

C-H Bond Activation of Decamethylcobaltocene Mediated by a Nitrogenase Fe₈S₇ P-Cluster Model

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Supporting Information

General Procedures. All reactions and the manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. THF, toluene, and hexane were purified by the method of Grubbs, where the solvents were passed over columns of activated alumina and a supported copper catalyst supplied by Hansen & Co. Ltd. Deuterated solvents were dried by sodium (toluene-*d*₈) or molecular sieves (acetone-*d*₆) and distilled prior to use. ¹H and ¹³C{¹H} NMR spectra were acquired on a JEOL ECA-600. The proton and carbon signals were referenced to the residual signals of deuterated solvents. Infrared spectra were recorded on a JASCO FT/IR-410 spectrometer. Elemental analyses were performed on a LECO-CHNS-932 elemental analyzer where the crystalline samples were sealed in silver capsules under nitrogen. The cyclic voltammogram was recorded in THF using glassy carbon as the working electrode with 0.2 M (Bu₄N)(PF₆) as the supporting electrolyte. The potentials are referenced to Ag/AgNO₃ (0.01M AgNO₃ with 0.1M (Bu₄N)(PF₆) in CH₃CN). X-ray fluorescence microanalyses were performed on a Horiba Emax-5770W. X-ray diffraction data were collected on a Rigaku AFC8 or a Rigaku AFC10 equipped with a CCD area detector by using graphite-monochromated MoK α radiation. Cp*₂Co and [Cp*₂Co](PF₆) were purchased from Aldrich. Crystals of [Fe₄S₃{N(SiMe₃)₂}{SC(NMe₂)₂}]₂(μ_6 -S){ μ -N(SiMe₃)₂}(C₇H₈) (**1**·toluene) were prepared as reported previously.¹

Reaction of 1 with Cp*₂Co. A cooled (*ca.* -40 °C) THF (7 mL) solution of Cp*₂Co (59 mg, 0.180 mmol) was added via syringe to a THF (7 mL) solution of **1**·toluene (150 mg, 0.090 mmol) at -40 °C within one minute. After being stirred for 1 min, the reaction mixture was centrifuged at room temperature to remove a small amount of insoluble solid, and the supernatant was transferred into a Schlenk tube. The black solution was layered with hexane (20 mL). After standing at room temperature for several days, black plates of [Fe₄S₃{N(SiMe₃)₂}{(CH₂C₅Me₄)CoCp*}]₂(μ₆-S){μ-N(SiMe₃)}₂·3THF (**2**·3THF, 2.4 mg, 1.2 %) and a black powder precipitated. After removal of the supernatant, hexane was added into the Schlenk tube. The tube was shaken, and the black powder was taken out together with hexane by a syringe. After repeating this process (removal of the black powder) twice, the black plates were dried under vacuum. UV-vis (toluene, rt): λ_{max} = 277 (ε 93000), 323 (sh, ε 42000), 418 (sh, ε 20000) nm. IR (nujol): 1601(w), 1466(s), 1390(m), 1366(s), 1231(m), 952(w), 917(w), 795(w), 756(m), 699(m), 615(w). Cyclic Voltammogram (1 mM in THF, rt, potential vs Ag/Ag⁺): E_{1/2} = -1.68 V ([Fe₈S₇] core), E_p^c = -2.03 V ((CH₂C₅Me₄)CoCp* unit). Anal. Calcd for C₆₄H₁₃₀Co₂Fe₈N₄S₇Si₈: C, 39.03; H, 6.65; N, 2.85; S, 11.40. Found: C, 39.03; H, 6.60; N, 2.77; S, 11.49.

Synthesis of Cp*Co(η⁴-C₅Me₄CH₂) (3**).** A toluene solution of KN(SiMe₃)₂ (0.5 M, 0.42 mL, 0.21 mmol) was slowly added to a THF (6 mL) suspension of [Cp*₂Co](PF₆) (100 mg, 0.211 mmol) at -40 °C. After stirring for 1 hr at -40 °C, the solvent was removed under reduced pressure. The dark green residue was extracted with cold hexane (6 mL). The solution was centrifuged to remove an insoluble solid. The solvent was removed under reduced pressure to afford Cp*Co(η⁴-C₅Me₄CH₂) (**3**, 48 mg, 69 %) as a dark green powder. Complex **3** was found to decompose slowly at room temperature. ¹H NMR (toluene-d₈, -30 °C): δ 3.15 (brs, 2H, C₅Me₄CH₂), 1.56 (s, 6H, C₅Me₄CH₂), 1.39 (s, 15H, Cp*), 1.05 (s, 6H, C₅Me₄CH₂). ¹³C{¹H} NMR (toluene-d₈, -30 °C): δ 130.48 (C=CH₂), 81.94 (C₅Me₅), 80.06 (C₅Me₄CH₂), 62.83 (C₅Me₄CH₂), 52.95 (C=CH₂), 4.25 (C₅Me₄CH₂), 3.78 (C₅Me₄CH₂), 2.43 (C₅Me₅). Cyclic Voltammogram (1 mM in THF, rt, potential vs Ag/Ag⁺): E_{1/2} = -1.70, -2.91 V. Anal. Calcd for C₂₀H₂₉Co: C, 73.15; H,

8.90. Found: C, 73.18; H, 8.42.

Synthesis of Cluster 2 from the Reaction of 1 with 3. Complex **3** was prepared from the reaction of a THF (20 mL) suspension of $[\text{Cp}^*_2\text{Co}](\text{PF}_6)$ (149 mg, 0.314 mmol) and a toluene solution of $\text{KN}(\text{SiMe}_3)_2$ (0.5 M, 0.63 mL, 0.32 mmol) at $-40\text{ }^\circ\text{C}$, followed by evaporation at room temperature, extraction of the residue with hexane (7.5 mL), centrifugation, and removal of hexane under reduced pressure. A THF (2 mL) solution of **3** was added to a THF (4 mL) solution of **1**·toluene (260 mg, 0.156 mmol) in a Schlenk tube at room temperature with stirring. After addition of **3**, the stirring was stopped and the reaction mixture was allowed to stand for several minutes, and a black crystalline powder appeared from the reaction mixture. After removal of the supernatant, the crystalline powder was washed with hexane to afford **2**·3THF (205 mg, 60 %). The supernatant of the reaction mixture was layered with hexane (5 mL) and kept standing at room temperature to afford crystalline **2**·3THF (36 mg, 11 %). Total amount of **2**·3THF was 241 mg (71 %). The identity of **2**·3THF was confirmed by the elemental analysis of crystalline powder. Anal. Calcd for $\text{C}_{64}\text{H}_{130}\text{Co}_2\text{Fe}_8\text{N}_4\text{S}_7\text{Si}_8$: C, 39.03; H, 6.65; N, 2.85; S, 11.40. Found: C, 39.39; H, 6.85; N, 2.84; S, 11.73. Single crystals of **2**·3THF obtained from THF and hexane were also analyzed by X-ray crystallography.

Reaction of 1 with $[\text{Cp}^*_2\text{Co}](\text{PF}_6)$. To a THF (6 mL) solution of **1**·toluene (546 mg, 0.327 mmol) was added a THF (5 mL) suspension of $[\text{Cp}^*_2\text{Co}](\text{PF}_6)$ (103 mg, 0.217 mmol). After stirring for 20 hrs at room temperature, the solvent was removed under reduced pressure. The residue was washed with hexane (10 mL x 2) and THF (10 mL) to remove unreacted **1**. The residue was dried under vacuum to afford unreacted $[\text{Cp}^*_2\text{Co}](\text{PF}_6)$ (99 mg, 96 %), which was characterized by the ^1H NMR spectrum and the X-ray fluorescence microanalysis. ^1H NMR (acetone- d_6 , rt): δ 1.82. X-ray fluorescence microanalysis: Co:P:Fe:S = 1:1.1-1.4:0.15-0.19:0.19-0.30.

X-ray Structural Determination. Crystal data and refinement parameters of **2** are summarized in Table S1. Single crystals were coated with oil (Immersion Oil, type B: Code 1248, Cargill

Laboratories, Inc.) and mounted on loops. Diffraction data were collected at -100 °C under a cold nitrogen stream on a Rigaku AFC10 equipped with Saturn CCD detector and a graphite monochromatized MoK α source ($\lambda = 0.71070 \text{ \AA}$). Six preliminary data frames were measured at 0.5° increments of ω , to assess the crystal quality and preliminary unit cell parameters. The intensity images were also measured at 0.5° intervals of ω . The frame data were integrated using Rigaku/MSM CrystalClear program package, and the data sets were corrected for absorption using the REQAB program. The calculations were performed with the Rigaku/MSM CrystalStructure program package. The structure was solved by direct methods and refined by full-matrix least squares procedures on F^2 . Anisotropic refinement was applied to all non-hydrogen atoms except for crystal solvents (THF, refined isotopically). Anisotropic refinement of THF gave inappropriate thermal ellipsoids of carbon and oxygen atoms. All of the hydrogen atoms were placed at calculated positions. The atomic coordinates, bond distances, bond angles, torsion angles, and crystal data are available as a CIF file.

Table S1. Crystal Data for $[\text{Fe}_4\text{S}_3\{\text{N}(\text{SiMe}_3)_2\}\{(\text{CH}_2\text{C}_5\text{Me}_4)\text{CoCp}^*\}_2]_2(\mu_6\text{-S})\{\mu\text{-N}(\text{SiMe}_3)\}_2$ (**2** · 3THF)

	2 · 3THF
Formula	$\text{C}_{76}\text{H}_{154}\text{O}_3\text{S}_7\text{Si}_8\text{Co}_2\text{Fe}_8$
Formula wt (g mol^{-1})	2185.82
Crystal color	black
Crystal system	orthorhombic
Space group	<i>Pbca</i> (No. 61)
<i>a</i> (\AA)	30.522(9)
<i>b</i> (\AA)	19.523(6)
<i>c</i> (\AA)	35.204(10)
<i>V</i> (\AA^3)	20978(11)
<i>Z</i>	8
D_{calcd} (g cm^{-3})	1.384
<i>Max</i> 2θ ($^\circ$)	54.6
No. of Reflections Measured	
Total	188604
Unique	24003
No. of Parameters Refined	423
<i>R1</i> ($I > 2.00\sigma(I)$) ^a	0.0809
<i>wR2</i> (All reflections) ^b	0.1804
GOF on F^2 ^c	0.895

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ($I > 2\sigma(I)$). ^b $wR2 = [(\sum(w(|F_o| - |F_c|)^2) / \sum wFo^2)]^{1/2}$ (all reflections). ^c GOF = $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$ (where N_o = number of observations, N_v = number of variables).

Figure S1. Molecular structure of **2** with thermal ellipsoids at the 50 % probability level. The methyl groups of N(SiMe₃)₂ are omitted for clarity.

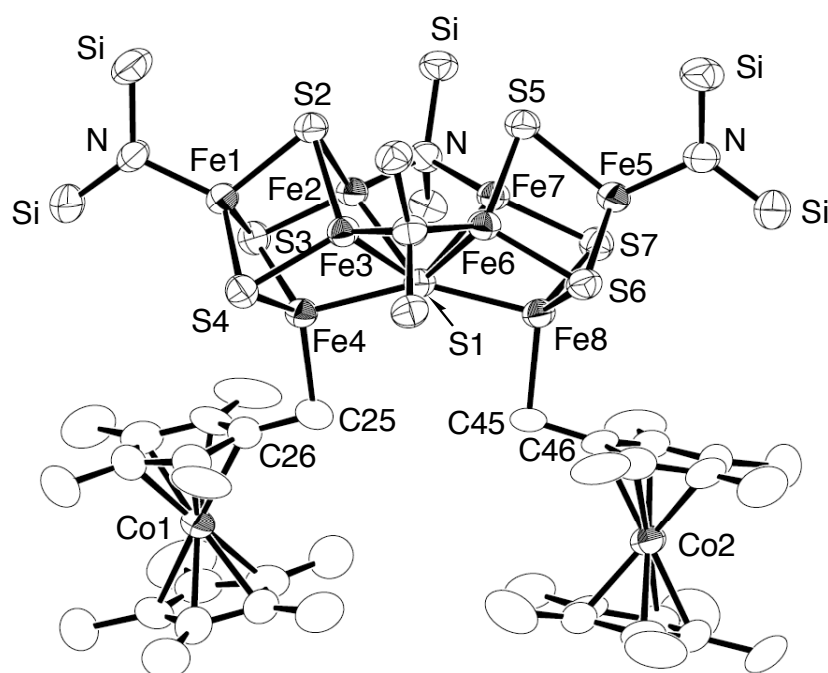
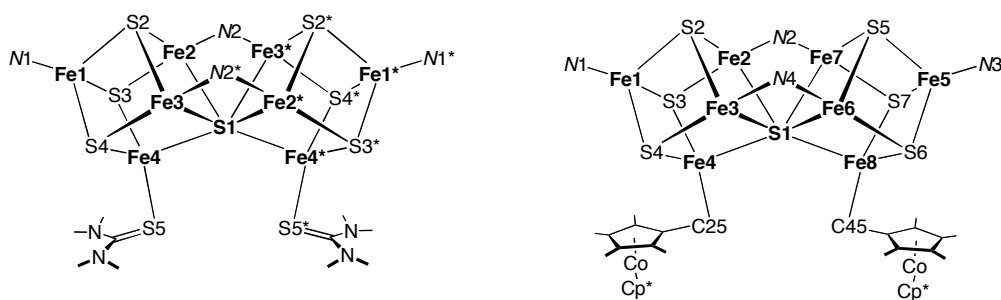


Table S2. Selected bond distances (Å) and angles (°) for **1** and **2**.^a



	1		2
Fe1-Fe2, Fe1-Fe3, Fe1-Fe4	2.8275(6), 2.8147(6), 2.7346(6)	Fe1-Fe2, Fe1-Fe3, Fe1-Fe4 Fe5-Fe6, Fe5-Fe7, Fe5-Fe8	2.7919(18), 2.7908(17), 2.7531(17) 2.7957(16), 2.7905(15), 2.7632(16)
Fe2-Fe3, Fe2-Fe4, Fe3-Fe4	2.7021(7), 2.6505(7), 2.6429(7)	Fe2-Fe3, Fe2-Fe4, Fe3-Fe4 Fe6-Fe7, Fe6-Fe8, Fe7-Fe8	2.6945(17), 2.6291(17), 2.6230(16) 2.6933(16), 2.6384(17), 2.6228(16)
Fe2-Fe3*, Fe3-Fe2*	2.7910(5)	Fe2-Fe7, Fe3-Fe6	2.7399(15), 2.7395(15)
Fe4-S1	2.3492(5)	Fe4-S1, Fe8-S1	2.381(2), 2.396(2)

Fe2-S1, Fe3-S1	2.3967(9), 2.3715(8)	Fe2-S1, Fe3-S1, Fe6-S1, Fe7-S1	2.415(2), 2.390(2) 2.421(2), 2.388(2)
Fe4-S5	2.3151(10)	Fe4-C25, Fe8-C45	2.126(7), 2.111(7)
Fe1-S2, Fe1-S3, Fe1-S4	2.2849(10), 2.2880(11), 2.2847(11)	Fe1-S2, Fe1-S3, Fe1-S4 Fe5-S5, Fe5-S6, Fe5-S7	2.269(2), 2.284(2), 2.307(2) 2.270(2), 2.292(2), 2.299(2)
Fe2-S2, Fe3-S2	2.2987(11), 2.2869(11)	Fe2-S2, Fe3-S2, Fe6-S5, Fe7-S5	2.287(2), 2.274(2) 2.288(2), 2.276(2)
Fe2-S3, Fe3-S4	2.3041(10), 2.2871(9)	Fe2-S3, Fe3-S4 Fe6-S6, Fe7-S7	2.274(2), 2.283(2) 2.277(2), 2.282(2)
Fe4-S3, Fe4-S4	2.2544(11), 2.2796(10)	Fe4-S3, Fe4-S4 Fe8-S6, Fe8-S7	2.277(2), 2.294(2) 2.283(2), 2.291(2)
Fe4-S1-Fe4*	143.61(6)	Fe4-S1-Fe8	150.67(9)
Fe2-S1-Fe3*, Fe3-S1-Fe2*	71.65(2)	Fe2-S1-Fe7, Fe3-S1-Fe6	69.56(6), 69.43(6)
S1-Fe4-S5	95.85(4)	S1-Fe4-C25, S1-Fe8-C45	98.4(2), 99.0(2)
Fe1-N1	1.921(2)	Fe1-N1, Fe5-N3	1.926(7), 1.918(6)
Fe2-N2, Fe3-N2	2.064(2), 2.064(2)	Fe2-N2, Fe7-N2 Fe3-N4, Fe6-N4	2.048(6), 2.059(6) 2.082(6), 2.054(6)
Fe2-N2-Fe3*	85.08(11)	Fe2-N2-Fe7, Fe3-N4-Fe6	83.7(2), 82.9(2)

^a Distances and angles for **1** were taken from reference 1.

Reference

1) Ohki, Y.; Sunada, Y.; Honda, M.; Katada, M.; Tatsumi, K. *J. Am. Chem. Soc.* **2003**, *125*, 4052-4053.