Low-Valent Iron(I) Amido Olefin Complexes as Promoters for Dehydrogenation Reactions**

Crispin Lichtenberg,* Liliana Viciu, Mario Adelhardt, Jörg Sutter, Karsten Meyer, Bas de Bruin,* and Hansjörg Grützmacher*

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Supporting Information

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[LiFe(trop$_2$dae)(L)(L’)]

(2b: L = OEt$_2$, L’ = thf; 2c: L = L’ = 2-Me-THF; 2d: L = L’ = thf)……………… S07

[Li$_2$Fe(CH$_2$SiMe$_3$)$_2$(trop$_2$dae)(TMEDA)] (3)…………………………………………… S08

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Experimental

**General considerations.** All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk techniques or in an MBraun inert atmosphere dry-box containing an atmosphere of purified argon. CD$_6$, THF, Et$_2$O, MTBE, 2-Me-THF, $n$-hexane, toluene, and $p$-xylene were distilled before use from sodium benzophenone ketyl or from sodium, respectively. MeOH was dried by addition of Na, distilled and degassed prior to use. 1-Octene was dried over CaH$_2$ and distilled prior to use. Anhydrous FeCl$_2$, DMAB, and Me$_3$NBH$_3$ were obtained from Sigma Aldrich and used as received. PhSiH$_3$ was obtained from Sigma Aldrich and dried with molecular sieves (4 Å). H$_2$trop$_2$dae, LiCH$_2$SiMe$_3$, NaCH$_2$SiMe$_3$, [FeCl$_2$(thf)$_1$$_3$], and [Fe(N(SiMe$_3$)$_2$)$_2$] were synthesized according to the literature. NMR spectra were recorded on Bruker instruments operating at 200, 250, 300, or 500 MHz with respect to $^1$H, $^1$H, $^{13}$C, and $^{29}$Si NMR chemical shifts are reported relative to SiMe$_4$ using the residual $^1$H and $^{13}$C chemical shifts of the solvent as a secondary standard or an external standard in case of $^{29}$Si. $^{11}$B NMR chemical shifts are reported relative to BF$_3$·OEt$_2$. $^{29}$Si NMR shifts were obtained from 2D $^1$H-$^{29}$Si correlated spectroscopy experiments. Infrared spectra were collected on a Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer. UV/vis spectra were recorded on UV/vis/NIR lambda-19-spectrometer in a cell with a 0.5 cm path length. Mass spectrometric analyses were performed on a Bruker UltraFlex II instrument (MALDI-TOF, mill, anhydrous sodium acetate, E-2-[3-(4-t-Butylphenyl)-2-methyl-2-propenylidene]-malononitrile). Elemental analyses were performed at the Mikrolabor of ETH Zürich. Reliable elemental analysis data for 1 and 2 proved difficult to obtain due to the sensitivity of the samples. Alternative bulk methods of characterization are provided as evidence of the efficacy of the syntheses.

Powder X-ray diffraction patterns of the samples were recorded with a STOE Stadi P diffractometer equipped with a germanium monochromator and CuKα1 radiation (operated at 35 mA, 35 kV). Powder spectra were simulated using WinXpow Version 3.0.1.13 (06-Dec-2010), STOE&Cie GmbH, 64295 Darmstadt, Germany. Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a dry-box, transferred to a nylon loop and then transferred to the goniometer of an Oxford XCalibur, a Bruker SMART APEX or a Bruker APEX II diffractometer equipped with a molybdenum X-ray tube ($\lambda = 0.71073$ Å). The structures were solved using direct methods (SHELXS) completed by Fourier synthesis and refined by full-matrix least-squares procedures.

$^{57}$Fe Mössbauer spectra were recorded on a WissEl Mössbauer spectrometer (MRG-500) at 77 K in constant acceleration mode. $^{57}$Co/Rh was used as the radiation source. WinNormos for Igor Pro software has been used for the quantitative evaluation of the spectral parameters (least-squares fitting to Lorentzian peaks). The minimum experimental line widths were 0.20 mm/s. The temperature of the samples was controlled by an MBBC-HE0106 MÖSSBAUER He/N$_2$ cryostat within an accuracy of ±0.3 K. Isomer shifts were determined relative to $\alpha$-iron at 298 K.

Magnetic susceptibility measurements were carried out with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-5S) in the temperature range of 2-300 K in fields of 100 Oe and 1 T. Both field-cooled (FC) and zero-field-cooled (ZFC) data were obtained.
Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer (Bruker BioSpin) equipped with a He temperature control cryostat system (Oxford Instruments). Simulations of the EPR spectra were performed by iteration of the anisotropic g-values and line widths using the EPR simulation program W95EPR developed by Prof. Dr. Frank Neese. The gas phase geometries of the complexes [Fe(trop₃dae)]⁺, [LiFe(trop₂dae)(OEt₂)₂] (Li bridged), [LiFe(trop₂dae)] (Li bridged), [LiFe(trop₂dae)] (Li terminal), [LiFe(trop₂dae)(thf)₂] (Li terminal), [LiFe(trop₂dae)(thf)₃] (Li terminal), [NaFe(trop₂dae)] (Na terminal), [NaFe(trop₂dae)] (Na bridged), and [NaFe(trop₂dae)(thf)₃] (Na terminal) were optimized with the Turbomole program package[1] coupled to the PQS Baker optimizer[2] via the BOpt package[3] at the ri-DFT[4]/BP86[5] level. We used the def2-TZVP basis set[6] for all atoms and a small grid (m4). The minima (no imaginary frequencies) were characterized by calculating the Hessian matrix. The Cartesian coordinates of the optimized geometries are supplied as a separated zip file (.pdb and .xyz format). EPR and Mössbauer parameters were calculated with the ORCA[7] program systems, using the coordinates from the structures optimized in Turbomole as input and the b3-lyp[8] functional. For the EPR property calculations we used the def2-TZVP basis set on all atoms. For the Mössbauer calculations we used the TVZP basis set on all atoms. The quadrupole splittings are directly plotted by the program. The isomer shifts (δ) were calculated from the calculated total electron density at the iron nucleus (ρ) using the linear relation δ = α(ρ – C) + β. Calibrated parameters derived for the TZVP basis set (α = –0.298, β = 1.118, and C = 11580) were taken from the literature.[9]

[NaFe(trop₃dae)(THF)₃] (1). NaCH₂SiMe₃ (74 mg, 0.67 mmol) was dissolved in THF (2 mL) at –30°C. The solution was added to a stirred suspension of [FeCl₂(thf)₃] (80 mg, 0.34 mmol) in THF (1.5 mL) at –30°C. H₂trop₂dae (150 mg, 0.34 mmol) was added as a solid after 5 min, upon which the reaction mixture turned deep red. After 5 min, NaCH₂SiMe₃ (37 mg, 0.34 mmol) was added as a solid. The reaction mixture was warmed to ambient temperature overnight and filtered. The filtrate was layered with MTBE (6 mL) and hexanes (6 mL) and cooled to –30°C. After 1 d deep red single crystals of 1 were isolated by filtration and dried in a stream of Argon. The filtrate was stored at –30°C to give a second crop of single crystalline 1 after 3 d. Combined yield: 88 mg, 0.12 mmol, 35%. 1 could be re-isolated as single crystals from a toluene solution by layering with hexanes at room temperature in 68% yield. 

[LiFe(trop₂dae)(Et₂O)₂] (2) and [LiFe(trop₂dae)(thf)(Et₂O)] (2b). A solution of LiCH₂SiMe₃ (85 mg, 0.90 mmol) in Et₂O (1.5 mL) was cooled to –30°C and added to a stirred suspension of an iron chloride precursor (for 2: FeCl₂, 29 mg, 0.23 mmol; for 2b: [FeCl₂(thf)₃], 53 mg, 0.23 mmol) in Et₂O (1.5 mL) at –30°C. H₂trop₂dae (100 mg, 0.23 mmol) was added as a solid after 5 min, upon which the reaction mixture turned deep red. The reaction mixture was warmed to ambient temperature overnight and filtered. The filtrate was cooled to –30°C and layered with hexanes (7 mL). After 2 d deep red single crystals of 2/2b were isolated by filtration and dried in a stream of Argon. The filtrate was stored at –30°C to
give a second crop of single crystalline 2/2b after 2 d. Combined yield of 2: 54 mg, 83 µmol, 36%. [10]

Analytical data for 2: 1H NMR (300 MHz, C₆D₆): δ = 1.07 (t, JHH = 6.8 Hz, β-Et₂O), 1.43 (br s), 3.25 (q, JHH = 6.8 Hz, α-Et₂O), 3.49 (br s), 11.62 (br s), 20.89 (br s) ppm. UV/VIS (THF): λmax = 224, 254, 327, 505 nm. ATR IR: v = 3060 (w), 2956 (w), 2816 (w), 1592 (m), 1574 (w), 1479 (m), 1456 (m), 1384 (m), 1294 (w), 1248 (m), 1179 (w), 1151 (w), 1062 (m), 1041 (m), 963 (w), 837 (m), 803 (m), 738 (s), 692 (m) cm⁻¹. m.p. = 119°C (decomp.). μeff = 2.0(1) μB (Evans' method). ⁵⁷Fe Mössbauer (δ, |ΔE₀| (mm/s)): (77 K) 0.28(1), 2.0(1) (ΓFWHM = 0.29(1) mm/s).

Analytical data for 2b: 1H NMR (300 MHz, C₆D₆): δ = 0.81 (br s), 2.11 (br s), 2.93 (br s), 20.87 (br s) ppm. μeff = 1.7(1) μB (Evans' method).

[LiFe(trop₂dace)(2-Me-THF)₂] (2c) and [LiFe(trop₂dace)(thf)₂] (2d). The experiments were carried out on the 45 µmol scale. Compound 2 was dissolved in the appropriate solvent (for 2c: 2 mL of 2-Me-THF; for 2d: 1 mL of THF). The reaction mixture was warmed to ambient temperature over 1 h. TMEDA (26 mg, 0.22 mmol) was added and the reaction mixture was filtered. The filtrate was layered with hexanes (6 mL). Deep red single crystals of 2c or 2d had formed after 14 h, were isolated by filtration and dried in a stream of Argon. Yield: 91% (2c), 76% (2d).

2c could be re-isolated as single crystals from a toluene solution by layering with hexanes at room temperature in 62% yield.

Analytical data for 2c: 1H NMR (300 MHz, C₆D₆): δ = 1H NMR (300 MHz, C₆D₆): δ = 0.81 (br s), 1.35 (br s), 2.95 (br s), 3.21 (br s), 20.52 (br s) ppm. ATR IR: v = 2957 (m), 2863(w), 2833 (m), 2800 (w), 2769 (w), 1593 (m), 1571 (w), 1479 (s), 1453 (s), 1376 (s), 1259 (m), 1177 (w), 1090 (w), 1077 (s), 1067 (s), 1040 (m), 1018 (m), 962 (m), 896 (w), 855 (m), 808 (m), 798 (m), 747 (s) cm⁻¹. μeff = 2.0(1) μB (Evans' method).

Analytical data for 2d: 1H NMR (300 MHz, C₆D₆): δ = 1H NMR (300 MHz, C₆D₆): δ = 1.34 (br s), 3.44 (br s), 8.84 (br s), 20.18 (br s) ppm. ATR IR: v = 3053 (w), 3010 (w), 2972 (m), 2955 (m), 2884 (w), 2836 (m), 2818 (m), 2793 (m), 2727 (w), 2697(w), 1590 (m), 1570 (w), 1478 (s), 1455 (s), 1385 (s), 1312 (w), 1292 (w), 1257 (m), 1175 (w), 1118(w), 1078 (m), 1036 (s), 1020 (m), 961 (w), 912 (w), 888 (m), 874 (s), 856 (m), 800 (m), 734 (s) cm⁻¹. μeff = 2.2(1) μB (Evans' method).

[Li₂Fe(CH₂SiMe₃)₂(trop₂dace)(TMEDA)] (3). A solution of LiCH₂SiMe₃ (85 mg, 0.90 mmol) in Et₂O (1.5 mL) was cooled to −30°C and added to a stirred suspension of [FeCl₃(thf)]₅ (53 mg, 0.23 mmol) in Et₂O (1.5 mL) at −30°C. H₂trop₂dace (100 mg, 0.23 mmol) was added as a solid after 5 min, upon which the reaction mixture turned deep red. The reaction mixture was warmed to ambient temperature over 1 h. TMEDA (26 mg, 0.22 mmol) was added and the reaction mixture was filtered. The filtrate was layered with hexanes (8 mL). After 1 d deep red single crystals of 3 were isolated by filtration and dried in a stream of Argon. Yield: 138 mg, 173 µmol, 67%.

1H NMR (300 MHz, C₆D₆): δ = 0.05 (br s), 0.18 (br s), 1.44 (br s), 2.07 (br s), 2.28 (br s), 3.49 (br s), 11.30 (br s), 20.92 (br s), 31.62 (br s) ppm. UV/VIS (THF): λmax = 213, 285 nm. ATR IR: v = 3062 (w), 3013 (w), 2946 (m), 2836 (m), 2803 (m), 2709 (m), 1592 (m), 1467 (s), 1434 (m), 1410 (m), 1384 (w), 1355 (w), 1320 (w), 1306 (m), 1287 (m), 1268 (w), 1234 (s), 1203 (w), 1182 (m), 1158 (m), 1128 (m), 1091 (m), 1063 (s), 1044 (w), 1033 (w), 1015 (m), 982 (m), 945 (m), 877 (s), 844 (s) cm⁻¹. m.p. = 207–210°C (decomp.). μeff = 4.7 μB (Evans' method). Anal. calc. for C₄₈H₆₄N₄Li₂Si₂Fe (798.94 g/mol): C, 69.16; H, 8.07; N, 7.01; found: C, 68.88; H, 7.89; N, 6.78.

Reaction of 1 with H₂. A solution of 1 (6 mg, 8 µmol) in C₆D₆ or THF-d₈ (0.5 mL) was degassed and pressurized with H₂ (1.5 bar) in a J. Young type NMR tube at −196°C and then warmed to room temperature.

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With C₆D₆ as a solvent, no color change was observed and the ¹H NMR spectrum was unchanged (except for the presence of a resonance for H₂) after reaction times of up to >7 h. With THF-d₅ as a solvent, the dark red solution turned yellow, when the frozen solution was warmed to ambient temperature under the H₂ atmosphere. A yellowish solid precipitated. Non-coordinate H₂trop₂dae was the only species that could be identified by ¹H NMR spectroscopy.

**Attempted hydrogenation of 1-octene.** A solution of 1 (10 mg, 14 µmol), 1-octene (15 mg, 134 µmol), and p-xylene (19 mg, internal standard) in C₆D₆ (0.5 mL) was degassed and pressurized with H₂ (1.5 bar) in a J. Young type NMR tube. No hydrogenation of 1-octene was observed by NMR spectroscopy after up to 6.5 h.

**Dehydrogenation of N,N-dimethylamine-borane (DMAB).** Method A (open system under Argon): Typical experiments were carried out on the 0.24 mmol scale (with respect to DMAB). The requested amount of 1, 2, 2d, or 3 was dissolved in toluene (3.0 mL). A solution of DMAB (14 mg, 0.24 mmol) in toluene (2.0 mL) was added through a rubber septum. The gas evolved was collected in a burette setup and its volume determined. In poisoning experiments a stock solution of the poison was added at the indicated reaction time. The total volume was corrected for the volume added in this process. For table 1, entry 3 (main part): After completion of the reaction, an aliquot of the reaction mixture was analyzed by ¹¹B NMR spectroscopy after addition of 1/3 (V/V) of C₆D₆. The main component (>98%) was (Me₂NBH₂)₂. ¹¹B NMR (96 MHz, Tol/C₆D₆ (2:1)): δ = 4.8 (t, ¹J_BH = 113.0 Hz) ppm.

Method B (closed system): Typical experiments were carried out on the 0.15 mmol scale (with respect to DMAB) in a J. Young type NMR tube. The requested amount of 1, 2, or 3 was dissolved in C₆D₆ (0.3 mL). A solution DMAB (9 mg, 0.15 mmol) in C₆D₆ (0.3 mL) was added and the reaction vessel closed.

- **3** (5 mol%, 231 min): 34% DMAB, 31% 4, 31% 5, 1% Me₂NBH₂, 3% BH containing species (possibly Me₂NBH).
- **2** (5 mol%, 229 min): 42% DMAB, 27% 4, 28% 5, 1% Me₂NBH₂, 2% BH containing species (possibly Me₂NBH).
- **1** (9 mol%, 52 min): 18% DMAB, 21% 4, 56% 5, 2% Me₂NBH₂, 3% BH containing species (possibly Me₂NBH).
- **1** (5 mol%, 75 min): 15% DMAB, 65% 4, 16% 5, 1% Me₂NBH₂, 3% BH containing species (possibly Me₂NBH).

¹¹B NMR chemical shifts for boron species: ¹¹B NMR (96 MHz, C₆D₆): δ = −13.7 (q, ¹J_BH = 93.0 Hz, 5), −11.8 (q, ¹J_BH = 96.4 Hz, DMAB), 1.4 (t, ¹J_BH = 108.2 Hz, 5), 4.8 (t, ¹J_BH = 113.3 Hz, 4), 28.5 (d, ¹J_BH = 123.4 Hz, BH containing species), 37.6 (t, ¹J_BH = 128.4 Hz, Me₂NBH₂) ppm.

For comparison, the dehydrogenation of DMAB with [Fe(N(SiMe₃)₂)₂] was tested. A solution of DMAB (16 mg, 0.27 mmol) in C₆D₆ (0.3 mL) was added to a solution of [Fe(N(SiMe₃)₂)₂] (5 mg, 13 µmol) in C₆D₆ (0.3 mL). The reaction vessel was closed. Gas evolution was observed and a suspension of a dark brown solid in a colorless liquid phase resulted. The reaction was monitored by ¹¹B NMR spectroscopy. After 6 h at ambient temperature, formation ca. 80% 4 was observed and the reaction did not proceed any further. Only trace amounts of 5 were detected in the course of the reaction.

**Reactions with N,N,N-trimethylamine-borane (Me₃NBH₃).** Reactions of equimolar amounts of 1 or 2 with Me₃NBH₃ were performed in toluene (1 mL) on the 41 µmol scale and
gave dark red solutions. $^{11}$B NMR spectroscopic analysis showed a quartet due to the BH$_3$
+ group as the only signal in both cases. In case of 2, the chemical shift (δ = -7.35 ppm) was
+ similar to that of a sample of Me$_3$NBH$_3$ alone (δ = -7.34 ppm). In case of 1, the chemical shift
+ was slightly altered (δ = -7.25 ppm). All volatiles were removed from the reaction with 1 to
+ give a red powder. Solid state IR spectroscopy showed a shift of the bands in the B–H
+ stretching region from $\tilde{v}$ = 2312, 2283, 2263 cm$^{-1}$ for pure Me$_3$NBH$_3$ to $\tilde{v}$ = 2387, 2314, 2266
+ cm$^{-1}$ for the product obtained from reaction of Me$_3$NBH$_3$ with 1.

**Dehydrogenative methanolation of PhSiH$_3$.** Method A (open system under Argon): Typical experiments were carried out on the 0.41 mmol scale (with respect to PhSiH$_3$). The requested amount of 1 (as a pure compound or as a freshly prepared stock solution in toluene) was dissolved in toluene to give a total volume of 2.0 mL. A solution of the requested amount of PhSiH$_3$ in toluene (1 mL) was added. The requested amount of methanol was added through a rubber septum using a microliter syringe. The gas evolved was collected in a burette setup and its volume determined.

In one run, all volatiles were removed from the reaction mixture and the residue dissolved in C$_6$D$_6$ (0.6 mL). The main component (>95% by $^1$H NMR) was PhSi(OMe)$_3$.$^{[11]}$ $^1$H NMR (300 MHz, C$_6$D$_6$): δ = 3.48 (s, 9H, OMe), 7.20 (br s, 2H, o/m-Ph), 7.79-7.95 (m, 3H, m/o-Ph, p-Ph) ppm. $^{13}$C NMR (100 MHz, C$_6$D$_6$): δ = 50.63 (s, OMe), 130.77 (s, o/m-Ph), 131.29 (s, ipso-Ph), 135.09 (s, p-Ph), 135.26 (s, m/o-Ph) ppm. $^{29}$Si NMR (80 MHz, C$_6$D$_6$): δ = 54.9 (s, PhSi(OMe)$_3$) ppm.

In poisoning experiments a stock solution of the poison was added at the indicated reaction time. The total volume was corrected for the volume added in this process.

In a deuteration experiment MeOH was replaced by MeOD (≥99% deuteration) and 6 mol% of 1 were used. After completion of the reaction, the collected gas was transferred into a J. Young NMR tube containing C$_6$D$_6$ (0.6 mL). $^1$H NMR spectroscopy showed the presence of H$_2$ and HD in a molar ratio of 1.0 : 6.2. The liquid phase of the reaction was subjected to aqueous workup. $^1$H and $^{13}$C NMR spectroscopic analysis revealed partial deuteration of the C$_2$H$_4$ backbone and of the benzylic positions of H$_2$trp$_2$dae.

Method B (closed system): Typical experiments were carried out on the 0.08 mmol scale (with respect to PhSiH$_3$) in a J. Young type NMR tube. The requested amounts of 1 (2 mg, 2.7 µmol) and PhSiH$_3$ (9 mg, 83 µmol) were dissolved in C$_6$D$_6$ (0.6 mL). MeOH (10 µL, 7.9 µg) was added and the reaction vessel closed. H$_2$ and PhSi(OMe)$_3$ were detected as the main species (>99%) by $^1$H NMR.$^{[12]}$ If intended, the reaction vessel was vented under inert gas atmosphere and recharged with PhSiH$_3$ and MeOH.

**Dehydrogenative alcoholysis of PhSiH$_3$ with 1,4-benzen-dimethanol.** Typical experiments were carried out in an open system under Argon on a 277 µmol scale (with respect to PhSiH$_3$). The requested amount of 1,4-benzene-dimethanol was suspended in toluene (3 mL). A solution of the requested amounts of 1 and PhSiH$_3$ in toluene (3 mL) was added with a syringe through a rubber septum. The gas evolved was collected in a burette setup and its volume determined.

After completion of the reaction, the collected gas was transferred into a J. Young NMR tube containing C$_6$D$_6$ (0.6 mL). $^1$H NMR spectroscopy confirmed the formation of H$_2$.

The precipitated off-white polymeric material 6 was isolated from the dark brown liquid phase by filtration under ambient conditions, washed with toluene (2 × 5 mL), and dried in

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vacuo. The material is poorly soluble in common solvents such as toluene, chloroform or dimethylformamide. Yield: 84 mg, 271 µmol, 98%.

ATR IR: \(\tilde{\nu} = 2918 \text{ (w)}, 2870 \text{ (w)}, 2946 \text{ (m)}, 2836 \text{ (m)}, 2803 \text{ (m)}, 1592 \text{ (w)}, 1515 \text{ (w)}, 1460 \text{ (w)}, 1430 \text{ (m)}, 1375 \text{ (m)}, 1260 \text{ (w)}, 1215 \text{ (m)}, 1051 \text{ (s)}, 1017 \text{ (s)}, 850 \text{ (s)}, 801 \text{ (s)}, 763 \text{ (s)}, 740 \text{ (s)}, 699 \text{ (s)} \, \text{cm}^{-1}.\) MALDI-TOF-MS \((m/z) = 1295.4 \, [C_{72}H_{72}NaO_{14}Si_{4}]^{+}; 1674.6 \, [C_{94}H_{94}NaO_{18}Si_{3}]^{+}; 2052.7 \, [C_{116}H_{116}NaO_{22}Si_{6}]^{+}; 2433.8 \, [C_{138}H_{138}NaO_{26}Si_{7}]^{+}; 2810.0 \, [C_{160}H_{160}NaO_{30}Si_{8}]^{+}; 3187.1 \, [C_{182}H_{182}NaO_{34}Si_{9}]^{+}.\)

**Dehydrogenative alcoholyis of Ph₂SiH₂ with 1,4-benzenediethanol.** Typical experiments were carried out in an open system under Argon on a 0.28 mmol scale. The requested amount of 1,4-benzenediethanol was suspended in toluene (3 mL). A solution of the requested amounts of 1 (2 mol%) and Ph₂SiH₂ (1.0 equiv.) in toluene (3 mL) was added with a syringe through a rubber septum. THF (1 mL) was added. The gas evolved was collected in a burette setup and its volume determined. After completion of the reaction, the reaction mixture was poured into hexanes (10 mL) under ambient conditions. All volatiles were removed under reduced pressure. The residue was washed with hexanes (5 mL) to give an off-white sticky solid, which was dried in vacuo. The product 7 is soluble in common organic solvents such as chloroform, THF or dimethylformamide. Yield: 90 mg, 0.28 mmol, quantitative.

\(^1\)H NMR (200 MHz, CDC\(_3\)): \(\delta = 4.65-4.80 \text{ (m, 4H, CH₂)}, 6.94-7.74 \text{ (m, 14H, H}^{\text{arom}}\) ppm. \(^{13}\)C NMR\(^\text{13}\) (50 MHz, CDC\(_3\)) \(\delta = 64.93-65.28 \text{ (s, CH₂)}, 126.02-127.10 \text{ (s, C}^{\text{arom}}\), 127.88-128.63 \text{ (s, C}^{\text{arom}}\), 130.36-130.59 \text{ (s, C}^{\text{arom}}\), 132.46-132.65 \text{ (s, C}^{\text{arom}}\), 134.47-135.12 \text{ (s, C}^{\text{arom}}\), 138.78-139.89 \text{ (s, C}^{\text{arom}}\)) ppm. \(^{29}\)Si NMR (79 MHz, CDC\(_3\)): \(\delta = -31 \text{ (br s) ppm. ATR IR: } \tilde{\nu} = 3068 \text{ (w)}, 3017 \text{ (w)}, 2870 \text{ (w)}, 1590 \text{ (w)}, 1515 \text{ (w)}, 1459 \text{(w)}, 1429 \text{ (m)}, 1375 \text{ (m)}, 1261 \text{ (w)}, 1214 \text{ (w)}, 1115 \text{ (s)}, 1056 \text{ (s)}, 1018 \text{ (s)}, 997 \text{ (m)}, 844(s), 801 \text{ (s)}, 740 \text{ (s)}, 718 \text{ (s)}, 699 \text{ (s)} \, \text{cm}^{-1}.\) MALDI-TOF-MS \((m/z) = 2070.7 \, [(C_{20}H_{18}O_{2}Si)_{6}(C_{8}H_{10}O_{2})Na]^{+}; 2388.8 \, [(C_{20}H_{18}O_{2}Si)_{7}(C_{8}H_{10}O_{2})Na]^{+}; 2707.9 \, [(C_{20}H_{18}O_{2}Si)_{8}(C_{8}H_{10}O_{2})Na]^{+}; 3026.0 \, [(C_{20}H_{18}O_{2}Si)_{9}(C_{8}H_{10}O_{2})Na]^{+}; 3345.1 \, [(C_{20}H_{18}O_{2}Si)_{10}(C_{8}H_{10}O_{2})Na]^{+}; 3663.2 \, [(C_{20}H_{18}O_{2}Si)_{11}(C_{8}H_{10}O_{2})Na]^{+}; 3981.4 \, [(C_{20}H_{18}O_{2}Si)_{12}(C_{8}H_{10}O_{2})Na]^{+}; 4300.5 \, [(C_{20}H_{18}O_{2}Si)_{13}(C_{8}H_{10}O_{2})Na]^{+}; 4618.6 \, [(C_{20}H_{18}O_{2}Si)_{14}(C_{8}H_{10}O_{2})Na]^{+}; 4936.7 \, [(C_{20}H_{18}O_{2}Si)_{15}(C_{8}H_{10}O_{2})Na]^{+}; 5255.8 \, [(C_{20}H_{18}O_{2}Si)_{16}(C_{8}H_{10}O_{2})Na]^{+}; 5574.9 \, [(C_{20}H_{18}O_{2}Si)_{17}(C_{8}H_{10}O_{2})Na]^{+}; 5893.0 \, [(C_{20}H_{18}O_{2}Si)_{18}(C_{8}H_{10}O_{2})Na]^{+}; 6211.2 \, [(C_{20}H_{18}O_{2}Si)_{19}(C_{8}H_{10}O_{2})Na]^{+}.\)
[LiFe(trop$_2$dae)(OEt)$_2$(thf)] (2b). Compound 2b was obtained as dark red single crystals, when the reaction protocol for the synthesis of 2 was performed with [FeCl$_2$(thf)$_{1.5}$] as a starting material instead of [FeCl$_2$]. It crystallized in the orthorhombic space group Pna2$_1$ with $Z = 4$ (Figure S1). The bonding parameters in 2b are highly similar to those in compound 2. The (C=C)$_{olefin}$ distances in 2b differ stronger than those in 2 ($\Delta = 0.013$ Å in 2b vs. no significant difference in 2). However, the average (C=C)$_{olefin}$ bond lengths in 2b and 2 are identical within limits of error. The only marked difference is the shorter Li–O$^{THF}$ distance in 2b ($1.95(11)$ Å) compared to the Li–O$^{Et_2O}$ distance in 2 ($2.017(12)$ Å), which is due to the higher Lewis basicity of THF compared to Et$_2$O. The $^1$H NMR spectrum of 2b is similar to that of 2 except for the resonances due to the neutral ligands. Magnetic susceptibility measurements by Evans’ method revealed an effective magnetic moment of $\mu_{\text{eff}} = 1.7(1)$ $\mu_B$ in agreement with the presence of one unpaired electron (d$^7$ low spin electron configuration).

Figure S1. Molecular structure of [LiFe(trop$_2$dae)(OEt)$_2$(thf)] (2b) in the solid state; displacement ellipsoids are shown at the 50% probability level; annulated C$_9$H$_4$ groups, one split position of disordered Et$_2$O and thf ligands, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–N1, 1.899(3); Fe1–N2, 1.954(3); Fe1–(C4–C5), 1.923(5); Fe1–(C19–C20), 1.931(4); C4–C5, 1.407(6); C19–C20, 1.420(7); Li1–N1, 2.178(9); Li1–N2, 2.072(9); Li1–O1, 1.95(11); Li1–O2, 2.03(12); (N/(C=C)–Fe1–N/(C=C), 79.19(15) - 96.94(18); angle sum around Fe1, 361.

[LiFe(trop$_2$dae)(L)$_2$] (2c: L = 2-Me-THF; 2d: L = thf). Compounds 2c and 2d were obtained as dark red single crystals upon recrystallization of 2 from 2-Me-THF/hexanes or THF/hexanes in 91% and 76% yield, respectively. After having been dissolved in toluene, compound 2c could be re-isolated in 62% yield by layering with hexanes. The solution effective magnetic moments of 2c/2d are slightly higher than that of 2b ($\mu_{\text{eff}} = 2.0(1)$ to 2.0(2) $\mu_B$), but still in agreement with a d$^7$ low spin electron configuration of the Fe center. Compounds 2c/2d crystallized in the orthorhombic space group P2$_1$2$_1$2$_1$ with $Z = 4$ (2c, Figure S2a) and in the monoclinic space group P2$_1$/c with $Z = 4$ (2d, Figure S2b). The solid state structures of 2c/d differ from those of the other lithium containing species 2 and 2b in
that the lithium counter ion interacts only with one of the nitrogen atoms of the \((\text{trop}_2\text{dae})^2^-\) ligand. This is resembling of the solid state structure of the sodium containing compound \([\text{NaFe}(\text{trop}_2\text{dae})\text{(thf)}_3]\) (1). Indeed, the bonding parameters of 2c/2d and 1 are highly similar in most respects. Although the average Fe–N distances in 1, 2c, and 2d are similar (1.880(4) Å in 1 – 1.8878(15) Å in 2c), the Fe–N bonds within one molecule are more asymmetric in case of 2c/2d (Δ = 0.09 Å in 2c/2d vs. 0.04 Å in 1). Further differences are related to the coordination geometry of the alkali counter ion. The coordination sphere of the lithium ion in 2c/2d is defined by one nitrogen atom of the \((\text{trop}_2\text{dae})^2^-\) ligand and two O\(^2\text{Me-THF}/O\text{THF}\) atoms (CN = 3). In contrast, the sodium ion in 1 interacts with one nitrogen atom of the \((\text{trop}_2\text{dae})^2^-\) ligand, three O\text{THF}\) atoms, and with an aromatic C–C bond of the trop moiety (CN = 5). The solid state structures of 2, 2b, 2c, and 2d demonstrate that the nature of the neutral ligands coordinating to Li sensitively effect the coordination chemistry of these compounds. DFT calculations revealed significant differences in their electronic structures (Table S2). In general the calculated g-values and spin densities are similar for compounds in which the alkali metal interacts with one nitrogen atom (terminal) or with both nitrogen atoms of the \((\text{trop}_2\text{dae})^2^-\) ligand (bridging). The nature of the alkali metal (Li vs. Na) seems less important in this respect.

**Figure S2.** Molecular structure of \([\text{LiFe}(\text{trop}_2\text{dae})(2\text{-Me-THF})_2]\) (2c) (a, left) and \([\text{LiFe}(\text{trop}_2\text{dae})(\text{thf})_2]\) (2d) (b, right) in the solid state; displacement ellipsoids are shown at the 50% probability level; annulated C\(_6\)H\(_4\) groups and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for 2c: Fe1–N1, 1.9311(15); Fe1–N2, 1.8444(14); Fe1–(C4–C5), 1.9217(18); Fe1–(C19–C20), 1.9323(17); C4–C5, 1.443(3); C19–C20, 1.427(3); Li1–N1, 2.056(4); Li1–O1, 1.905(17); Li1–O2, 1.934(4); (N/(C=C)–Fe1–N/(C=C), 84.39(6) - 97.32(7); angle sum around Fe1, 368. Selected bond lengths [Å] and angles [°] for 2d: Fe1–N1, 1.9286(12); Fe1–N2, 1.8439(16); Fe1–(C4–C5), 1.925(2); Fe1–(C19–C20), 1.9294(16); C4–C5, 1.434(2); C19–C20, 1.432(2); Li1–N1, 2.004(3); Li1–O1, 1.942(3); Li1–O2, 1.877(4); (N/(C=C)–Fe1–N/(C=C), 84.22(6) - 98.14(7); angle sum around Fe1, 368.
[Li$_2$Fe(CH$_2$SiMe$_3$)$_2$(trop$_2$dae)(TMEDA)] (3). Compound 3 was isolated in 67% yield as dark red single crystals. It possesses a magnetic moment of $\mu_{\text{eff}} = 4.7$ $\mu_B$ at 298 K, corresponding to four unpaired electrons for an Fe(II) species with a d$^6$ high spin electron configuration. Hence, in this mixed trinuclear alkyl amide, the metal centers Li$^+$ and Fe$^{2+}$ have retained their original oxidation states and we suggest 3 as a possible intermediate en route to the formation of species analogous to 1 and 2. It is noteworthy, that (trop$_2$dae)$^2$ can accommodate two metal centers in its binding pocket suggesting that a rich heterobimetallic chemistry based on this ligand should be possible. Compound 3 crystallizes in the triclinic space group $P\bar{1}$ with $Z = 4$. Distorted tetrahedral coordination geometries are observed for Fe1 and Li1 which are bridged by one (CH$_2$SiMe$_3$)$_2^-$ ligand and one amido group (N1) forming a four membered ring (Figure S3). As expected, the Fe–C distance is larger for the bridging (CH$_2$SiMe$_3$)$_2^-$ ligand than for the terminal one. The difference in these bond lengths of 0.085 Å is much larger than the corresponding value of 0.032 Å found in [(Me$_3$SiCH$_2$)Fe(µ-TMP)(µ-CH$_2$SiMe$_3$)Na(TMEDA)] (TMP = 2,2,6,6-tetramethylpiperidid). The Fe1–(C4=C5) distance is larger than in compounds 1 and 2 reflecting the less electron rich nature of the Fe(II) center in compound 3. The Fe1–N1 distance in 3 (1.964(3) Å is longer than that in 2 (1.899(3) Å), which is due to a shortened Li1–N1 distance in 3 (2.054(4) Å) compared to 2 (2.160(11) Å). The third metal center, Li2, interacts with the TMEDA ligand and with a bridging amido group (N2) resulting in a trigonal planar coordination geometry.

Figure S3. Molecular structure of [Li$_2$Fe(CH$_2$SiMe$_3$)$_2$(trop$_2$dae)(TMEDA)] (3) in the solid state; displacement ellipsoids are shown at the 50% probability level; methyl groups of SiMe$_3$ substituents and TMEDA ligand are drawn as wireframe; annelated C$_8$H$_4$ groups and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Fe1–N1, 1.964(3); Fe1–C33, 2.059(3); Fe1–C37, 2.144(2); Fe1–(C4–C5), 2.044(2); Li1–N1, 2.054(4); Li1–N2, 1.926(5); Li1–C37, 2.356(6); Li1–(C19–C20), 2.388(6); C4–C5, 1.407(3); C19–C20, 1.360(4).
Powder X-ray diffraction.

**Figure S4.** Experimental (blue) and calculated (magenta) X-ray powder diffractogram for [NaFe(trop$_2$dae)(thf)$_3$] (1) at room temperature.

**Figure S5.** Experimental (blue, room temperature) and calculated (magenta, 100 K) X-ray powder diffractogram for [LiFe(trop$_2$dae)(Et$_2$O)$_2$] (2).
Zero field Mössbauer spectroscopy.

Figure S6. Zero field Mössbauer spectrum of [NaFe(trop$_2$dae)(thf)$_3$] (1) at 77 K. δ = 0.20(1) mm/s; |ΔE$_Q$| = 2.87(1) mm/s; Γ$_{FWHM}$ = 0.34(1) mm/s.

Figure S7. Zero field Mössbauer spectrum of [LiFe(trop$_2$dae)(Et$_2$O)$_2$] (2) at 77 K. δ = 0.28(1) mm/s; |ΔE$_Q$| = 2.01(1) mm/s; Γ$_{FWHM}$ = 0.29(1) mm/s.
The DFT calculated Mössbauer isomer shifts (Table S1) are in good agreement with the experimental parameters (1: DFT 0.22 mm/s, Exp. 0.20 mm/s; 2: DFT 0.35 mm/s, Exp. 0.28 mm/s). The absolute values of the computed quadrupole splitting (QS) parameters (1: 2.07 mm/s; 2: 2.49 mm/s) moderately correspond with the experimental values (1: 2.87(1) mm/s; 2: 2.01(1) mm/s), but predict a somewhat larger QS for [LiFe(trop2dae)(OEt2)2] (2) compared to [NaFe(trop2dae)(thf)3] (1), while experimentally the reverse is observed. This is not caused by small differences in the X-ray coordination geometries compared to the optimized geometries in the gas phase, as the DFT calculated Mössbauer parameters using the X-ray geometries without any prior geometry optimization are similar (Table S1). We thus speculate that either the experimental Mössbauer parameters are influenced by weak intermolecular exchange interactions between the [Fe(trop2dae)]− anions in the solid state, or the QS parameters are simply not predicted accurately enough by the applied DFT method.

Table S1. Experimental and DFT calculated Mössbauer parameters(a), (b)

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<th>Experimental</th>
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<th>δ(d) (mm/s)</th>
<th>Quadrupole splitting (mm/s)</th>
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<tr>
<td></td>
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<tr>
<td></td>
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<td>Terminal (f)</td>
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<td>[LiFe(trop2dae)] (g) (X-ray)</td>
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(a) Geometries optimized with Turbomole (BP86, def2-TZVP).
(b) Mössbauer parameters calculated with Orca (b3-lyp, TZVP) using the Turbomole optimized geometries.
(c) Calculated total electron density at the iron nucleus.
(d) Isomer shift δ = αρ − C + β, with α = −0.298, β = 1.118 and C = 11580.15
(e) Alkali metal bridged over both N-donors, like in the X-ray structure of 2.
(f) Alkali metal bound to only one N-donor, like in the X-ray structure of 1.
(g) Geometry of the X-ray structure, not optimized with DFT.
**SQUID analysis.** Representative plots of the susceptibility, the effective magnetic moment and inverse susceptibility at 1 T of compound 1 are shown in Figure S8. 1 shows paramagnetic behavior over the whole temperature range of 2-300 K and follows the Curie-Weiss law (see inset, Figure S8). The data were fitted with the equation \( \chi = \chi_0 + \chi_{TI} \) with \( \chi_0 = C/(T-\theta) \), the temperature dependent contribution to the susceptibility (C = Curie constant; \( \theta = \) Weiss constant), and \( \chi_{TI} \), the temperature independent term. The constants calculated from the fit are C = 0.5323(4) cm\(^3\)K/mol, \( \theta = -0.39 \) K and \( \chi_{TI} = -8.3(1) \times 10^{-6} \) cm\(^3\)/mol. The effective magnetic moment at room temperature after data correction for temperature independent contributions is \( \mu_{eff} (300 \text{ K}) = 1.96 \mu_B \), which is slightly larger than the expected spin only value for one unpaired electron (1.73 \( \mu_B \)). A very subtle increase up to 2.05 \( \mu_B \) in the effective magnetic moment is observed when cooled from room temperature. Overall, the magnetic moment is consistent with Fe(I) in low spin configuration and \( S = 1/2 \).

At 100 Oe, the magnetic moment at room temperature \( \mu_{eff} (300 \text{ K}) = 3.25 \mu_B \), is higher than the one observed at 1 T (Figure S9). The discrepancy observed between the moment at 100 Oe and 1 T might be explained by the presence of uncompensated interfacial ferromagnetically aligned spins oriented by small magnetic fields. A higher magnetic field will suppress the surface effects and only the bulk property will be observed. This could be an intrinsic property of 1 or result from a superparamagnetic trace impurity. However, single crystals of 1, which could be used to further investigate this effect by single crystal magnetic analysis, were too small for such measurements. Field dependent susceptibilities were observed in Re(III) complexes with bifunctional single amino acid chelates, but the lack of single crystal magnetic analysis hindered a more detailed study of these observations.\(^{[16]}\)
**Figure S9.** Temperature dependence of the magnetic susceptibility at 100 Oe for 1 (only ZFC is shown - ZFC and FC curves were equivalent). Empty circles represent the molar susceptibility while the solid blue line is the result of fitting a Curie-Weiss law (see text). The empty triangles represent the effective magnetic moment with a Cuire-Weiss fit (blue line). The inset shows the reciprocal molar susceptibility (empty symbols) with a linear fit (solid line).

**EPR spectroscopy and DFT calculations.** EPR spectra of undiluted powdered solids or frozen glasses \((c = 6 \cdot 10^{-3} \text{ M})\) were recorded at 20 K. When THF was used as a solvent, 0.1 M \([\text{N}(n\text{Bu})_4][\text{PF}_6]\) was added. Experimental conditions for the spectrum shown in the main text (2 in THF/0.1 M \([\text{N}(n\text{Bu})_4][\text{PF}_6]\), Figure 2b): microwave power 0.2 mW, field modulation amplitude = 2 Gauss, microwave frequency = 9.365782 GHz. The simulated spectrum was obtained with the parameters shown in Table S2.

**EPR spectra of 1 and 2 as powdered solids.** X-band EPR spectra of the (undiluted) powdered solids of 1 and 2 at 20K revealed signals of reasonable quality (Figure S10). The spectra are clearly different, pointing to a distinct crystal packing. In agreement with the Mössbauer results, also the g-values appear to be different, suggestive of a somewhat different electronic structure. These electronic differences could well be caused by differences in the interaction between the \((\text{trop}_2\text{dae})^2^-\) ligand and the \([\text{Na}(\text{thf})_3]^+\) and \([\text{Li}(\text{OEt})_2)_2]^+\) complex ions (although intermolecular exchange interactions in the solid state may also have their influence). According to DFT calculations the electronic structures of \([\text{NaFe}(\text{trop}_2\text{dae})(\text{thf})_3]\) (1) and \([\text{LiFe}(\text{trop}_2\text{dae})(\text{OEt})_2)_2]\) (2) and are indeed significantly different, with a larger g-anisotropy a higher Fe spin density and a higher NBO charge at Fe for 2 (in agreement with the Mössbauer data). The effect is due to the different binding modes of the \((\text{trop}_2\text{dae})^2^-\) ligand to Fe, which in turn is induced by the different binding modes of \([\text{Na}(\text{thf})_3]^+\) and \([\text{Li}(\text{OEt})_2)_2]^+\) to the N-donors. \([\text{Na}(\text{thf})_3]^+\) binds in a terminal manner to only one of the two N-donors, leaving the chelating ethylenediamido moiety bound to iron in its preferred \((\delta\text{ or } \lambda)\) twisted manner. In contrast, \([\text{Li}(\text{OEt})_2)_2]^+\) binds in a bridging manner to both N-donors, pushing the ethylenediamido moiety in a non-twisted, more symmetrical binding mode. The
resulting different orientation of the nitrogen lone pairs (up-down for 1, up-up for 2) affects electronic properties of the iron(I) center (directly or indirectly by affecting the \( \pi \)-interaction with the trop moieties). Indeed, DFT calculations revealed smaller electronic differences between the assemblies [NaFe(trop\(_2\)dae)(thf)\(_x\)] and [LiFe(trop\(_2\)dae)(thf)\(_x\)] (\( x = 0, 2 \) or 3), which in all cases were optimized with the alkali metals bound in a terminal manner to only one N-donor of the (trop\(_2\)dae\(^2\))\(^-\) ligand (see Table S2).

**Figure S10.** Left: Experimental X-band EPR spectrum of 1 as a solid material. Experimental conditions: Temperature = 20 K, microwave power 0.632 mW, field modulation amplitude = 2 Gauss, microwave frequency = 9.378312 GHz. Right: Experimental X-band EPR spectrum of 2 as a solid material. Experimental conditions: Temperature = 20 K, microwave power 0.0063 mW, field modulation amplitude = 4 Gauss, microwave frequency = 9.379990 GHz. In both cases the spectrum of the solid is sensitive to rotation of the EPR tube, leading to differences in intensities of specific EPR transitions.

**EPR spectrum of 1 in THF/0.1 M \([N(nBu)\(_4\)][PF\(_6\)].**

**Figure S11.** Experimental and simulated X-band EPR spectra of 1 in frozen THF/0.1 M \([N(nBu)\(_4\)][PF\(_6\)]. Experimental conditions: Temperature = 20 K, microwave power 0.063 mW, field modulation amplitude = 2 Gauss, microwave frequency = 9.365337 GHz. The simulated spectrum was obtained with the parameters shown in Table S2.
EPR spectrum of 2 in THF/0.1 M [N(nBu)₄][PF₆].

Figure S12. Experimental and simulated X-band EPR spectra of 2 in frozen THF/0.1 M [N(nBu)₄][PF₆]. Experimental conditions: Temperature = 20 K, microwave power 0.2 mW, field modulation amplitude = 2 Gauss, microwave frequency = 9.365782 GHz. The simulated spectrum was obtained with the parameters shown in Table S2.

EPR spectra of 1 and 2 in toluene glass.

Figure S13. Left: Experimental X-band EPR spectrum of 1 in a frozen toluene glass. Experimental conditions: Temperature = 20 K, microwave power 0.632 mW, field modulation amplitude = 4 Gauss, microwave frequency = 9.368429 GHz. Right: Experimental X-band EPR spectrum of 2 in a frozen toluene glass. Experimental conditions: Temperature = 20 K, microwave power 0.2 mW, field modulation amplitude = 4 Gauss, microwave frequency = 9.364132 GHz.
Figure S14. ‘Half-field’ signal observed in the EPR spectrum of 2 recorded in a toluene glass. Experimental conditions: Temperature = 20 K, microwave power 2 mW, field modulation amplitude = 4 Gauss, microwave frequency = 9.364135. Complex 1 reveals a similar ‘half-field’ signal in a toluene glass at $T = 20$ K.

Table S2. Experimental g-values and DFT calculated g-values and Fe spin densities\(^{(a),(b)}\)

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<th>$g_y$</th>
<th>$g_z$</th>
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<td>2.160</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Bridged (^{(e)})</td>
<td>2.009</td>
<td>2.060</td>
<td>2.160</td>
<td>-</td>
</tr>
<tr>
<td>DFT (^{(a),(b)})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe(trop$_2$dae)]$^{-}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[NaFe(trop$_2$dae)(thf)$_3$] (^{1})</td>
<td>Terminal (^{(d)})</td>
<td>2.019</td>
<td>2.069</td>
<td>2.116</td>
<td>1.122 (0.585)</td>
</tr>
<tr>
<td>[LiFe(trop$_2$dae)(OEt)$_2$] (^{2})</td>
<td>Bridged (^{(e)})</td>
<td>2.020</td>
<td>2.071</td>
<td>2.126</td>
<td>1.168 (0.590)</td>
</tr>
<tr>
<td>[NaFe(trop$_2$dae)]</td>
<td>Bridged (^{(e)})</td>
<td>2.023</td>
<td>2.085</td>
<td>2.157</td>
<td>1.273 (0.588)</td>
</tr>
<tr>
<td>[NaFe(trop$_2$dae)]</td>
<td>Terminal (^{(d)})</td>
<td>2.022</td>
<td>2.076</td>
<td>2.135</td>
<td>1.166 (0.563)</td>
</tr>
<tr>
<td>[LiFe(trop$_2$dae)]</td>
<td>Bridged (^{(e)})</td>
<td>2.024</td>
<td>2.091</td>
<td>2.153</td>
<td>1.316 (0.6076)</td>
</tr>
<tr>
<td>[LiFe(trop$_2$dae)]</td>
<td>Terminal (^{(d)})</td>
<td>2.024</td>
<td>2.082</td>
<td>2.135</td>
<td>1.199 (0.567)</td>
</tr>
<tr>
<td>[LiFe(trop$_2$dae)(thf)$_3$]</td>
<td>Terminal (^{(d)})</td>
<td>2.021</td>
<td>2.073</td>
<td>2.131</td>
<td>1.173 (0.584)</td>
</tr>
<tr>
<td>[LiFe(trop$_2$dae)(thf)$_3$]</td>
<td>Terminal (^{(d)})</td>
<td>2.020</td>
<td>2.071</td>
<td>2.126</td>
<td>1.185 (0.613)</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Geometries optimized with Turbomole (BP86, def2-TZVP).
\(^{(b)}\) EPR parameters calculated with Orca (b3-lyp, def2-TZVP) using the Turbomole optimized geometries.
\(^{(c)}\) Alkali metal bridged over both N-donors, like in the X-ray structure of 2
\(^{(d)}\) Alkali metal interacting only with one N-donor, like in the X-ray structure of 1
Figure S15. Top: Spin density plot of [Fe(trop$_2$_dae)]$^-$ (cf, Figure 2a in main part); Bottom left: spin density plot of [NaFe(trop$_2$_dae)(thf)$_3$] (1) with ‘terminal’ Na$^+$ ion. Bottom right: spin density plot of [LiFe(trop$_2$_dae)(OEt)$_2$] (2) with ‘bridging’ Li$^+$ ion (positive spin densities in blue, negative spin densities in red).

Cyclic voltammetry.

Figure S16. Cyclic voltammogram of [NaFe(trop$_2$_dae)(thf)$_3$] in 0.1 M solution of [$n$Bu$_4$N][PF$_6$] in THF vs. Fc/Fc$^+$ at a scan rate of 200 mV/s; working electrode: glassy carbon; counter electrode: Pt; reference electrode: Ag; $E_{1/2} = -2.24$ V.
Dehydrogenation of $N,N$-dimethylamine-borane (DMAB).

Figure S17 Dehydrogenation of DMAB in open system at 23°C in toluene catalyzed by 5 mol% of 1, 2 or 3, respectively.

The rate of reaction for the dehydrogenation of DMAB with 5 mol% 1 as a catalyst in toluene solution in an open system under Argon is increased by a factor of 2.1(2), when the overall concentrations are increased from $c_0$(DMAB) = 0.048 mol/L to $c_0$(DMAB) = 0.096 mol/L (Figures S18, S19). Further lowering or increasing the initial concentration of DMAB (by a factor of 2.0 in each case) did not have a strong influence on the rate of reaction. The plots of concentrations of DMAB versus time were divided into three phases (Figure S19, left). At early stages of the reactions, they show a high initial rate. Then they show a linear correlation (Figure S19, right). After that they could be described by exponential decay. The rate constants were deduced from the linear correlation (vide supra). It has to be pointed out that these rate constant only relate to reaction times of $240 \text{s} \leq t \leq 900 \text{s}$.

Figure S18. Dehydrogenation of DMAB in open system at 23°C in toluene catalyzed by 5 mol% 1 with $c_0$(DMAB) = 0.048 mol/L (triangles) or $c_0$(DMAB) = 0.096 mol/L (circles).
Figure S19. Plot of concentration vs. time for dehydrogenation of DMAB in open system at 23°C with 5 mol% of 1 at $c_0$(DMAB) = 0.096 mol/L and $c_0$(DMAB) = 0.048 mol/L, respectively; left: all data; right: phase of reaction with linear correlation.

Dehydrogenation of [D$_1$]-DMAB.

Figure S20. Dehydrogenation of [Me$_2$DN–BH$_3$] ([D$_1$]-DMAB) in open system at 23°C in toluene catalyzed by 5 mol% 1.

The plots of concentrations of DMAB or [D$_1$]-DMAB versus time were divided into three phases (Figure S21, left). At early stages of the reactions, they show a high initial rate. Then they show a linear correlation (Figure S21, right). After that they could be described by exponential decay. The kinetic isotope effect was deduced from rate constants obtained from the linear correlation. It has to be pointed out that the rate constant only relate to reaction times of $240 \text{s} \leq t \leq 900 \text{s}$. 
Figure S21. Plot of concentration vs. time for dehydrogenation of DMAB and [D₁]-DMAB, respectively, in open system at 23°C with 5 mol% of 1 at c₀(DMAB) = 0.096 mol/L; left: all data; right: phase of reaction with linear correlation.

Dehydrogenation of DMAB in the presence of additives.

Figure S22. Dehydrogenation of DMAB in open system at 23°C in toluene catalyzed by 5 mol% 1 without additives and in the presence of equimolar amounts (with respect to Fe) of [N(nBu)₄]Br or 15-c-5.
Figure S23. Dehydrogenation of DMAB in open system at 23°C in toluene catalyzed by 5 mol% 1. After liberation of the first equiv. of H₂, a second equivalent of DMAB was added. After liberation of the second equiv. of H₂, a third equivalent of DMAB was added.

Figure S24. Dehydrogenation of DMAB in open system at 23°C in toluene catalyzed by 5 mol% 1 without catalyst poison and with PPh₃ or [P(OMe)₃] as catalyst poisons (0.2 or 0.1 equiv., respectively, with respect to Fe).

In order to prove the efficiency of P(OMe)₃ as a catalyst poison, 2 equivalents were added to a running reaction (dehydrogenation of DMAB with 5 mol% of 1) at early stages of the reaction. Indeed, the reaction essentially came to a halt after the poison had been added (Figure S25).
Dehydrogenative alcoholyis of silanes with MeOH or 1,4-benzene-dimethanol.

Compound 1 catalyzes the stoichiometric methanolysis of PhSiH₃ at room temperature in toluene in the absence of a co-catalyst (Table S3). With a catalyst loading of 3 mol% (corresponding to 1 mol% per Si–H bond), the reaction went to completion within 5 min (entry 1). Furthermore, the catalyst remained active after completion of the reaction as demonstrated by consecutive addition of fresh silane and methanol. At least 3 × 30 equiv. of PhSiH₃ were converted without apparent loss of activity (entry 2). Lowering the catalyst loading to 0.3 mol% revealed that the first two equivalents of H₂ are much faster liberated than the third equivalent (10.5 min vs. 280 min under these conditions). This can be rationalized by a lower reactivity of in situ generated tertiary methoxysilane PhSi(OMe)₂H. When PhSiH₃ was added to a toluene solution of 1, no reaction could be detected by ¹H NMR spectroscopy. After addition of MeOH to this mixture, however, new paramagnetically shifted resonances appear. This indicates that 1 acts as a pre-catalyst rather than being directly the active species. Indeed, an induction period for the evolution of H₂ was observed when the catalyst loading was lowered to 0.03 mol%. The addition of 0.1 equivalents of P(OMe)₃ as a catalyst poison did not cause any inhibition (entry 3) and no Fe particles were detected in the reaction mixture by scanning electron microscopy (SEM) after completion of the reaction. Experiments using MeOD instead of MeOH as a substrate resulted in partial deuteration of the ethylene unit and the benzylic positions of the (trop₂dae)²⁻ ligand as indicated by NMR spectroscopic analysis of the material obtained after aqueous workup. This suggests chemical non-innocence of the ligand as previously observed for a related Ru-system in the production of H₂ from methanol/water mixtures.
Table S3. Dehydrogenative coupling of alcohols with silanes initiated by 1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Silane</th>
<th>Alcohol</th>
<th>Poison (equiv.)</th>
<th>t / min</th>
<th>Conv. / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1[a]</td>
<td>PhSiH₃</td>
<td>MeOH</td>
<td>-</td>
<td>5</td>
<td>&gt; 99</td>
</tr>
<tr>
<td>2[b,c]</td>
<td>PhSiH₃</td>
<td>MeOH</td>
<td>-</td>
<td>3 × 5</td>
<td>3 × &gt; 99</td>
</tr>
<tr>
<td>3[a]</td>
<td>PhSiH₃</td>
<td>MeOH</td>
<td>P(OMe)$_3$ (0.1)</td>
<td>5</td>
<td>&gt; 99</td>
</tr>
</tbody>
</table>

[a]: open system, conversion determined volumetrically (liberation of H$_2$); [b]: closed system, C$_6$D$_6$ as a solvent; $^{[21]}$ conversion determined by NMR spectroscopy, [c]: 3 x 30 equiv. PhSiH$_3$ and 3 x 90 equiv. MeOH (consecutive additions).

Figure S26. Dehydrogenative methanolysis of PhSiH$_3$ in open system at 23°C in toluene with 3 mol% 1 (poison = 0.1 P(OMe)$_3$ per Fe).

Figure S27. Dehydrogenative methanolysis of PhSiH$_3$ in open system at 23°C in toluene with 0.3 mol% 1.
Figure S28. Dehydrogenative methanolysis of PhSiH$_3$ in open system at 23°C in toluene with 0.03 mol% 1.

Figure S29. Dehydrogenative alcoholysis of PhSiH$_3$ with 1,4-benzene-dimethanol in open system at 23°C in toluene with 3 mol% 1.

Figure S30. Dehydrogenative alcoholysis of Ph$_2$SiH$_2$ with 1,4-benzene-dimethanol in open system at 23°C in toluene/THF (6:1) with 2 mol% 1.
References.

1. R. Ahlrichs, Turbomole Version 6.5, Theoretical Chemistry Group, University of Karlsruhe.
10. For compound 2b, yields similar to those of 2 were observed.
12. New paramagnetically shifted resonances of low intensity (compared to those due to PhSi(OMe)₃) were detected: ¹H NMR (300 MHz, C₆D₆): δ = 9.19 (s), 16.64 (br s), 43.26 (br s), 44.58 (br s), 48.07 (br s) ppm.
13. Multiple resonances were observed for each carbon atom of one repeating unit; the corresponding ranges of chemical shifts are reported.
15. Deviations of calculated from experimentally determined quadrupol splittings up to 0.34 mm/s and 0.70 mm/s have been reported for mono- and dinuclear Fe compounds, respectively: T. Liu, T. Lovell, W.-G. Han, L. Noodleman, Inorg. Chem. 2003, 42, 5244-5251.
17. This analysis was suggested in earlier work. In the previously published data, the reactions showed an induction period and therefore the reaction rates were smaller in the early phase of the reaction (opposite to our case): T. J. Williams, B. L. Conley, US patent 0201744 A1, 2012.
18. Using THF as a solvent gave the same result within limits of error.
19. No H₂ is generated from C₆D₆ solutions containing 1 and PhSiH₃ at temperatures up to 80°C.
21. PhSi(OMe)₃ and H₂ were detected by ¹H NMR spectroscopy as the only products.