

Supporting Information

Synthesis of Sulfur- and Nitrogen-Bridged Diiron Complexes and Catalytic Behavior toward Hydrazines

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General Procedures. All manipulations were carried out under inert atmosphere using standard Schlenk-line techniques or in a glovebox. Solvents were dried over appropriate agents under an atmosphere of dinitrogen. Compound such as 2-trimethylsilylbenzenethiol (ArSH)^{S1} and 2,6-bistrimethylsilylbenzenethiol (Ar'SH)^{S1} and complexes such as [Cp*FeCl(tmeda)]^{S2} and [Cp*RuCl]₄^{S3} were prepared by the literature methods. Other reagents were purchased from commercial sources and were used as received. NMR spectra were recorded on JEOL JNM-EX270 spectrometer, and chemical shifts are quoted in ppm. Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. Elemental analyses were performed on an Exeter Analytical CE-440 elemental analyzer.

Preparation of [Cp*Fe(μ -SAr)]₂ (1). To a THF (2 mL) solution of ArSH (183 mg, 1.00 mmol) was added KN(SiMe₃)₂ (199 mg, 0.998 mmol) in THF (3 mL). After 30 min at room temperature, the volatiles were removed in vacuo. The resulting white powder was dissolved in THF (5 mL), and was added to a THF (5 mL) solution of [Cp*FeCl(tmeda)] (344 mg, 1.00 mmol). The mixture was stirred at room temperature for 24 h. After filtration, the purple-red solution was concentrated to dryness. Recrystallization from hexane at -30 °C afforded purple-red plates of [Cp*Fe(μ -SAr)]₂·1.5C₆H₁₄ (**1**·1.5C₆H₁₄). The crystals were dried in vacuo to give purple-red powder of solvent-free **1** (287 mg, 77%). Data for **1**: Anal Calcd for C₃₈H₅₆Fe₂S₂Si₂: C, 61.28; H, 7.58%. Found: C, 61.30; H, 7.26%. ¹H NMR (THF-*d*₈, 293 K) δ 9.87 (br. s, 30H, Cp*), 8.85 (br. s, 2H, Ar-H), 2.97 (br. t, *J* = 7 Hz, 2H, Ar-H), 0.65 (br. d, *J* = 7 Hz, 2H, Ar-H), -1.02 (br. s, 18H, SiMe₃), -23.47 (br. s, 2H, Ar-H). Magnetic moment (Evans' method): $\mu_{\text{eff}} = 2.2 \mu_{\text{B}}$ /iron atom at 293 K.

Reaction of 1 with Methylhydrazine. To a THF (5 mL) solution of [Cp*Fe(μ -SAr)]₂ (**1**; 74.5 mg, 0.100 mmol) was added methylhydrazine (5.8 mg, 0.13 mmol). The mixture was stirred at room temperature for 20 h. The volatiles were trap-to-trap distilled into ethereal solution of HCl (2 M, 10 mL). The distillate was concentrated to dryness, and the amounts of MeNH₃Cl (0.043 mmol; 57% yield based on **1**; 57% = 0.043 mmol/(0.1 mmol x 0.75) x 100) and NH₄Cl (0.043 mmol; 57% yield based on **1**; 57% = 0.043 mmol/(0.1 mmol x 0.75) x 100) were determined by ¹H NMR in DMSO-*d*₆ with mesitylene as an internal standard. For example, 3 mol of methylamine

were produced from 4 mol of **1** when methylamine achieved 100% yield based on **1** (See Scheme 2). The ^1H NMR analysis of the distillation residue showed the formation of $[(\text{Cp}^*\text{Fe})_2(\mu\text{-SAr})(\mu\text{-}\eta^2\text{:}\eta^2\text{-NNMe})]$ (**2**) (0.032 mmol; 64% yield based on **1**; $64\% = 0.032 \text{ mmol}/(0.1 \text{ mmol} \times 0.5) \times 100$) and $[(\text{Cp}^*\text{Fe})_2(\mu\text{-SAr})_3]$ (**3**) (0.018 mmol; 36% yield based on **1**; $36\% = 0.018 \text{ mmol}/(0.1 \text{ mmol} \times 0.5) \times 100$). Independently, $[(\text{Cp}^*\text{Fe})_2(\mu\text{-SAr})_3]$ (**3**) (0.017 mmol; 34% yield based on **1**; $34\% = 0.017 \text{ mmol}/(0.1 \text{ mmol} \times 0.5) \times 100$) was isolated from the reaction mixture by crystallization from cold hexane. For example, 2 mol of **2** were produced from 4 mol of **1** when **2** achieved 100% yield based on **1** (See Scheme 2). Data for **3**: Anal Calcd for $\text{C}_{47}\text{H}_{69}\text{Fe}_2\text{S}_3\text{Si}_3$: C, 60.95; H, 7.51%. Found: C, 60.66; H, 7.57%. ^1H NMR(C_6D_6 , 293 K) δ 9.59 (br. s, 3H, Ar), 9.05 (br. s, 3H, Ar), 0.10 (br. s, 30H, Cp*), -1.14 (br. s, 27H, SiMe₃). The other signals corresponding to aromatic protons (3H x 2) were not observed. Magnetic moment (Evans' method): $\mu_{\text{eff}} = 1.9 \mu_{\text{B}}$ /iron atom at 293 K.

Isolation of 2. To a THF (5 mL) solution of **1** (49.0 mg, 65.8 μmol) were added 2 equivalents of methylhydrazine (6.1 mg, 132 μmol) in THF (5 mL). The solution was stirred at room temperature for 20 h. The resulting brown solution was concentrated to dryness. The residue was extracted with hexane and cooled at -30 °C to afford brown crystals of **2** (22 mg, 49%). Data for **2**: Anal. Calcd for $\text{C}_{30}\text{H}_{46}\text{N}_2\text{Fe}_2\text{SSi}$: C, 59.41; H, 7.64; N, 4.62%. Found: C, 59.45; H, 7.46; N, 4.66%. ^1H NMR (C_6D_6) δ 7.40 (dd, $J = 7 \text{ Hz}$ and 1 Hz , 1H, Ar-H), 7.06 (td, $J = 7 \text{ Hz}$ and 1 Hz , 1H, Ar-H), 6.75 (td, $J = 8 \text{ Hz}$ and 1 Hz , 1H, Ar-H), 5.36 (dd, $J = 8 \text{ Hz}$ and 1 Hz , 1H, Ar-H), 2.26 (s, 3H, NMe), 1.59 (s, 30H, Cp*), 0.88 (s, 9H, SiMe₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) δ 153.5 (quarternary aryl carbon), 141.6 (Ar-H), 141.4 (quarternary aryl carbon), 133.0, 128.0, 124.9 (aromatic CH x 3), 88.2 (C_5Me_5), 36.4 (NMe), 10.8 (C_5Me_5), 1.3 (SiMe₃).

Catalytic Reduction of Hydrazines. A typical procedure (Table 1, entry 1) is as follows. To a THF (10 mL) solution containing **2** (18.2 mg, 0.030 mmol) and MeNHNH₂ (27.6 mg, 0.60 mmol) were added [LutH]BPh₄ (513 mg, 1.20 mmol) and Cp₂Co (227 mg, 1.20 mmol) under argon atmosphere. The mixture was stirred at room temperature for 1 h. An aliquot of gas phase was analyzed by GC to estimate the amounts of formation of H₂ and N₂. The volatile materials of the solution were transferred to an ethereal solution of HCl (2 M, 10 mL) by bulb-to-bulb distillation.

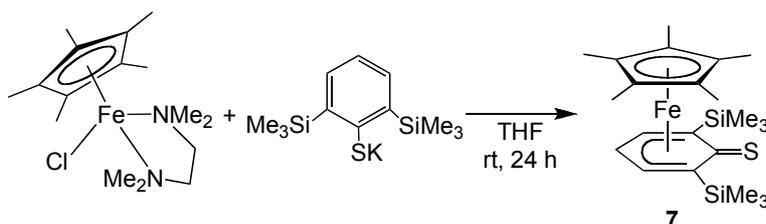
The residue was treated with KO^tBu (540 mg, 4.81 mmol) in THF (5 mL), and then the volatiles were distilled again. The distillates were concentrated to dryness to give white solid containing MeNH₃Cl, NH₄Cl, and LutHCl. The amounts of MeNH₃Cl and NH₄Cl were determined by ¹H NMR (DMSO-*d*₆) using mesitylene as an internal standard. For example, 1 mol of methylamine was produced from 1 mol of methylhydrazine when methylamine achieved 100% yield based on methylhydrazine (See Table 1).

Preparation of [Cp*Ru(μ -SAr)]₂ (5). To a THF (2 mL) solution of ArSH (183 mg, 1.00 mmol) was added KN(SiMe₃)₂ (198 mg, 0.993 mmol) in THF (3 mL). After 1 h, pale yellow solution was concentrated to dryness. The residue dissolved in THF (5 mL), was added to a THF (5 mL) solution of [Cp*RuCl]₄ (271 mg, 0.249 mmol). The mixture was stirred at room temperature for 24 h. After filtration, the blue solution was concentrated to dryness. Recrystallization from hexane at -30 °C afforded blue crystalline solid, which was dried in vacuo to give a dark blue powder of **5** (328 mg, 79%). A X-ray quality crystal was obtained by recrystallization from hexamethyldisiloxane at -30 °C. Data for **5**: Anal Calcd for C₃₈H₅₆Ru₂S₂Si₂: C, 54.64; H, 6.76%. Found: C, 54.34; H, 6.52%. ¹H NMR (THF-*d*₈) δ 8.36 (d, *J* = 7 Hz, 2H, Ar-H), 7.53-7.45 (m, 4H, Ar-H), 7.34 (t, *J* = 7 Hz, 2H, Ar-H), 1.48 (s, 30H, Cp*), 0.29 (s, 18H, SiMe₃). ¹³C{¹H} NMR (THF-*d*₈) δ 151.5 (quaternary aryl carbon), 143.6 (quaternary aryl carbon), 135.9 (aromatic CH), 134.2 (aromatic CH), 129.2 (aromatic CH), 126.8 (aromatic CH), 78.3 (C₅Me₅), 11.6 (C₅Me₅), 0.3 (SiMe₃).

Preparation of [(Cp*Fe)₂(μ -SAr)(μ - η^2 : η^2 -HNNMe)]OTf (6). To a THF (5 mL) solution of **2** (50.2 mg, 0.0828 mmol) was added LutHOTf (20.7 mg, 80.5 mmol), and then the mixture was stirred at room temperature for 10 min. The mixture was concentrated to dryness. Recrystallization from dimethoxyethane-hexane afforded brown rods of **6** (51.2 mg, 84%). Data for **6**: Anal. Calcd for C₃₁H₄₇N₂F₃Fe₂O₃S₂Si: C, 49.21; H, 6.26; N, 3.70. Found: C, 48.74; H, 6.02; N, 3.73%. ¹H NMR (THF-*d*₈) δ 14.67 (s, 1H, NH), 7.51 (d, *J* = 7 Hz, 1H, Ar), 7.27 (t, *J* = 7 Hz, 1H, Ar), 6.82 (t, *J* = 7 Hz, 1H, Ar), 4.29 (d, *J* = 7 Hz, 1H, Ar), 2.09 (s, 3H, NMe), 1.49 (s, 30H, Cp*), 0.75 (s, 9H, SiMe₃).

Preparation of [Cp*Fe(η^5 -Ar'S)] (7) (Scheme S1). To a THF (5 mL) solution of Ar'SH (510 mg, 2.00 mmol) was added KN(SiMe₃)₂ (400 mg, 2.01 mmol) in THF (5 mL). After 30 min, yellow solution was dried in vacuo. The resulting white powder of KSAr' was redissolved to THF (10 mL) and was transferred to a flask containing [Cp*FeCl(tmeda)] (686 mg, 2.00 mmol) in THF (10 mL). The mixture was stirred at room temperature for 24 h. After filtration, the dark red solution was concentrated to dryness. Recrystallization from THF-hexane afforded orange-red leaflets of 7·0.25THF (666 mg, 72%). Data for 7: Anal. Calcd for C₂₃H₃₈FeO_{0.25}SSi₂ (7·0.25THF): C, 59.71; H, 8.28%. Found: C, 59.68; H, 8.15%. ¹H NMR (THF-*d*₈) δ 5.40 (t, ³J = 6 Hz, 1H, 4-position of Ar'), 5.23 (d, ³J = 6 Hz, 2H, 3,5-positions of Ar'), 1.78 (s, 15H, Cp*), 0.40 (s, 18H, SiMe₃). ¹³C{¹H} NMR (THF-*d*₈) δ 149.9 (1-position of Ar'), 97.3 (2,6-positions of Ar'), 92.1 (C₅Me₅), 86.5 (3,5-positions of Ar'), 82.6 (4-position of Ar'), 10.2 (C₅Me₅), 1.7 (SiMe₃).

Scheme S1



X-ray Crystallography. Summary of crystallographic data are given in Table S1. The paraffin-coated crystals were placed on a nylon loop and mounted on a Rigaku RAXIS RAPID imaging plate system. Data were collected under a cold nitrogen stream using graphite monochromated MoK α radiation ($\lambda = 0.71069 \text{ \AA}$). Data were corrected for Lorenz, polarization, and absorption effects. Structures were solved by direct methods (SIR97)^{S4} and refined on F^2 by full-matrix least-squares techniques. Anisotropic thermal parameters were introduced for all non-hydrogen atoms. The structure of **3** was refined as a racemic twin with a Flack parameter of 0.5. The unit cell of **7** contains a solvent accessible void of 185 \AA^3 . The ^1H NMR spectrum and elemental analysis of the crystals indicated that the void was occupied by a THF molecule, which could not be located appropriately. The diffused electron density associated with the solvent molecule was removed by SQUEEZE routine in PLATON.^{S5} The large anisotropy of thermal factors indicates the disordered structure of one Cp* ligand in **3** and one triflate anion in **6** but could not found appropriate modeling. The N-H hydrogen (H1) of **6** was located by difference-Fourier map and refined isotropically, while the other hydrogen atoms were placed in idealized positions and treated as riding atoms. All calculations were carried out using WinGX/SHELXL software suites.^{S6, S7} The thermal ellipsoid plots were drawn with ORTEP3.^{S8} Crystallographic data are given in a CIF file.

The checkCIF report contains several alerts of level A and B. However, these alerts can be explained reasonably as follows, and do not affect the validity of our X-ray results. (1) All level B alerts for the data of complexes **3** are due to unresolved disorder of a Cp* ligand. (2) For the data of complex **6**, the checkCIF generated two level A alerts which "suspect" O-H bonds. These are "true" hydrogen bond between the hydrogen atom of diazene ligand and the oxygen atom of the triflate anion. (3) The level B alerts of complex **6** are due to unresolved disorder of a triflate anion.

References

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Table S1. Summary of Crystallographic Data.

	1 ·1.5C ₆ H ₁₄	2	3
formula	C ₄₇ H ₇₇ Fe ₂ S ₂ Si ₂	C ₃₀ H ₄₆ N ₂ Fe ₂ SSi	C ₄₇ H ₆₉ Fe ₂ S ₃ Si ₃
formula weight	874.09	606.54	926.17
crystal size/mm	0.65 x 0.30 x 0.20	0.50 x 0.25 x 0.10	0.50 x 0.30 x 0.30
color, habit	purple plate	brown plate	dark green prism
crystal system	<i>triclinic</i>	<i>monoclinic</i>	<i>hexagonal</i>
space group	<i>P1</i> - (No. 2)	<i>P2</i> ₁ / <i>n</i> (No. 14)	<i>P6</i> ₃ (No. 173)
<i>a</i> /Å	12.4295(6)	11.1305(4)	24.6933(5)
<i>b</i> /Å	13.8048(8)	18.4097(6)	24.6933(5)
<i>c</i> /Å	15.5245(8)	15.4573(5)	13.8075(3)
α /deg	89.869(2)	90	90
β /deg	71.536(1)	103.257(1)	90
γ /deg	76.876(2)	90	120
<i>V</i> /Å ³	2453.7(2)	3082.94(18)	7291.3(3)
<i>Z</i>	2	4	6
<i>T</i> /K	173	173	173
<i>d</i> _c /g cm ⁻³	1.183	1.307	1.266
μ (Mo K α)/mm ⁻¹	0.754	1.068	0.830
No. of data collected	24020	28946	66521
No. of unique data (<i>R</i> _{int})	11033 (0.029)	7015 (0.047)	11049 (0.033)
No. of parameters refined	521	339	515
<i>R1</i> ^a (<i>F</i> ² > 2 σ)	0.039	0.034	0.035
<i>wR2</i> ^b (all data)	0.116	0.088	0.084
goodness of fit indicator ^c	1.08	1.09	1.06
residual electron density/e Å ⁻³	+0.53 to -0.40	+0.43 to -0.40	+0.33 to -0.27

$${}^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, {}^b wR2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o)^2]^{1/2}}{[\sum w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}}.$$

Table S1. Continued.

	5	6	7
formula	C ₃₈ H ₅₆ Ru ₂ S ₂ Si ₂	C ₃₁ H ₄₇ N ₂ F ₃ Fe ₂ O ₃ S ₂ Si	C ₂₃ H ₃₈ FeO _{0.25} SSi ₂
formula weight	835.27	756.62	462.63
crystal size/mm	0.10 x 0.03 x 0.03	0.20 x 0.20 x 0.01	0.30 x 0.30 x 0.03
color, habit	blue rod	brown plate	orange red plate
crystal system	<i>monoclinic</i>	<i>triclinic</i>	<i>triclinic</i>
space group	<i>P2</i> ₁ / <i>c</i> (No. 14)	<i>P1</i> - (No. 2)	<i>P1</i> - (No. 2)
<i>a</i> /Å	12.763(2)	11.072(2)	10.9850(10)
<i>b</i> /Å	18.570(3)	15.416(3)	15.8855(14)
<i>c</i> /Å	16.934(3)	21.854(4)	15.9669(16)
<i>α</i> /deg	90	95.023(4)	92.938(2)
<i>β</i> /deg	93.351(3)	98.802(3)	107.854(3)
<i>γ</i> /deg	90	101.281(4)	107.113(2)
<i>V</i> /Å ³	4006.7(12)	3588.4(18)	2503.8(2)
<i>Z</i>	4	4	4
<i>T</i> /K	173	103	173
<i>d</i> _c /g cm ⁻³	1.390	1.401	1.227
<i>μ</i> (Mo Kα)/mm ⁻¹	0.942	1.007	0.789
No. of data collected	32212	29261	19942
No. of unique data (<i>R</i> _{int})	8949 (0.088)	15732 (0.059)	8998 (0.096)
No. of parameters refined	413	829	491
<i>R1</i> ^a (<i>F</i> ² > 2σ)	0.070	0.058	0.080
<i>wR2</i> ^b (all data)	0.156	0.163	0.252
goodness of fit indicator ^c	1.13	0.94	1.04
residual electron density/e Å ⁻³	+1.52 to -0.95	+1.69 to -1.80	+0.56 to -0.72

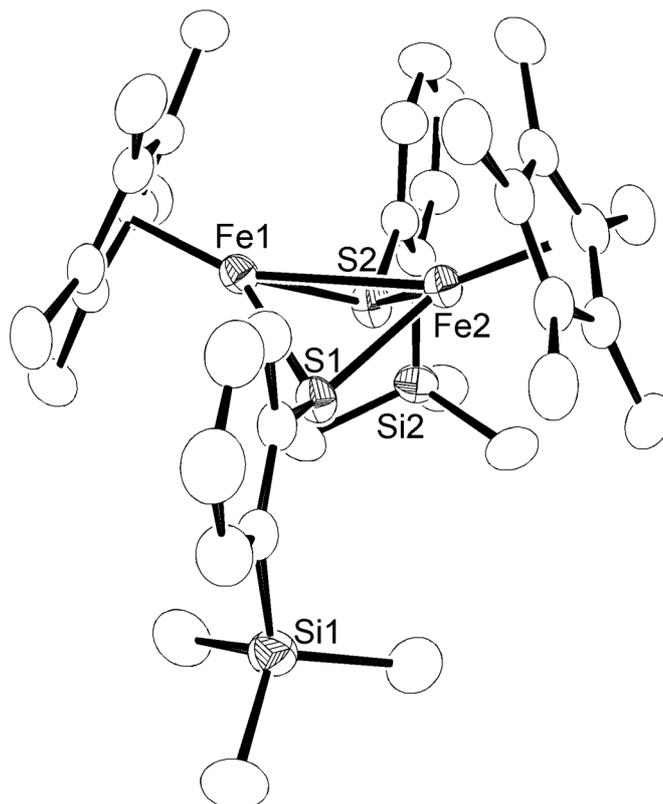


Figure S1. ORTEP view of $[\text{Cp}^*\text{Fe}(\mu\text{-SAr})]_2$ (**1**) drawn with 50% ellipsoids.

Table S2. Selected Interatomic Distances (Å) and Bond Angles (deg) for **1**

Distances			
Fe1-Fe2	2.7429(4)		
Fe1-S1	2.2203(6)	Fe1-S2	2.2138(6)
Fe2-S1	2.2216(6)	Fe2-S2	2.2133(6)
Angles			
S1-Fe1-S2	78.81(2)	S1-Fe2-S2	78.79(2)
Fe1-S1-Fe2	76.268(19)	Fe1-S2-Fe2	76.568(19)

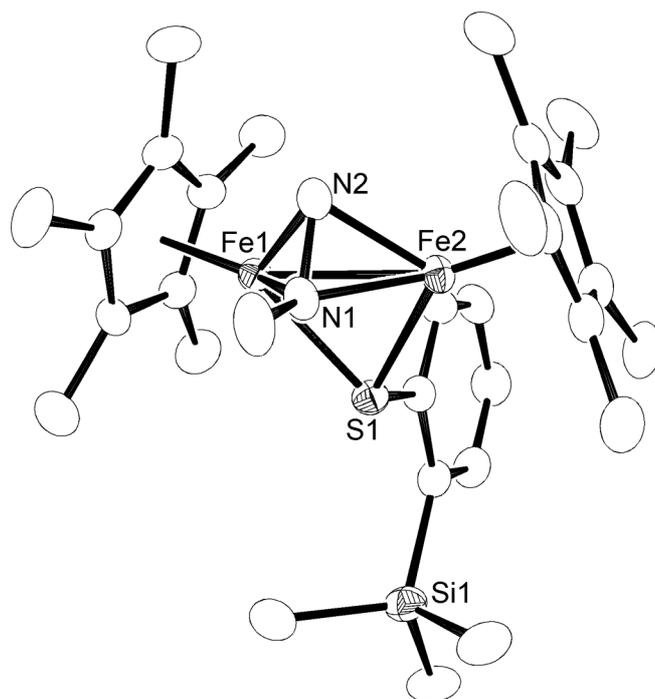


Figure S2. ORTEP view of $[(\text{Cp}^*\text{Fe})_2(\mu\text{-SAr})(\mu\text{-}\eta^2\text{:}\eta^2\text{-NNMe})]$ (**2**) drawn with 50% ellipsoids.

Table S3. Selected Interatomic Distances (Å) and Bond Angles (deg) for **2**

Distances			
N1-N2	1.331(3)	N1-C30	1.464(3)
Fe1-N1	1.9504(17)	Fe2-N1	1.9470(17)
Fe1-N2	1.8940(18)	Fe2-N2	1.8911(18)
Fe1-S1	2.2457(6)	Fe2-S1	2.2496(6)
Fe1-Fe2	2.5532(4)		
Angles			
N1-Fe1-N2	40.49(8)	N1-Fe2-N2	40.56(8)
Fe1-N1-Fe2	81.85(7)	Fe1-N2-Fe2	84.84(7)
Fe1-S1-Fe2	69.217(18)		
N2-N1-C30	120.71(19)		

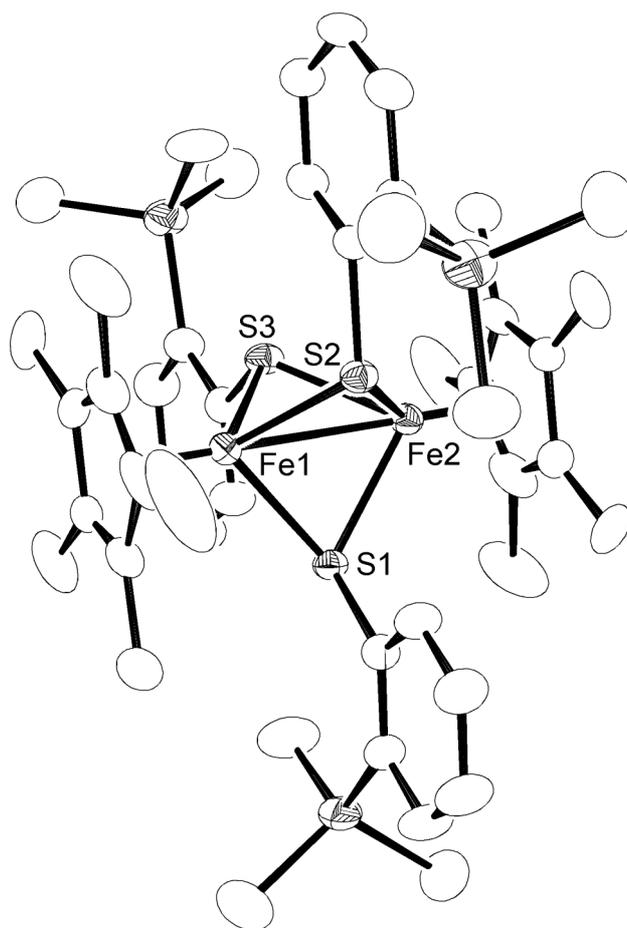


Figure S3. ORTEP view of $[(\text{Cp}^*\text{Fe})_2(\mu\text{-SAr})_3]$ (**3**) drawn with 50% ellipsoids.

Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) for **3**

Distances			
Fe1-S1	2.2820(10)	Fe2-S1	2.2768(9)
Fe1-S2	2.2829(9)	Fe2-S2	2.2766(10)
Fe1-S3	2.2837(10)	Fe2-S3	2.2733(10)
Fe1-Fe2	2.7058(3)		
Angles			
Fe1-S1-Fe2	72.82(2)	Fe1-S2-Fe2	72.81(2)
Fe1-S3-Fe2	72.85(2)		

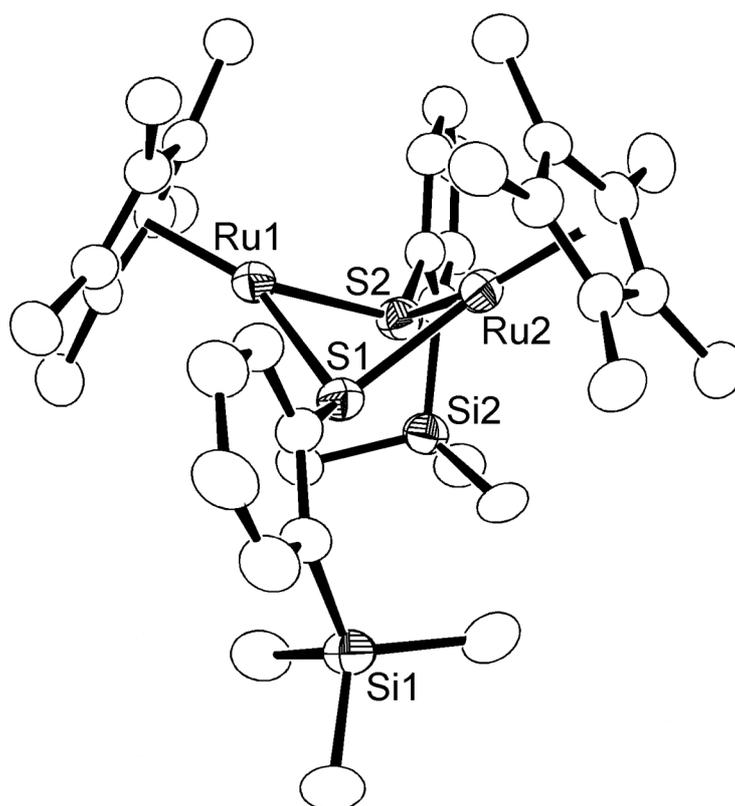


Figure S4. ORTEP view of $[\text{Cp}^*\text{Ru}(\mu\text{-SAr})]_2$ (**5**) drawn with 50% ellipsoids.

Table S5. Selected Interatomic Distances (Å) and Bond Angles (deg) for **5**

Distances			
Ru1-S1	2.3252(15)	Ru1-S2	2.3186(15)
Ru2-S1	2.3319(15)	Ru2-S2	2.3218(15)
Ru1-Ru2	3.0832(8)		
Angles			
S1-Ru1-S2	75.16(5)	S1-Ru2-S2	74.98(5)
Ru1-S1-Ru2	82.91(5)	Ru1-S2-Ru2	83.28(5)

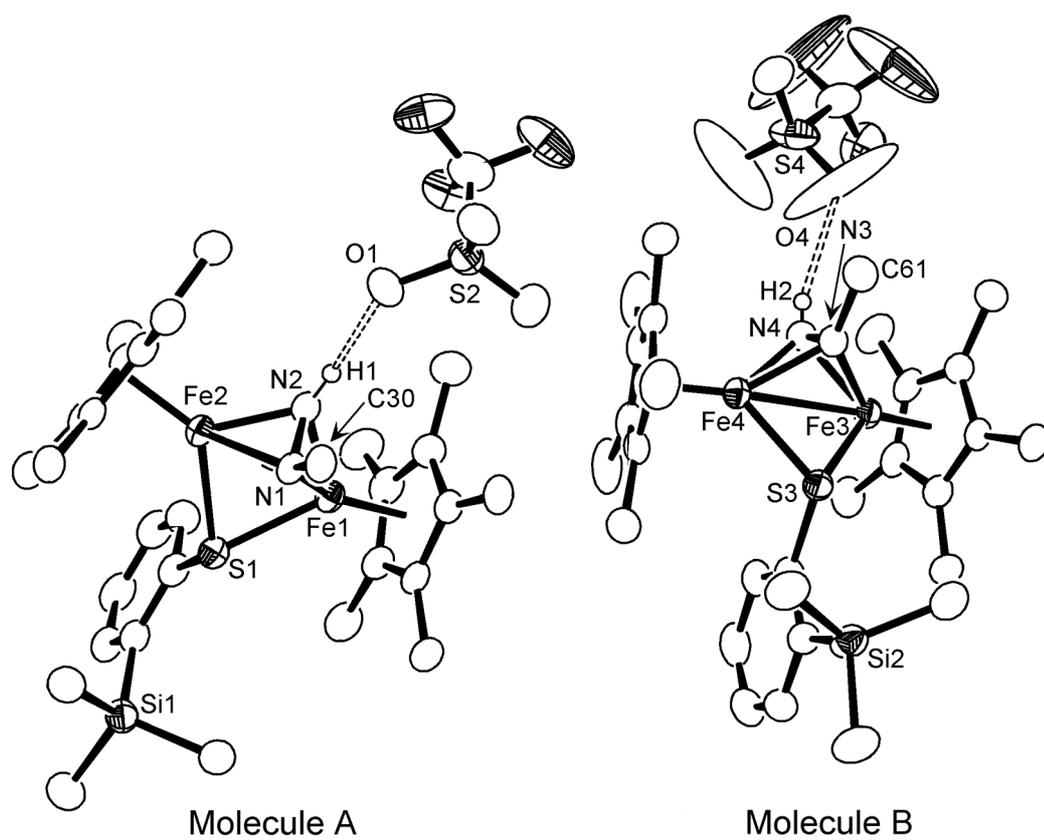


Figure S5. ORTEP view of $[(\text{Cp}^*\text{Fe})_2(\mu\text{-SAr})(\mu\text{-}\eta^2\text{:}\eta^2\text{-HNNMe})]\text{OTf}$ (**6**) drawn with 50% ellipsoids.

Table S6. Selected Interatomic Distances (Å) and Bond Angles (deg) for **6**

	Molecule A		Molecule B
		Distances	
N1-N2	1.373(4)	N3-N4	1.365(5)
N1-C30	1.468(4)	N3-C61	1.470(5)
N2-H1	0.85(4)	N4-H2	0.66(5)
H1···O1	2.04(4)	H2···O4	2.41(5)
N2···S2	4.124(4)	N4···S4	3.947(4)
Fe1-N1	1.995(3)	Fe3-N3	1.980(3)
Fe2-N1	1.991(3)	Fe4-N3	1.971(3)
Fe1-N2	1.865(3)	Fe3-N4	1.868(4)
Fe2-N2	1.868(3)	Fe4-N4	1.867(4)
Fe1-S1	2.2449(12)	Fe3-S3	2.2548(12)
Fe2-S1	2.2460(11)	Fe4-S3	2.2551(11)
Fe1-Fe2	2.6264(9)	Fe3-Fe4	2.6340(9)
		Angles	
N1-Fe1-N2	41.51(13)	N3-Fe3-N4	41.42(14)
N1-Fe2-N2	41.54(13)	N3-Fe4-N4	41.55(15)
Fe1-N1-Fe2	82.45(11)	Fe3-N3-Fe4	83.64(11)
Fe1-N2-Fe2	89.44(14)	Fe3-N4-Fe4	89.69(17)
Fe1-S1-Fe2	71.58(3)	Fe3-S3-Fe4	71.47(4)
N2-N1-C30	119.1(3)	N4-N3-C61	120.2(3)
N1-N2-H1	108(3)	N3-N4-H2	109(5)

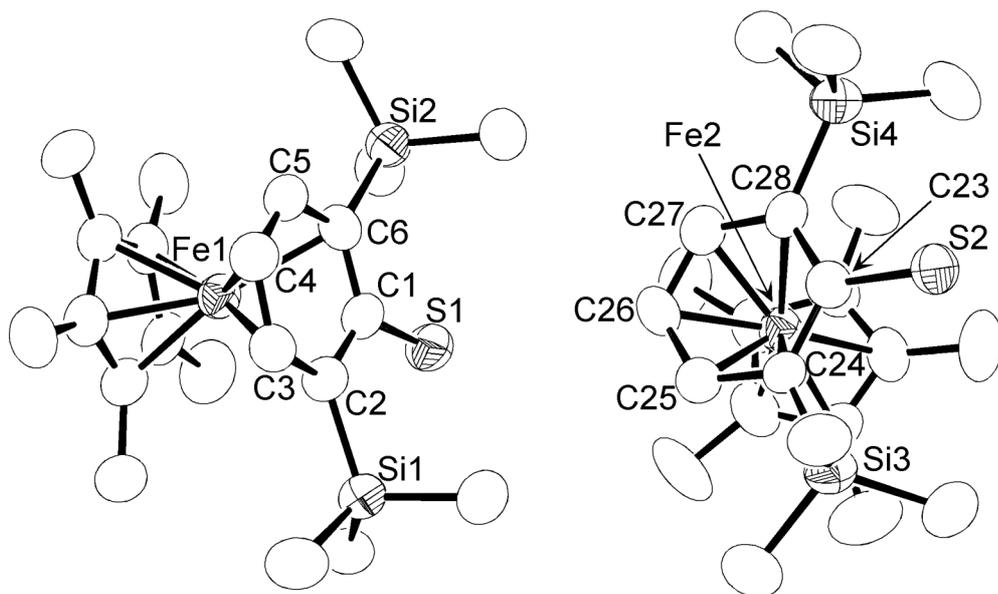


Figure S6. ORTEP view of $[\text{Cp}^*\text{Fe}(\eta^5\text{-Ar'S})]$ (7) with 50% ellipsoids.

Table S7. Selected Interatomic Distances (Å) for 7

	Molecule A		Molecule B
S1-C1	1.735(7)	S2-C23	1.721(7)
Fe1···C1	2.244(7)	Fe2···C23	2.246(6)
Fe1-C2	2.156(7)	Fe2-C24	2.156(7)
Fe1-C3	2.057(8)	Fe2-C25	2.058(7)
Fe1-C4	2.063(8)	Fe2-C26	2.044(7)
Fe1-C5	2.056(6)	Fe2-C27	2.061(7)
Fe1-C6	2.147(6)	Fe2-C28	2.161(7)