Electronic Supplementary Material (ESI) for Dalton Transactions.

C-Halide Bond Activation by a Two-Coordinate Iron(I) Complex

C. G. Werncke,[a,*] J. Pfeiffer,[a] I. Müller,[a] L. Vendier,[b] S. Sabo-Etienne,[b] Sébastien Bontemps[b]

a) Philipps-University Marburg, Hans-Meerwein-Straße 4, D-35032 Marburg, Germany

b) CNRS, LCC (Laboratoire de Chimie de Coordination) 205 route de Narbonne, 31077 Toulouse and Université de Toulouse, UPS, INPT 31077 Toulouse, France

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Spectra of complexes 1-6

1. K{18-crown-6}[Fe(Br)(N(SiMe$_3$)$_2$)$_2$] (1a)

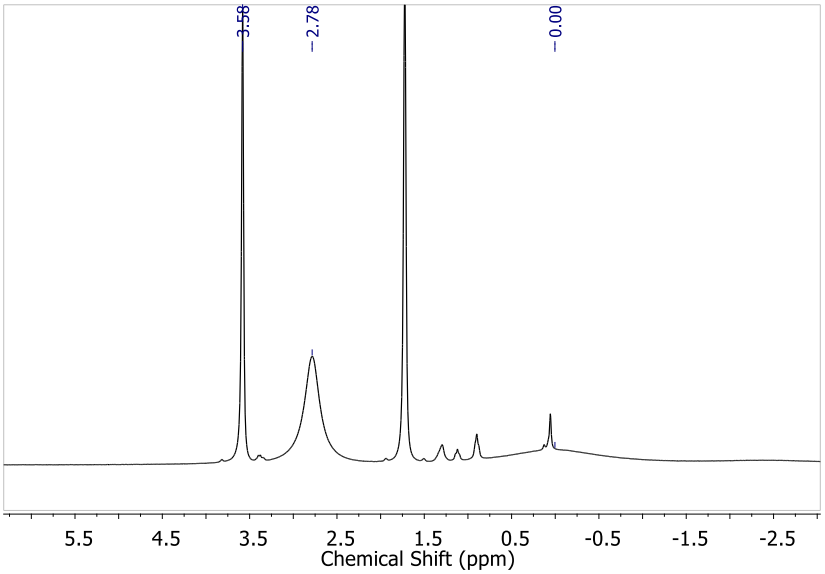

Figure S1. ^{1}H NMR spectrum of **K{18-crown-6}[Fe(Br)(N(SiMe$_3$)$_2$)$_2$** (**1a**) in THF-d$_8$ (500.1 MHz).

2. K{18-crown-6}[Fe(Cl)(N(SiMe$_3$)$_2$)$_2$] (1b)

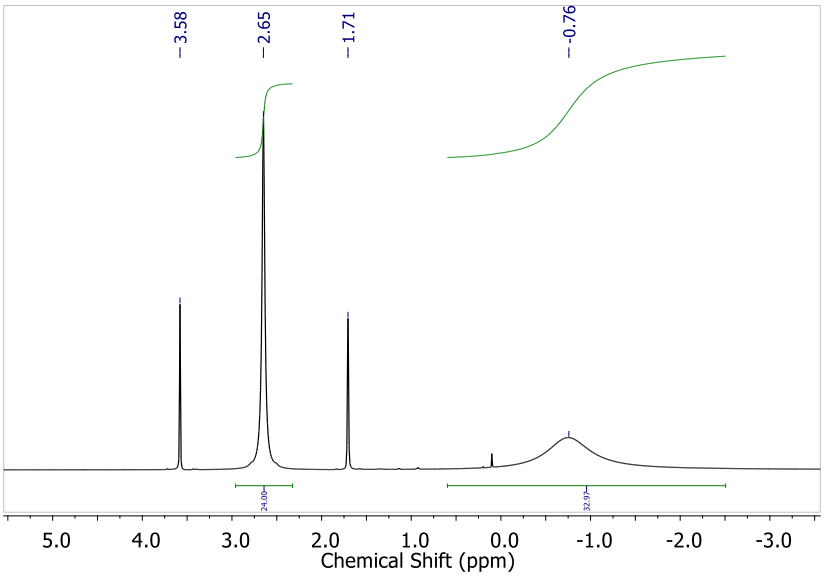

Figure S2. ^{1}H NMR spectrum of **K{18-crown-6}[Fe(Cl)(N(SiMe$_3$)$_2$)$_2$** (**1b**) in THF-d$_8$ (500.1 MHz).

3. K{18-crown-6}[Fe(Bz)(N(SiMe$_3$)$_2$)$_2$] (2)

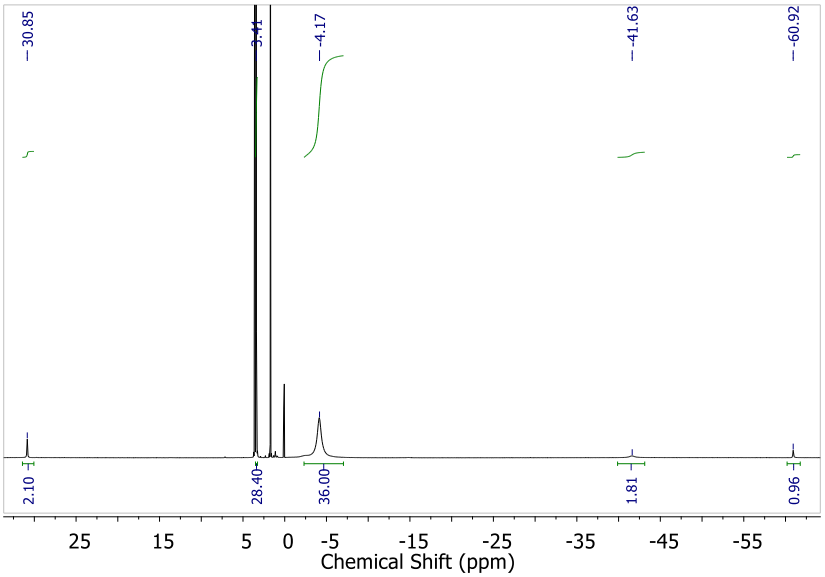

Figure S3. ^{1}H NMR spectrum of **K{18-crown-6}[Fe(Bz)(N(SiMe$_3$)$_2$)$_2$** (**2**) in THF-d$_8$ (500.1 MHz).

4. K{18-crown-6}[Fe(Br)$_2$(N(SiMe$_3$)$_2$)$_2$ (3a)

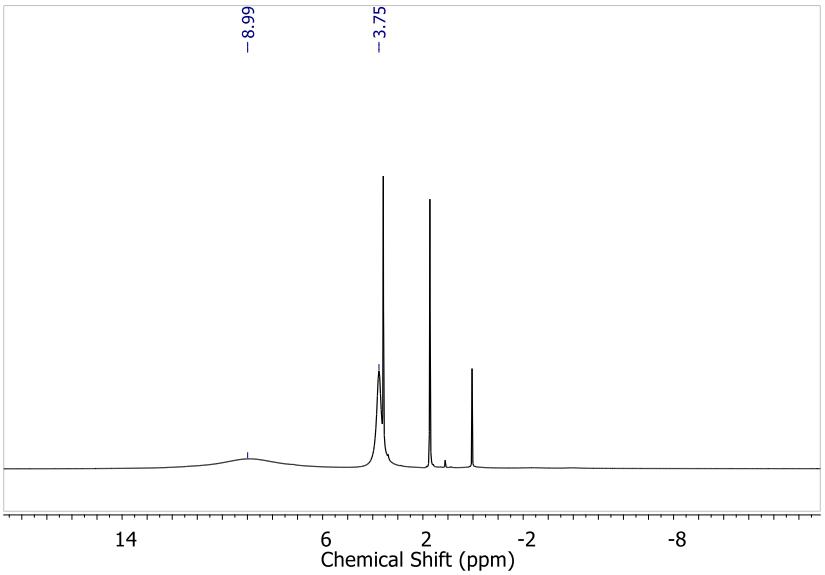

Figure S4. ^{1}H NMR spectrum of **K{18-crown-6}[Fe(Br)$_2$(N(SiMe$_3$)$_2$)$_2$** (**3a**) in THF-d$_8$ (500.1 MHz).

5. K{18-crown-6}[Fe(Cl)$_2$(N(SiMe$_3$)$_2$)$_2$] (3b)

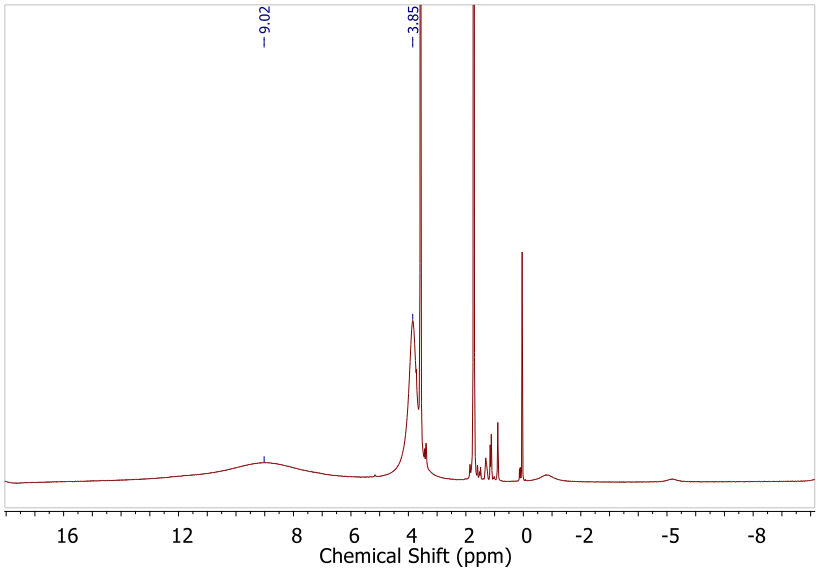

Figure 5. ^{1}H NMR spectrum of **K{18-crown-6}[Fe(Cl)$_2$(N(SiMe$_3$)$_2$)$_2$** (**6**)in [D8]THF (500.1 MHz).

6. KFe(Bz)(N(SiMe$_3$)$_2$)$_2$ (4)

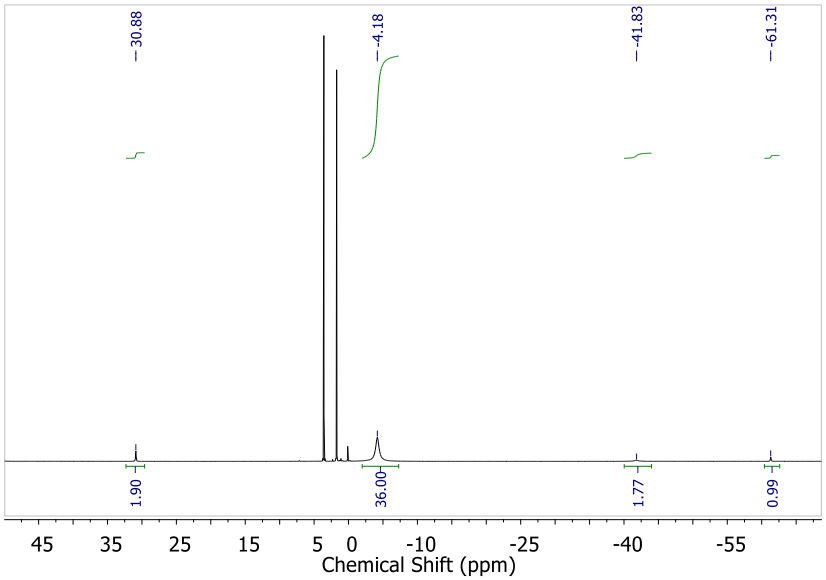

Figure S6. ^{1}H NMR spectrum of **K[Fe(Bz)(N(SiMe$_3$)$_2$)$_2$** (**4**) in THF-d$_8$ (500.1 MHz).

7. K{18-crown-6}[Fe(^{n}Bu)(N(SiMe$_3$)$_2$)$_2$] (5a)

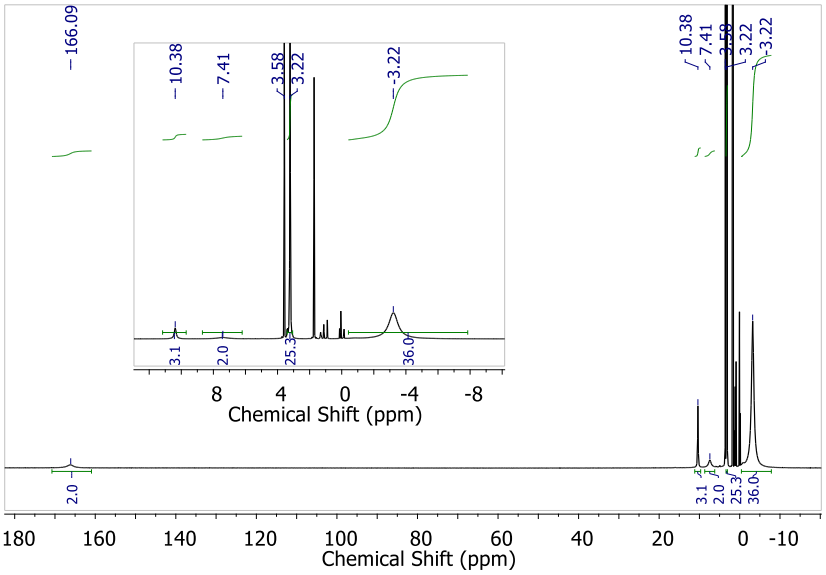

Figure S7. ^{1}H NMR spectrum of **K{18-crown-6}[Fe(*n*Bu)(N(SiMe$_3$)$_2$)$_2$** (**5a**) in THF-d$_8$ (500.1 MHz).

8. K{18-crown-6}[Fe(Ph)(N(SiMe$_3$)$_2$)$_2$] (6)

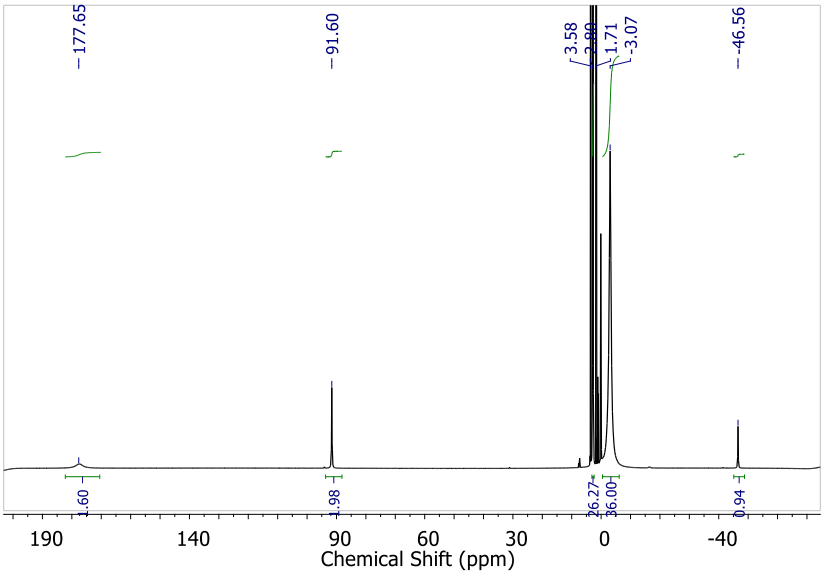

Figure S8. ^{1}H NMR spectrum of **K{18-crown-6}[Fe(Ph)(N(SiMe$_3$)$_2$)$_2$** (**6**) in THF-d$_8$ (500.1 MHz).

Spectra of NMR-scale reactions

Reaction of A with benzyl bromide

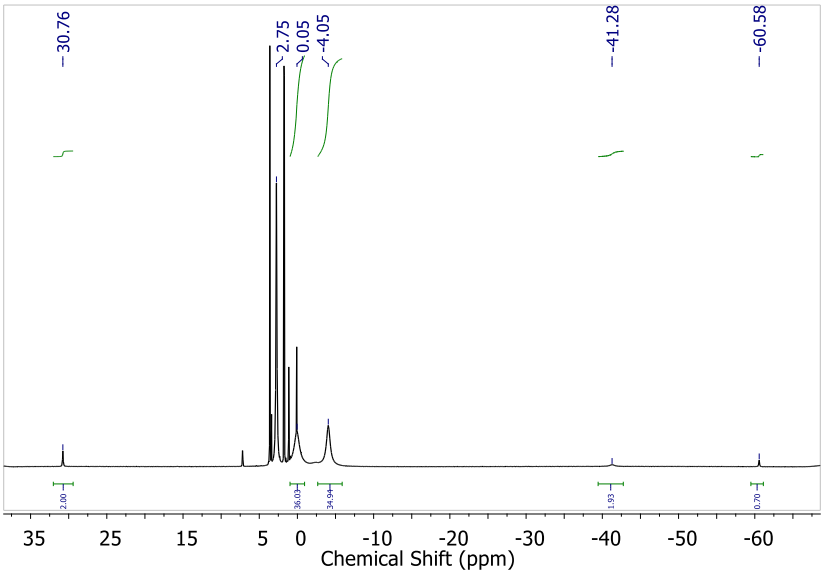

Figure S9. ^{1}H NMR spectrum of a reaction of **A** with approx. 0.5 equiv. benzyl bromide in THF-d$_8$ (500.1 MHz). **[Fe(Br)(N(SiMe$_3$)$_2$)$_2$]$^-$**: δ = 0.08 ppm. Fe(Bz)(N(SiMe$_3$)$_2$)$_2$]$^-$: δ(ppm) = 30.76 (C$_{Ar}$-H), -4.05 (SiMe$_3$), -41.28 (C$_{Ar}$-H), -60.58 (C$_{Ar}$-H).

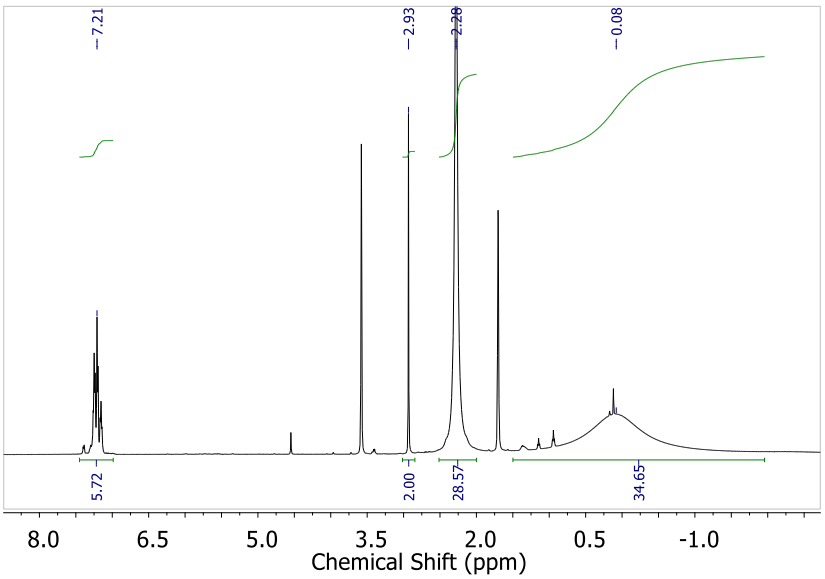

Figure S10. ^{1}H NMR spectrum of a reaction of **A** with 1 equiv. benzyl bromide in THF-d_8 (500.1 MHz). **[Fe(Br)(N(SiMe$_3$)$_2$)$_2$]$^-$** : δ = 0.08 ppm. Signals at 7.21 and 2.93 ppm belongs to the homo-coupling product Ph-CH_2-CH_2-Ph.

Reaction of A with Benzyl chloride

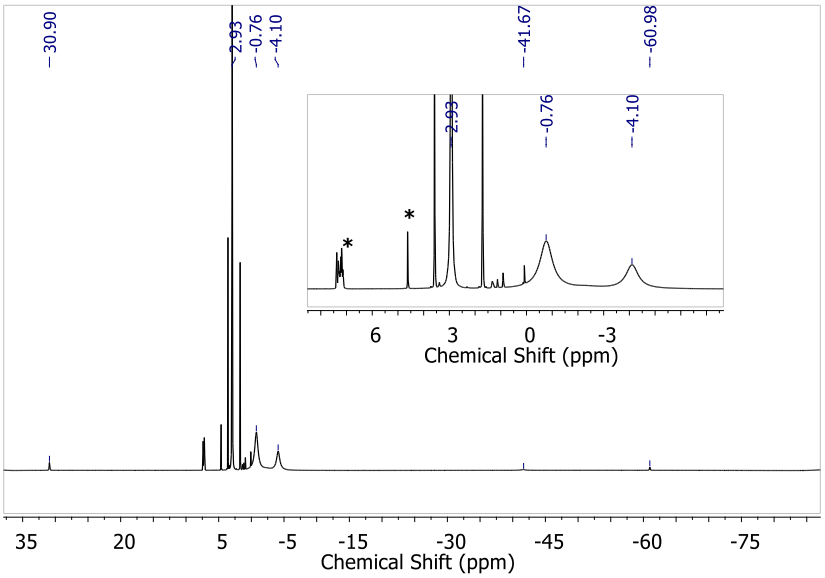

Figure S11. ^{1}H NMR spectrum of a reaction of **A** with 1 equiv. benzyl chloride in THF-d_8 (500.1 MHz) after 15 min. **[Fe(Cl)(N(SiMe$_3$)$_2$)$_2$]$^-$**: δ = -0.76 ppm. **[Fe(Bz)(N(SiMe$_3$)$_2$)$_2$]$^-$**: δ(ppm) = 30.90 (C_{Ar}-H), -4.10 ($SiMe_3$), -41.67 (C_{Ar}-H), -60.98 (C_{Ar}-H). (*) denotes unreacted benzylchloride.

Reaction of A with Benzyl fluoride

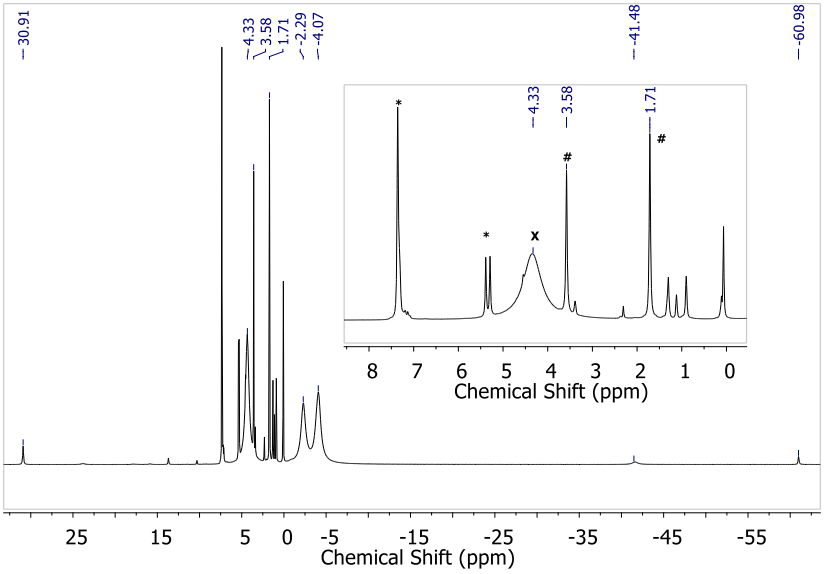

Figure S12. ^{1}H NMR spectrum of a reaction of **A** with 1 equiv. benzyl fluoride in THF-d_8 after 1 h (500.1 MHz). **[Fe(F)(N(SiMe$_3$)$_2$)$_2$]$^-$** : δ (ppm) = -2.29 ($w_{1/2}$ = 715 Hz, SiMe$_3$). **[Fe(Bz)(N(SiMe$_3$)$_2$)$_2$]$^-$** : δ (ppm) = 30.91 (C_{Ar}-H), -4.07 (SiMe$_3$), -41.48 (C_{Ar}-H), -60.98 (C_{Ar}-H). (*) unreacted benzyl fluoride; (#)THF-d_8; (x) K^+{18-crown-6}.

Reaction of A with 1-Bromobutane

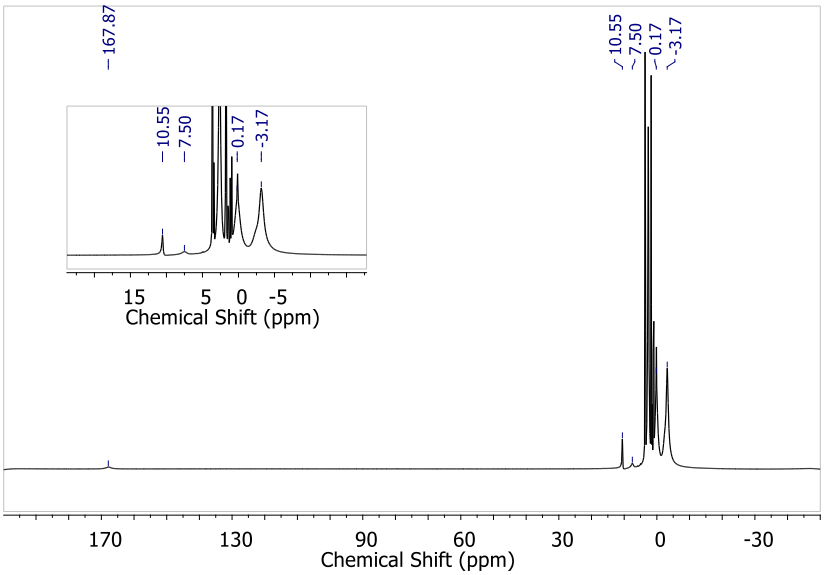

Figure S13. ^{1}H NMR spectrum of a reaction of **A** with 0.6 equiv. 1-bromobutane in THF-d_8 (500.1 MHz). **[Fe(Br)(N(SiMe$_3$)$_2$)$_2$]$^-$** : δ (ppm) = -0.17 (36H, SiMe$_3$). **[Fe(*n*Bu)(N(SiMe$_3$)$_2$)$_2$]$^-$** : δ (ppm) = 167.9, 10.55, 7.50, -3.17 (36H, SiMe$_3$).

Reaction of A with 1-Chlorobutane

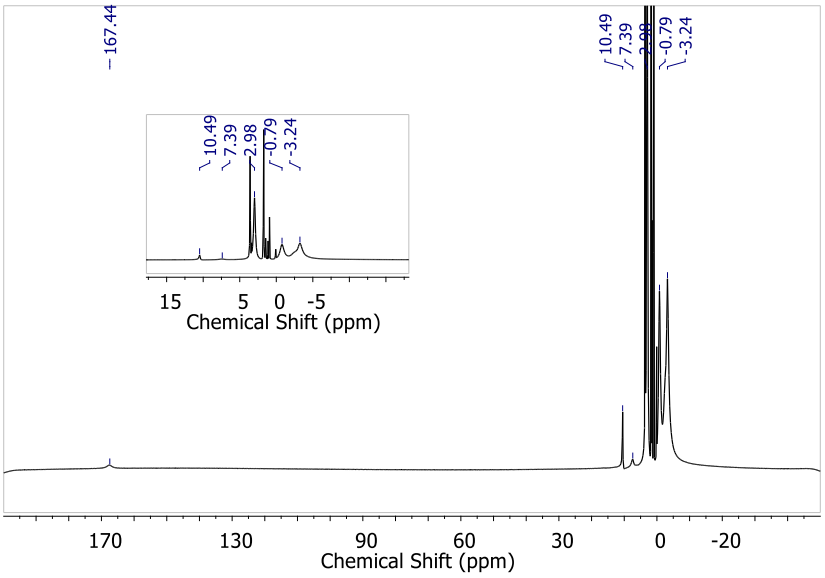

Figure S14. ^{1}H NMR spectrum of a reaction of **A** with 1 equiv. 1-chlorobutane in THF-d_8 (500.1 MHz). **[Fe(Cl)(N(SiMe$_3$)$_2$)$_2$]$^-$** : δ (ppm) = -0.79 (SiMe$_3$). **[Fe(*n*Bu)(N(SiMe$_3$)$_2$)$_2$]$^-$** : δ (ppm) = -167.4, 10.49, 7.39, -3.24 (SiMe$_3$).

Reaction of A with pentyl fluoride

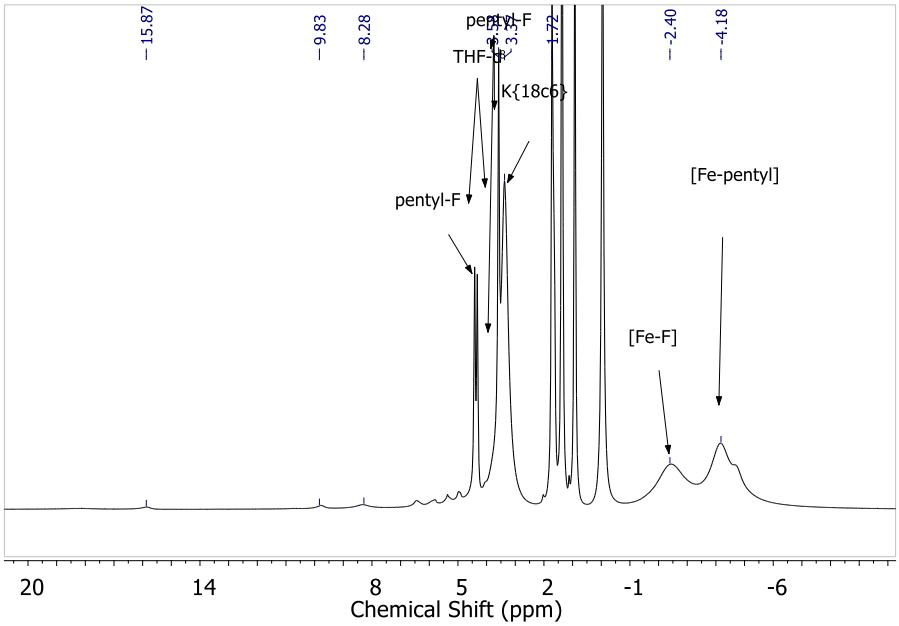

Figure S15. ^{1}H NMR spectrum of a reaction of **A** with 1 equiv. pentyl fluoride in THF-d_8 after 48 h of heating at 60°C and after filtration to remove the black paramagnetic decomposition products (500.1 MHz). **[Fe(pentyl)(N(SiMe$_3$)$_2$)$_2$]$^-$**: δ (ppm) = 15.87, 9.8, 8.28, -4.18 ($w_{1/2}$ = 450 Hz, SiMe$_3$, SiMe$_3$), **[Fe(F)(N(SiMe$_3$)$_2$)$_2$]$^-$** : δ (ppm) = -2.40 (SiMe$_3$). The small shoulder at around -4.7 ppm belongs to an unknown product (<5%).

Reaction of A with bromobenzene

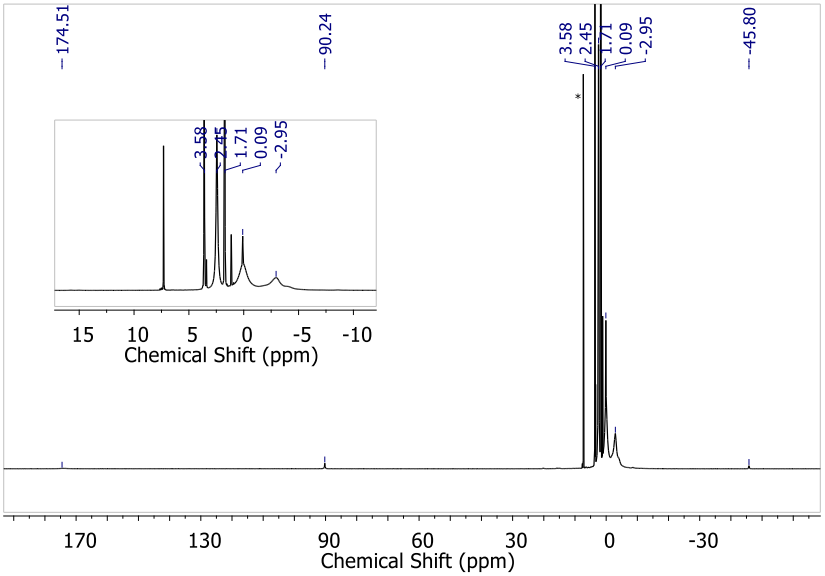

Figure S16. ^{1}H NMR spectrum of a reaction of **A** with approx. 0.6 equiv. bromobenzene (500.1 MHz, THF-d_8). **[Fe(Ph)(N(SiMe$_3$)$_2$)$_2$]$^-$**: δ(ppm) = 174.5 (C^{Ar}-H) 90.2 (2H, C^{Ar}-H), -2.95 (36H, $SiMe_3$), -45.8 (2H, C^{Ar}-H). **[Fe(Br)(N(SiMe$_3$)$_2$)$_2$]$^-$**: δ(ppm) = -0.09 (36H, $SiMe_3$). (*) denotes unreacted bromobenzene.

Reaction of A with chlorobenzene

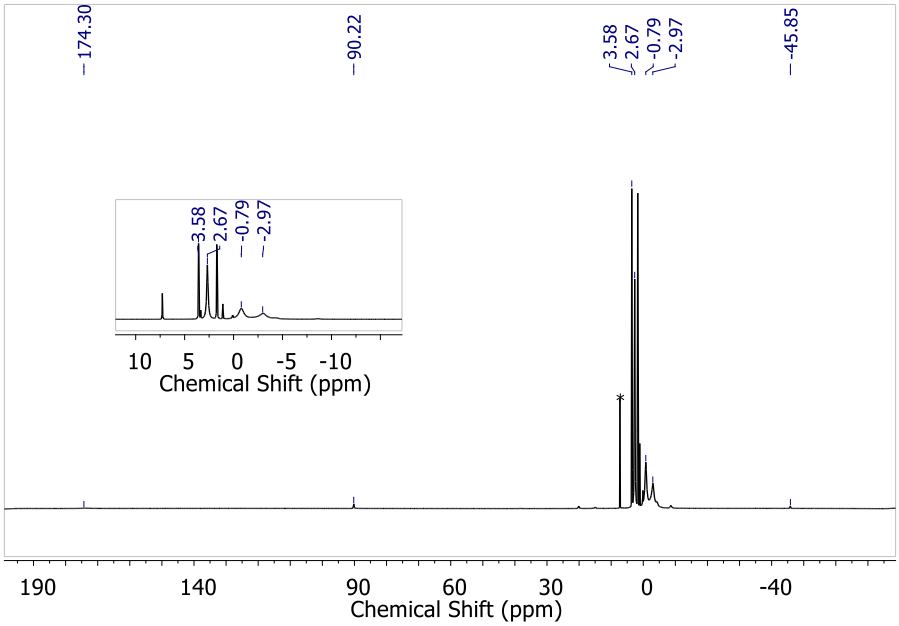

Figure S17. ^{1}H NMR spectrum of a reaction of **A** with approx. 0.6 equiv. chlorobenzene (500.1 MHz, THF-d_8). **[Fe(Ph)(N(SiMe$_3$)$_2$)$_2$]$^-$**: δ(ppm) = 174.5 (C_{Ar}-H) 90.2 (2H, C_{Ar}-H), -2.95 (36H, $SiMe_3$), -45.8 (2H, C_{Ar}-H). **[Fe(Cl)(N(SiMe$_3$)$_2$)$_2$]$^-$**: δ(ppm) = -0.79 ($SiMe_3$). (*) denotes unreacted chlorobenzene.

Reaction of A with fluorobenzene

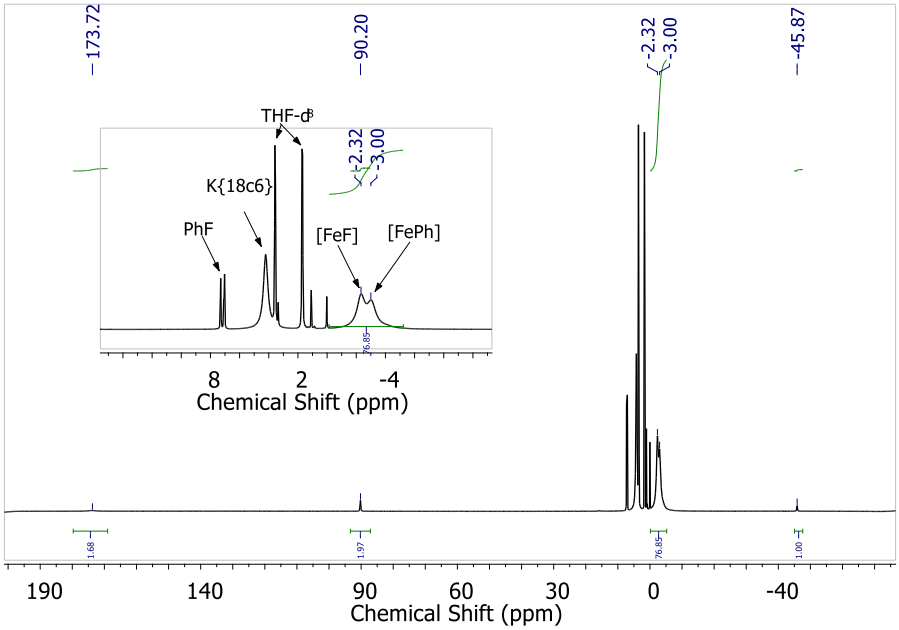

Figure S18. ^{1}H NMR spectrum of a reaction of **A** with 0.5 equiv. fluorobenzene (500.1 MHz, THF-d_8). **[Fe(Ph)(N(SiMe$_3$)$_2$)$_2$]$^-$** : δ (ppm) = 173.7 (C^{Ar}-H), 91.5 (C^{Ar}-H), -3.00 (SiMe$_3$), 46.5 (C^{Ar}-H). **[Fe(F)(N(SiMe$_3$)$_2$)$_2$]$^-$**: δ(ppm) = -2.29 (SiMe$_3$).

Reaction of A with Radical Clocks

Reaction of A with cyclopropyl methyl bromide

34 mg (0.05 mmol, 1.0 equiv.) **A** were reacted with 3.4 mg (0.025 mmol, 0.5 equiv.) cyclopropyl methyl bromide in THF-d_8.

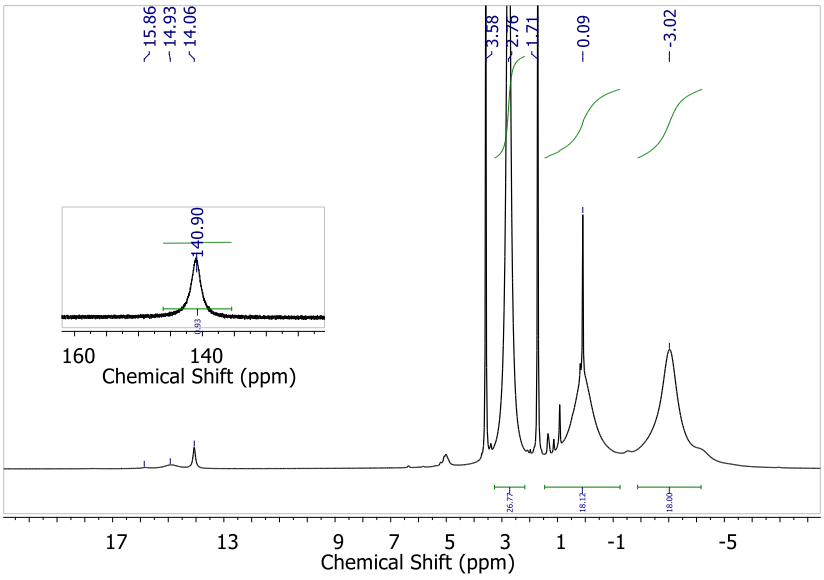

Figure S19. ^{1}H-NMR spectrum of the reaction of **A** with 1 equiv. cyclopropyl methylbromide (500.1 MHz, THF-d_8). **Fe(Br)(N(SiMe$_3$)$_2$)$_2$]$^-$** : δ = -0.09 ppm. **Fe(R)(N(SiMe$_3$)$_2$)$_2$]$^-$** : δ = 140.9, 15.9, 14.9, 14.1, -3.02 ppm.

NMR-spectroscopic examination after quenching with D_2O and subsequent distillation showed quantitative formation of 1-Deutero-3-butene. ^{1}H-NMR (500.1 MHz, THF-d_8, 300 K, ppm): δ = 5.83 (1H, ddt, $^3J_{HH}$ = 17.0 Hz, $^3J_{HH}$ = 17.5 Hz, $^3J_{HH}$ = 6.5 Hz, H_2C=C*H*-CH_2), 4.98-4.93 (1H, ddt, $^3J_{HH}$ = 17.0 Hz, $^2J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 1.5 Hz, *H*$_2$C=CH), 4.88-4.85 (1H, ddt, $^3J_{HH}$ = 10.5 Hz, $^2J_{HH}$ = 2.0 Hz, $^3J_{HH}$ = 1.5 Hz, *H*$_2$C=CH), 2.05-2.00 (2H, m, C*H*$_2$-CH_2D),0.95 (2H, dt*, $^3J_{HH}$ = 7.5 Hz, $^2J_{HD}$ = 2.0 Hz, CH_2D). ^{13}C{^{1}H}-NMR (125.8 MHz, THF-d_8, 300 K, ppm): δ = 141.3 (H_2C=*C*H), 113.37 (H_2*C*=CH), 27.5 (CH_2), 13.3 (t, $^1J_{CD}$ = 18.9 Hz, *C*H_2D).

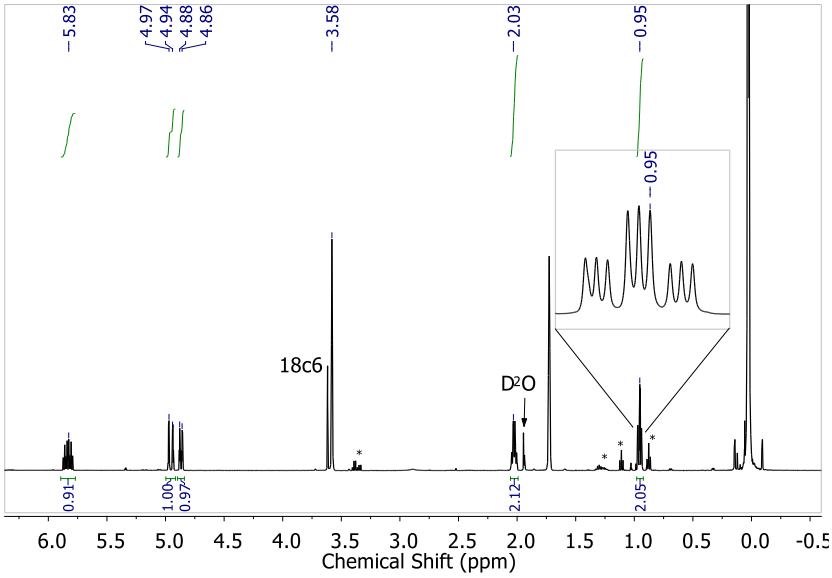

Figure S20. ^{1}H-NMR spectrum of the reaction of **A** with cyclopropyl methylbromide after quenching with D_2O and subsequent distillation (500 MHz, THF-d_8). (*) denotes residual pentane and Et_2O.

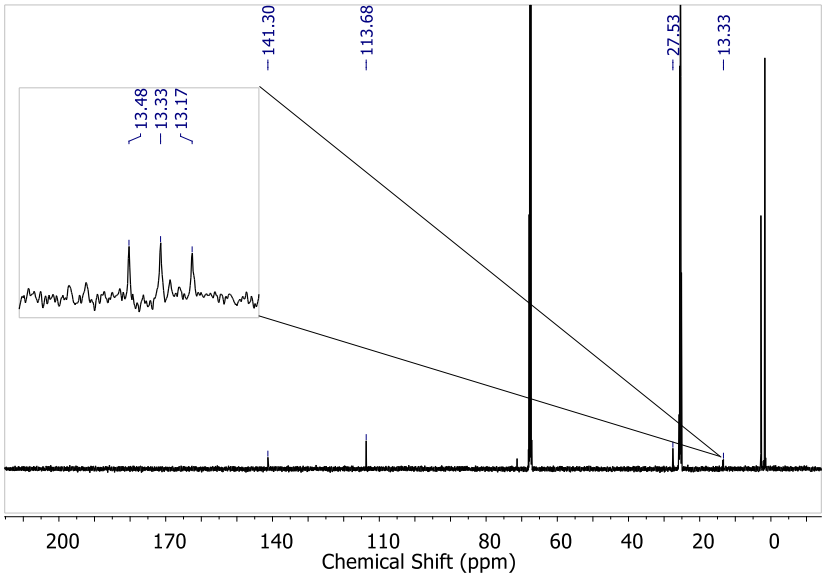

Figure S21. ^{13}C{^{1}H} NMR spectrum of the reaction of **A** with cyclopropyl methylbromide after quenching with D_2O and subsequent distillation (500 MHz, THF-d_8). The small frame depicts the triplet signal of the terminal CH_2D-group.

Reaction of A with 6-bromo-1-hexene

34 mg (0.05 mmol, 1.0 equiv.) **A** was reacted with 3.3 μl (0.025 mmol, 0.5 equiv.) 6-bromo-1-hexene in THF-d_8.

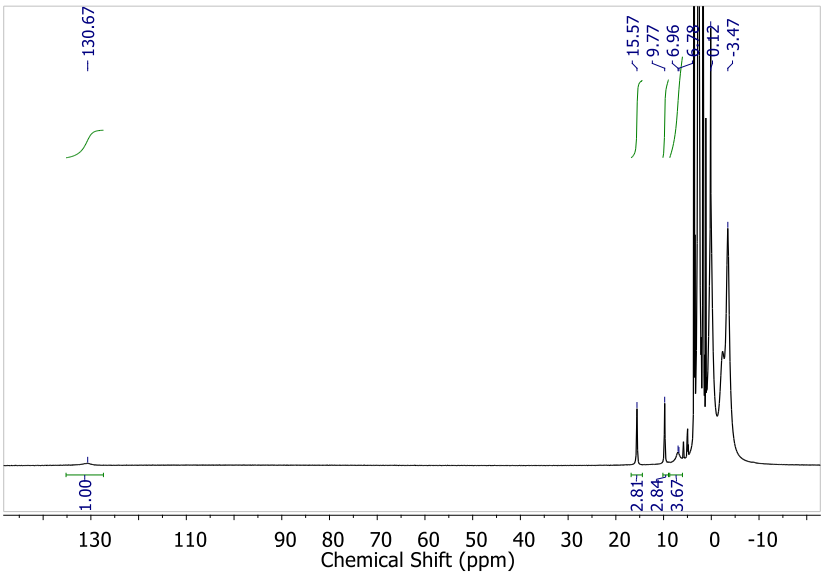

Figure S22. ^{1}H-NMR spectrum of the reaction of **A** with 1 equiv. 6-Bromo-1-hexene (500 MHz, THF-d_8). **Fe(Br)(N(SiMe$_3$)$_2$)$_2$]$^-$**: δ= -0.12 ppm. **Fe(R)(N(SiMe$_3$)$_2$)$_2$]$^-$**: δ[ppm] = 130 ($w_{1/2}$ = 1050 Hz, C*H*), 15.57 ($w_{1/2}$ = 80 Hz), 9.77 ($w_{1/2}$ = 78 Hz), 6.96 ($w_{1/2}$ = 715 Hz), -3.02 ($w_{1/2}$ = 400 Hz, SiMe$_3$).

NMR-spectroscopic examination after quenching with D_2O and subsequent distillation showed formation of cyclopentyl deutero methane (90%) as the main product with small amounts of 6-Deutero-1-hexene (10%).

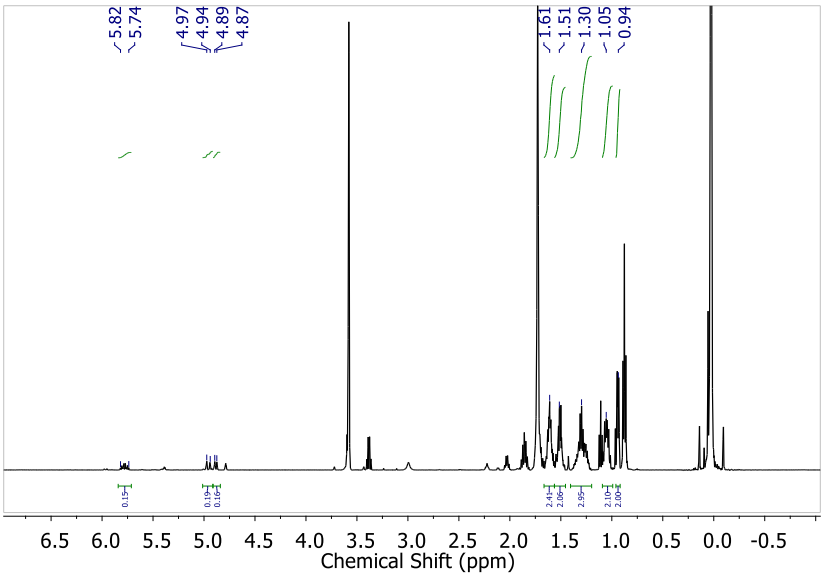

Figure S23. ^{1}H-NMR spectrum of the reaction of **A** with 6-bromo-1-hexene after quenching with D_2O and subsequent distillation (500 MHz, THF-d_8).

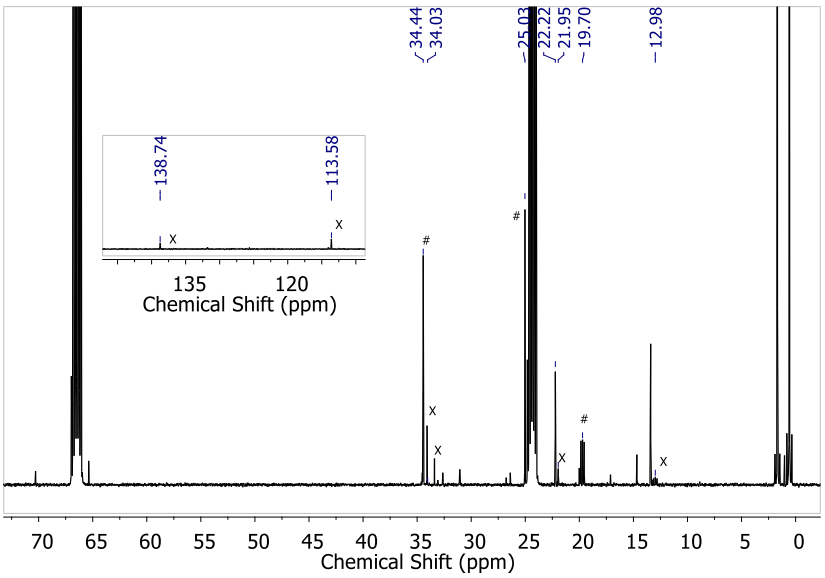

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of the reaction of **A** with 6-bromo-1-hexene after quenching with D_2O and subsequent distillation (500 MHz, THF-d_8). (#) denotes cyclopentyl deuteromethane. (x) denotes 6-deutero-1-hexene.

Reaction of 3a with one equivalent Ph-Li

3a and Ph-Li were each dissolved in 0.5 ml THF-d_8 and precooled to -80°C. Both solutions were combined leading to a bright red solution and immediately measured afterwards

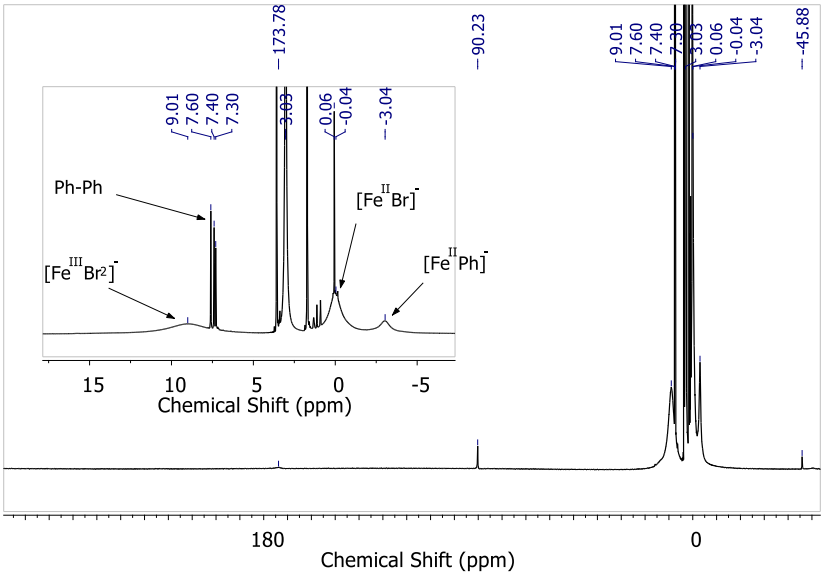

Figure S25. ^{1}H NMR spectrum of a reaction of **3a** with 1 equiv. Ph-Li after 5 minutes (500.1 MHz, THF-d_8). Fe(**Ph**)$(N(SiMe_3)_2)_2^-$: δ (ppm) = 173.8 (C_{Ar}-H), 90.23 (C_{Ar}-H), -3.0 ($SiMe_3$), -45.9 (C_{Ar}-H). Fe(**Br**)$(N(SiMe_3)_2)_2^-$: δ(ppm) = 0.04 ($SiMe_3$). Fe(**Br**)$_2(N(SiMe_3)_2)_2^-$: δ(ppm) = 9 ($SiMe_3$).

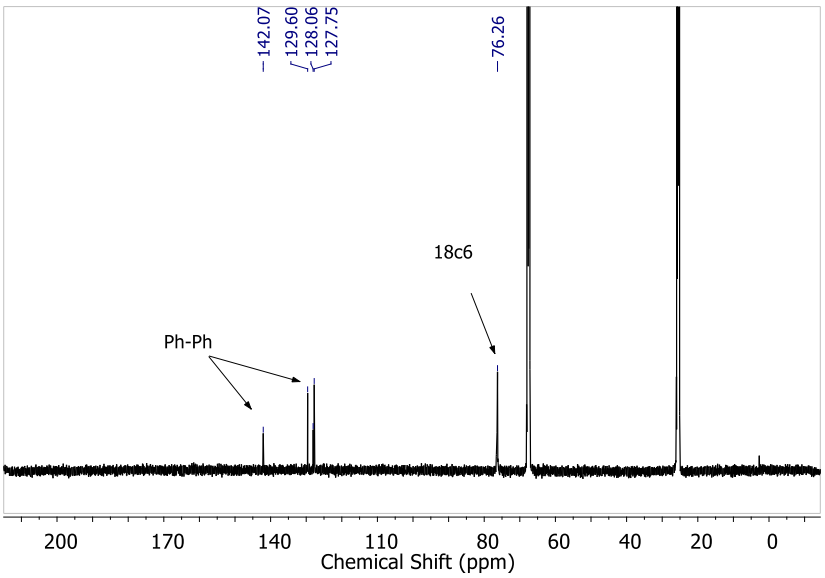

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of a reaction of **3a** with 1 equiv. Ph-Li after 5 minutes (500.1 MHz, THF-d_8). Ph-Ph: δ(ppm) = 142.1 (C_q), 129.6 ($C_{ortho/meta}$-H), 128.1 (C_{para}-H), 127.8 ($C_{ortho/meta}$-H).

X-Ray diffraction analysis and molecular structures

Data for **1a** (CCDC 1858772), **1b** (CCDC 1858774), **1c** (CCDC 1858775), **2** (CCDC 1858795), **3a** (CCDC 1858797), **3b** (CCDC 1858796), **5** (CCDC 1858800), **6** (CCDC 1858798) were collected at 100 K on a Bruker Quest D8 diffractometer using a graphite-monochromated Mo-Kα radiation and equipped with an *Oxford Instrument Cooler Device*. Data for **4** (CCDC 1858801) was collected at 100 K a STOE IPDS2T diffractometer using a graphite-monochromated Mo-Kα radiation (λ = 0.71073Å) and equipped with an *Oxford Cryosystems Cryostream Cooler Device*. The structures have been solved using either OLEX SHELXT V2014/1 [i] and refined by means of least-squares procedures on a F^2 with the aid of the program SHELXL-2016/6 [ii] include in the softwares package WinGX version 1.63[ii] or using CRYSTALS.[iii]

The Atomic Scattering Factors were taken from *International Tables for X-Ray Crystallography*.[iv] All non-hydrogen atoms were refined anisotropically. All hydrogens atoms were refined by using a riding model. Absorption corrections were introduced by using the MULTISCAN and X-Red program.[v, ix] Drawings of molecules are performed with the programs DIAMOND and POV-Ray with 50% probability displacement ellipsoids for non-H atoms. Depiction of H atoms is omitted for clarity.

Table S1. Crystal data and structure refinement for **1a.**

Identification code	k(18c6)_febr(1a)
Empirical formula	$C_{24}H_{60}BrFeKN_2O_6Si_4$
Formula weight	759.96
Temperature/K	100.01
Crystal system	triclinic
Space group	P-1
a/Å	11.8367(6)
b/Å	12.8422(7)
c/Å	15.1912(9)
α/°	81.153(2)
β/°	72.566(2)
γ/°	65.531(2)
Volume/Å^3	2004.08(19)
Z	2
ρ_{calc}g/cm^3	1.259
μ/mm^{-1}	1.629
F(000)	804.0
Crystal size/mm^3	0.589 × 0.236 × 0.172
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.278 to 52.34
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -17 ≤ l ≤ 18
Reflections collected	45143
Independent reflections	7988 [R_{int} = 0.0605, R_{sigma} = 0.0412]
Data/restraints/parameters	7988/0/373
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0309, wR_2 = 0.0630
Final R indexes [all data]	R_1 = 0.0457, wR_2 = 0.0673
Largest diff. peak/hole / e Å^{-3}	0.36/-0.56

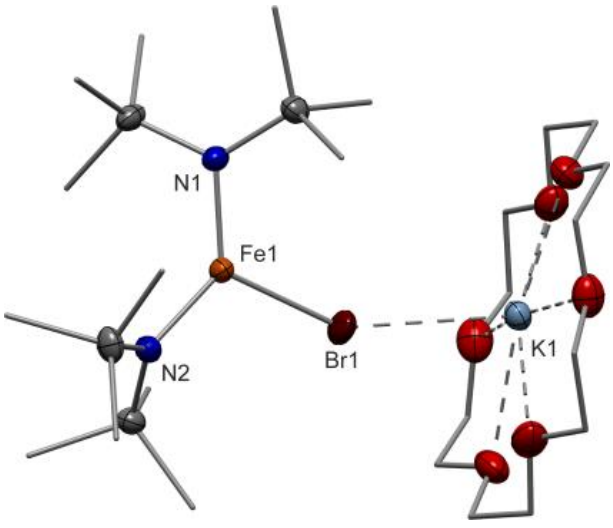

Figure S27. Molecular structure of **1a** within the crystal.

Table S2. Crystal data and structure refinement for **1b.**

Identification code	k(18c6)_fecl(1b)
Empirical formula	$C_{24}H_{60}ClFeKN_2O_6Si_4$
Formula weight	715.50
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.6580(4)
b/Å	19.6164(9)
c/Å	23.2135(10)
α/°	90
β/°	91.518(2)
γ/°	90
Volume/Å^3	3941.2(3)
Z	4
ρ_{calc}g/cm^3	1.206
μ/mm^{-1}	0.711
F(000)	1536.0
Crystal size/mm^3	0.574 × 0.166 × 0.131
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.508 to 52.152
Index ranges	-10 ≤ h ≤ 10, -24 ≤ k ≤ 24, -28 ≤ l ≤ 28
Reflections collected	118672
Independent reflections	7820 [R_{int} = 0.0910, R_{sigma} = 0.0330]
Data/restraints/parameters	7820/0/364
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0351, wR_2 = 0.0725
Final R indexes [all data]	R_1 = 0.0458, wR_2 = 0.0759
Largest diff. peak/hole / e Å^{-3}	0.45/-0.37

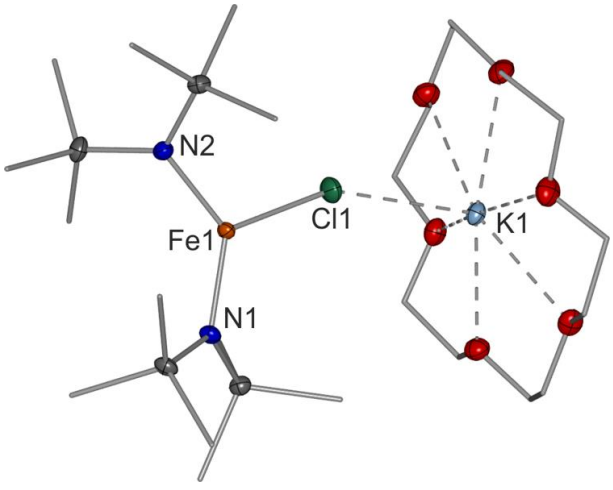

Figure S28. Molecular structure of **1b** within the crystal.

Table S3. Crystal data and structure refinement for **1c.**

Identification code	k(18c6)_fef(1c)
Empirical formula	$C_{72}H_{180}F_3Fe_3K_3N_6O_{18}Si_{12}$
Formula weight	2097.14
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.1913(5)
b/Å	12.5055(3)
c/Å	47.8877(13)
α/°	90
β/°	92.6170(10)
γ/°	90
Volume/Å^3	11480.9(5)
Z	4
ρ_{calc}g/cm^3	1.213
μ/mm^{-1}	0.667
F(000)	4512.0
Crystal size/mm^3	0.341 × 0.276 × 0.115
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.506 to 50
Index ranges	-22 ≤ h ≤ 22, -14 ≤ k ≤ 14, -56 ≤ l ≤ 56
Reflections collected	237019
Independent reflections	20179 [R_{int} = 0.0753, R_{sigma} = 0.0244]
Data/restraints/parameters	20179/0/1101
Goodness-of-fit on F^2	1.095
Final R indexes [I>=2σ (I)]	R_1 = 0.0317, wR_2 = 0.0772
Final R indexes [all data]	R_1 = 0.0364, wR_2 = 0.0790
Largest diff. peak/hole / e Å^{-3}	0.49/-0.30

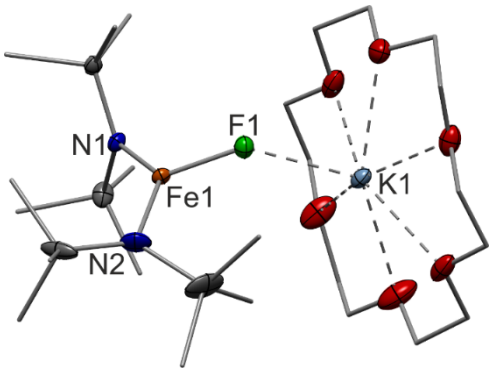

Figure S29. Molecular structure of **1c** within the crystal.

Table S4. Crystal data and structure refinement for **2.**

Identification code	k(18c6)_febz(2)
Empirical formula	$C_{31}H_{67}FeKN_2O_6Si_4$
Formula weight	771.17
Temperature/K	100.01
Crystal system	triclinic
Space group	P-1
a/Å	9.0328(9)
b/Å	19.980(2)
c/Å	24.078(3)
α/°	91.857(4)
β/°	94.986(4)
γ/°	92.202(4)
Volume/Å^3	4323.0(8)
Z	4
ρ_{calc}g/cm^3	1.185
μ/mm^{-1}	0.593
F(000)	1664.0
Crystal size/mm^3	0.498 × 0.196 × 0.056
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.366 to 49.998
Index ranges	-10 ≤ h ≤ 10, -23 ≤ k ≤ 23, -28 ≤ l ≤ 28
Reflections collected	94329
Independent reflections	15131 [R_{int} = 0.0607, R_{sigma} = 0.0484]
Data/restraints/parameters	15131/177/841
Goodness-of-fit on F^2	1.168
Final R indexes [I>=2σ (I)]	R_1 = 0.1083, wR_2 = 0.2652
Final R indexes [all data]	R_1 = 0.1230, wR_2 = 0.2697
Largest diff. peak/hole / e Å^{-3}	2.06/-0.77

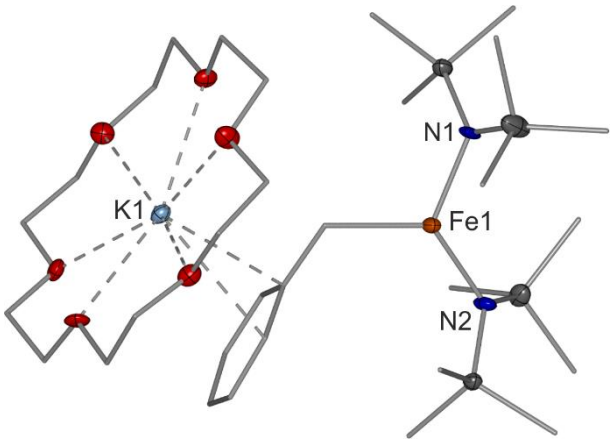

Figure S30. Molecular structure of **2** within the crystal. A disorder on one of the $SiMe_3$ group is and the second molecule of **2** in the unit cell is not depicted.

Table S5. Crystal data and structure refinement for **3a.**

Identification code	k(18c6)_febr2_(3a)
Empirical formula	$C_{24}H_{60}Br_2FeKN_2O_6Si_4$
Formula weight	839.87
Temperature/K	100.02
Crystal system	triclinic
Space group	P-1
a/Å	12.1198(5)
b/Å	18.0228(7)
c/Å	20.7923(9)
α/°	111.8930(10)
β/°	98.352(2)
γ/°	99.4360(10)
Volume/Å^3	4050.1(3)
Z	4
ρ_{calc}g/cm^3	1.377
μ/mm^{-1}	2.600
F(000)	1748.0
Crystal size/mm^3	0.255 × 0.201 × 0.148
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.42 to 49.994
Index ranges	-14 ≤ h ≤ 14, -21 ≤ k ≤ 21, -24 ≤ l ≤ 24
Reflections collected	131290
Independent reflections	14259 [R_{int} = 0.0480, R_{sigma} = 0.0223]
Data/restraints/parameters	14259/281/957
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0300, wR_2 = 0.0664
Final R indexes [all data]	R_1 = 0.0406, wR_2 = 0.0695
Largest diff. peak/hole / e Å^{-3}	0.64/-0.77

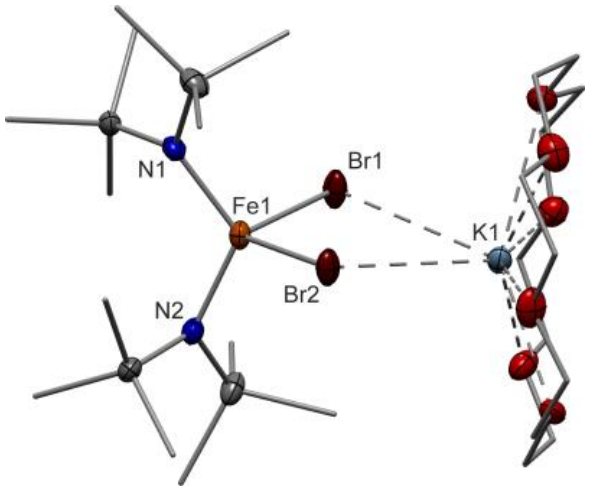

Figure S31. Molecular structure of **3a** within the crystal.

Table S6. Crystal data and structure refinement for **3b.**

Identification code	K(18c6)_FeCl2_(3b)
Empirical formula	$C_{24}H_{60}Cl_2FeKN_2O_6Si_4$
Formula weight	750.95
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	11.9279(8)
b/Å	17.7448(12)
c/Å	20.9599(15)
α/°	111.463(2)
β/°	97.733(2)
γ/°	99.677(2)
Volume/Å^3	3975.9(5)
Z	4
ρ_{calc}g/cm^3	1.255
μ/mm^{-1}	0.773
F(000)	1604.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.274 to 49.998
Index ranges	-14 ≤ h ≤ 13, -21 ≤ k ≤ 19, 0 ≤ l ≤ 24
Reflections collected	13943
Independent reflections	13943 [R_{int} = ?, R_{sigma} = 0.0646]
Data/restraints/parameters	13943/1950/1060
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0485, wR_2 = 0.1069
Final R indexes [all data]	R_1 = 0.0657, wR_2 = 0.1141
Largest diff. peak/hole / e Å^{-3}	0.59/-0.72

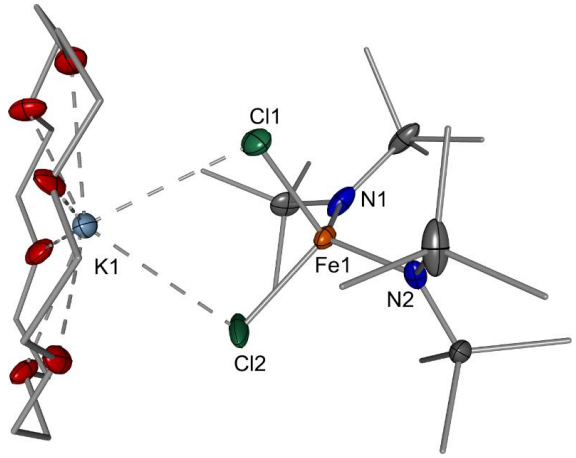

Figure 32. Molecular structure of **3b** within the crystal. Disorders at K{18c6} unit and at one of the hmds ligand are not depicted.

Table S6. Crystal data and structure refinement for **4.**

Identification code	kfebz_(4)
Empirical formula	$C_{19}H_{43}FeKN_2Si_4$
Formula weight	506.86
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.1546(5)
b/Å	20.9176(17)
c/Å	15.0072(9)
α/°	90
β/°	91.405(5)
γ/°	90
Volume/Å^3	2872.9(3)
Z	4
ρ_{calc}g/cm^3	1.172
μ/mm^{-1}	0.844
F(000)	1088.0
Crystal size/mm^3	0.74 × 0.413 × 0.347
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.156 to 52.998
Index ranges	-11 ≤ h ≤ 9, -26 ≤ k ≤ 25, -18 ≤ l ≤ 18
Reflections collected	18141
Independent reflections	5941 [R_{int} = 0.0990, R_{sigma} = 0.0706]
Data/restraints/parameters	5941/0/256
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0273, wR_2 = 0.0661
Final R indexes [all data]	R_1 = 0.0349, wR_2 = 0.0687
Largest diff. peak/hole / e Å^{-3}	0.42/-0.34

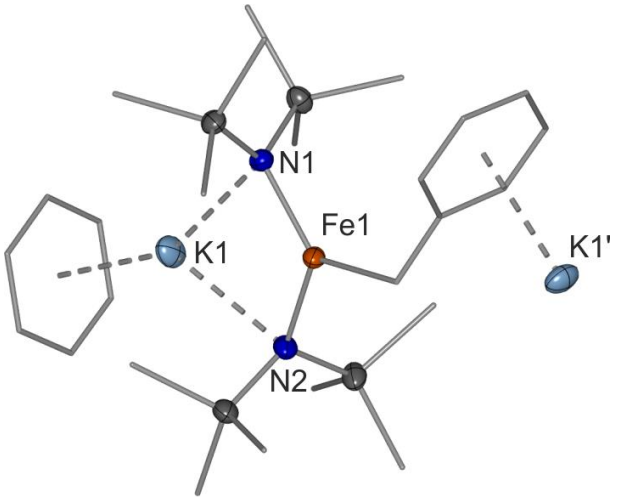

Figure S33. Molecular structure of **4** within the crystal. Each molecule of **4** is connected by the potassium ion to the benzyl unit of the next molecule giving overall a chain-like structure in solid state.

Table S7. Crystal data and structure refinement for **5a.**

Identification code	k(18c6)_fenbu(5a)
Empirical formula	$C_{28}H_{69}FeKN_2O_6Si_4$
Formula weight	737.16
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	9.1092(4)
b/Å	19.7540(9)
c/Å	23.9066(9)
α/°	94.5940(10)
β/°	96.9240(10)
γ/°	96.112(2)
Volume/Å^3	4227.3(3)
Z	4
ρ_{calc}g/cm^3	1.158
μ/mm^{-1}	0.604
F(000)	1600.0
Crystal size/mm^3	0.425 × 0.166 × 0.124
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.356 to 53.612
Index ranges	-11 ≤ h ≤ 11, -25 ≤ k ≤ 25, -30 ≤ l ≤ 30
Reflections collected	126701
Independent reflections	18048 [R_{int} = 0.0600, R_{sigma} = 0.0378]
Data/restraints/parameters	18048/57/811
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0356, wR_2 = 0.0695
Final R indexes [all data]	R_1 = 0.0557, wR_2 = 0.0756
Largest diff. peak/hole / e Å^{-3}	0.70/-0.85

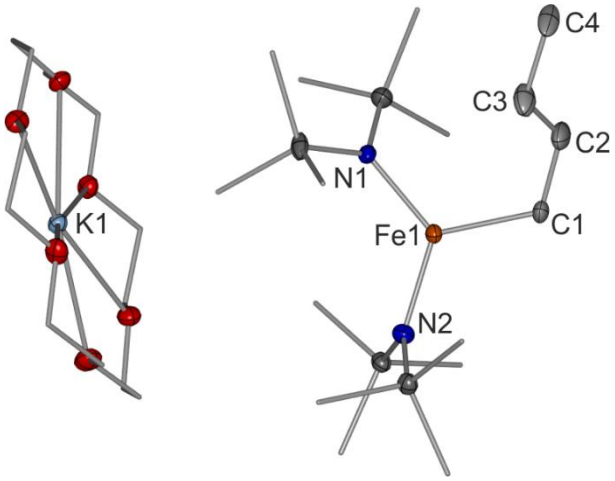

Figure S34. Molecular structure of **5a** within the crystal. Disorder at C4 is omitted for clarity.

Table S8. Crystal data and structure refinement for **6.**

Identification code	k(18c6)_feph_(6)
Empirical formula	$C_{30}H_{65}FeKN_2O_6Si_4$
Formula weight	757.15
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.1672(4)
b/Å	23.7130(9)
c/Å	17.7834(9)
α/°	90
β/°	92.968(2)
γ/°	90
Volume/Å^3	4281.7(3)
Z	4
ρ_{calc}g/cm^3	1.175
μ/mm^{-1}	0.598
F(000)	1632.0
Crystal size/mm^3	0.325 × 0.21 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.516 to 53.998
Index ranges	-12 ≤ h ≤ 12, -30 ≤ k ≤ 30, -22 ≤ l ≤ 20
Reflections collected	53588
Independent reflections	9340 [R_{int} = 0.0567, R_{sigma} = 0.0398]
Data/restraints/parameters	9340/0/439
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0446, wR_2 = 0.0977
Final R indexes [all data]	R_1 = 0.0685, wR_2 = 0.1049
Largest diff. peak/hole / e Å^{-3}	0.89/-0.49

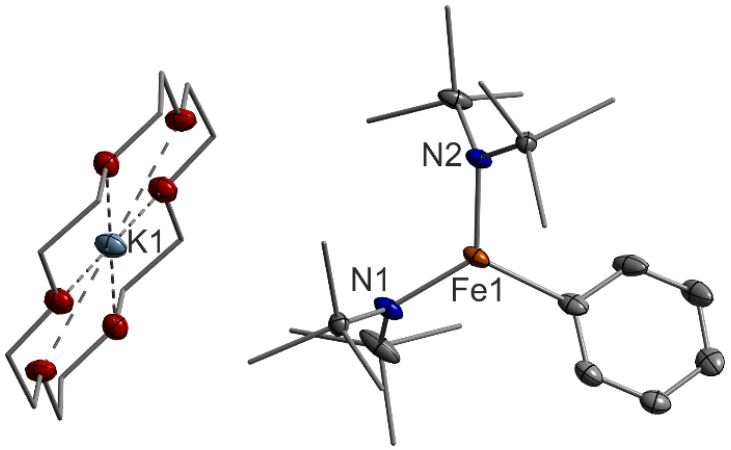

Figure S35. Molecular structure of **6** within the crystal. Disorder at the 18c6 unit is omitted for clarity.

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