (CDCl$_3$, 151 MHz) of 2e.
SUPPORTING INFORMATION

**1H NMR spectra (CDCl₃, 400 MHz) of 3a.**

**13C NMR spectra (CDCl₃, 101 MHz) of 3a.**
SUPPORTING INFORMATION

\[^{1}\text{H NMR spectra (CDCl}_3, 600 MHz) of 3b.}

\[^{13}\text{C NMR spectra (CDCl}_3, 101 MHz) of 3b.}
\( ^1H \) NMR spectra (CDCl\(_3\), 600 MHz) of 3c.

\( ^{13}C \) NMR spectra (CDCl\(_3\), 151 MHz) of 3c.
\(^1\)H NMR spectra (CDCl\(_3\), 400 MHz) of 3d (n-hexane in crystals, see elemental analysis).

\(^{13}\)C NMR spectra (CDCl\(_3\), 101 MHz) of 3d (n-hexane in crystals, see elemental analysis).
$^1$H NMR spectra (CDCl$_3$, 400 MHz) of 3e (n-hexane in crystals, see elemental analysis).

$^{13}$C NMR spectra (CDCl$_3$, 101 MHz) of 3e (n-hexane in crystals, see elemental analysis).
$^{1}$H NMR spectra (CDCl$_3$, 600 MHz) of 4.

$^{13}$C NMR spectra (CDCl$_3$, 151 MHz) of 4.
SUPPORTING INFORMATION

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