Supporting information for:

Desulfurization of N,N-dimethylthioformamide by hydrosilane with the help of an iron complex. Isolation and characterization of an iron-carbene complex as an intermediate of C=S double bond cleavage.

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1. General Remarks. NMR spectra (^{1}H, ^{13}C, ^{29}Si) were recorded on a JEOL JNM-AL400 spectrometer. The residual peaks of the solvent were used as the reference for ^{1}H NMR spectra. For ^{13}C NMR spectra, solvent signals were used as the chemical-shift reference. Peak positions of the ^{29}Si NMR spectra were referenced to external tetramethylsilane (δ = 0 ppm). IR spectra were recorded on a Perkin Elmer FTIR-Spectrum One.

2. Spectroscopic characterization

$Me_2NC(S)Ph$: Anal. Calc. for $C_9H_{11}NS$: C, 46.56; H, 8.79; N, 13.57. Found: C, 46.95; H, 8.85; N, 13.32.

$Me_2NC(S)Me$: Anal. Calc. for C_4H_9NS: C, 65.41; H, 6.71; N, 8.48. Found: C, 65.13; H, 6.73; N, 8.25.

$Cp(CO)Fe(C(H)NMe_2)(SSiEt_3)$ (3): ^{1}H NMR (399.65 MHz, +20 °C, in C_6D_6): 0.92 (m, 6H, SiCH_2CH$_3$), 1.24 (m, 9H, SiCH$_2$CH_3), 2.42 (s, 3H, NCH_3), 3.20 (s, 3H NCH_3), 4.49 (s, 5H C_5H_5), 11.99 (s, 1H Fe=CH). ^{13}C{^{1}H } NMR (100.40 MHz, +20 °C, in C_6D_6): 8.74 (s, SiCH_2CH$_3$), 9.59 (s, SiCH$_2$$CH_3$), 44.4 (s, NCH$_3$), 53.6 (s, NCH$_3$), 86.0 (s, C_5H_5), 223.77 (s, CO), 256.0 (s, Fe=C). ^{29}Si

NMR (79.30 MHz, +20 °C, in C_6D_6): 22.6 (s). IR (cm^{-1}, in toluene): ν (CO): 1932. Sufficient element analysis data could not be obtained because of its instability.

Cp(CO)Fe(C(H)NMe$_2$)(SSiPh$_3$) (5): ^{1}H NMR (399.65 MHz, +20 °C, in C_6D_6): 2.17 (s, 3H, NCH_3), 3.05 (s, 3H NCH_3), 4.19 (s, 5H C_5H_5), 7.21-8.03 (m, 15H, Ph), 11.74(s, 1H Fe=CH). $^{13}C\{^1H\}$ NMR (100.40 MHz, +20 °C, in C_6D_6): 44.4 (s, NCH_3), 53.4 (s, NCH_3), 85.7 (s, C_5H_5), 127.62 (s, Ph), 128.8(s, Ph), 136.5 (s, Ph), 140.8 (s, Ph), 222.9 (s, CO), 255.8 (s, Fe=C). ^{29}Si NMR (79.30 MHz, +20 °C, in C_6D_6): 1.8 (s). IR (cm^{-1}, in toluene): ν (CO): 1937. Anal. Calc. for $C_{27}H_{27}FeNOSSi$: C, 65.18; H, 5.47; N, 2.82. Found: C, 65.04; H, 5.41; N, 2.75.

3. X-ray Crystal structure determination of 5: Dark-red crystals of **5** suitable for an X-ray diffraction study were obtained through crystallization from CH_2Cl_2/hexane. The single crystal was mounted in a glass capillary. Data for **5** were collected at 20 ºC on Rigaku/MSC Mercury CCD area-detector diffractometer equipped with monochromated MoKα radiation (λ = 0.71070 Å). Calculations for **5** were performed with the teXane crystallographic software package of Molecular Structure Corporation. Crystal Data: $C_{22}H_{27}FeNOSSi$, M = 497.51, red block, 0.45 × 0.30 × 0.30 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 16.037(2) Å, b = 9.3525(11) Å, c = 16.402(3) Å, β = 101.572(3)°, V = 2410.0(5) $Å^3$, Z = 4, μ(MoKα) = 7.813 mm^{-1}, D_{calc} = 1.371 g/cm^3, 16617 reflections collected, 5411 ($I > 3\sigma I$) unique reflections were used in all calculations, number of variables = 373, R = 0.0328, R_w = 0.1051, and goodness of fit = 1.007.

Table S1 Crystal data and structure refinement for **5**.

	5
Empirical formula	$C_{22}H_{27}FeNOSSi$
Formula weight	497.51
Crystal system	Monoclinic
Crystal size(mm^3)	0.45 × 0.30 × 0.30
Space group	$P2_1/c$ (No. 14)
a, Å	16.037(2)
b, Å	9.3525(11)
c, Å	16.402(3)
β, deg	101.572(3)
V, $Å^3$	2410.0(5)
Z	4
μ, mm^{-1}	7.813
F(000)	1040.00
D_{calcd}, g cm^{-1}	1.371
No. of unique reflections	5411
No. of used reflections	16617
No. of variables	373
^aR	0.0328
^bR_W	0.1051
Goodness-of-fit	1.007

$^aR = \Sigma||Fo|-|Fc||/\Sigma|Fo|$.

$^bRw = [\Sigma w(|Fo|-|Fc|)^2/\Sigma wFo^2]^{0.5}$

Weighting scheme $[\sigma(F_O)^2]^{-1}$

Table S2 Selected bond distances (Å), bond angles (°), and torsion angles (°) for **5**.

Fe-S	2.3371(3)
Fe-C(3)	1.8891(5)
S-Si	2.1016(5)
N-C(1)	1.466(2)
N-C(2)	1.473(2)
N-C(3)	1.306(2)
S-Fe-C(3)	96.42(5)
C(3)-Fe-C(4)	97.34(7)
S-Fe-C(4)	87.39(5)
Fe-S-Si	115.482(19)
Fe-C(3)-N	135.96(12)
C(1)-N-C(2)	113.75(13)
C(1)-N-C(3)	123.56(13)
C(2)-N-C(3)	122.54(14)
C(1)-N-C(3)-Fe	-6.2(2)
C(2)-N-C(3)-Fe	169.06(12)