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C−H Bond Activation of Decamethylcobaltocene Mediated by a Nitrogenase Fe_8S_7 P-Cluster Model

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A C−H bond of Cp^*_2Co was found to be cleaved by a $[Fe_8S_7]$ cluster model of the nitrogenase P-cluster. This is the first example of C−H bond activation mediated by a biologically relevant Fe/S cluster. The reaction mechanism probably consists of electron transfer from Cp^*_2Co to the $[Fe_8S_7]$ cluster and subsequent proton abstraction by the reduced form of the cluster.

The P-cluster and the FeMo-cofactor in the MoFe protein of nitrogenase consist of unusual iron (molybdenum)−sulfide clusters, and the active sites are thought to play key roles in promoting the electron transfer and reduction of N_2.[1] Understanding these intriguing clusters and their functions has been a long-standing challenge for chemists. Although a good number of Mo(or V)/Fe/S and Fe/S clusters have been synthesized as structural models of the nitrogenase active sites, experimental demonstration of their reactivity, in particular that mimicking the enzymatic function, is still very limited. A breakthrough was made by Coucouvanis et al., who found that $[MFe_3S_4]$ (M = V, Mo) cubane clusters catalyze the reduction/hydrogenation of hydrazine and acetylene.[2] The intriguing electrochemical reduction of carbon dioxide mediated by $[Mo_2Fe_6S_8(SR)_9]^{3-}$ and $[Fe_4S_4(SR)_4]^{2-3}$ and the stoichiometric reduction of protons and acetylene by reduced $[Fe_4S_4(SR)_4]$ clusters have also been reported.[4] These reactions indicate that iron (molybdenum)−sulfide clusters may effect the reductive transformation of substrates by way of coupled electron- and proton-transfer steps, which are thought to be a common feature of reducing biocatalysts.[5]

As a result of our continuing research into the synthesis of iron (molybdenum)−sulfide clusters,[6] we reported isolation of the $[Fe_8S_7]$ cluster $[Fe_4S_3\{N(SiMe_3)_2\}\{SC(NMe_2)_2\}]_2(\mu_6\text{-}S)\{\mu\text{-}N(SiMe_3)\}_2$ (**1**),[6b] the core of which reproduces the reduced form of the P-cluster (P^N) in nitrogenase. Because the cluster core of **1** has two electrons less than that of P^N, the chemical reduction of **1** by decamethylcobaltocene was attemped.[7] Although isolation of a reduced species of **1** has not been successful, we have found that C−H bond activation of decamethylcobaltocene occurs, generating $[Fe_4S_3\{N(SiMe_3)_2\}\{(CH_2C_5Me_4)CoCp^*\}]_2(\mu_6\text{-}S)\{\mu\text{-}N(SiMe_3)\}_2$ (**2**). This paper reports the synthesis and structure of **2**, and a mechanism for the reaction is proposed.

A 1:2 mixture of **1** and decamethylcobaltocene (Cp^*_2Co; $Cp^* = \eta^5\text{-}C_5Me_5$) was held at −40 °C in tetrahydrofuran (THF) under a nitrogen atmosphere for 1 min. After centrifugal separation, hexane was added to the resulting supernatant, from which black plates of **2** (Scheme 1) grew and a black powder precipitated. The molecular structure of

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(7) Complex **1** shows two quasi-reversible redox couples at $E_{1/2} = -1.29$ and -1.69 V (vs Ag/Ag^+, THF), and the $Cp^*_2Co/Cp^*_2Co^+$ redox potential of -1.68 V (vs Ag/Ag^+, THF) is more negative than the first reduction potential of **1**. For the redox data of Cp^*_2Co, see: Connelly, N. G.; Gieger, W. E. *Chem. Rev.* **1996**, *96*, 877–910.

10.1021/ic900284f CCC: $40.75

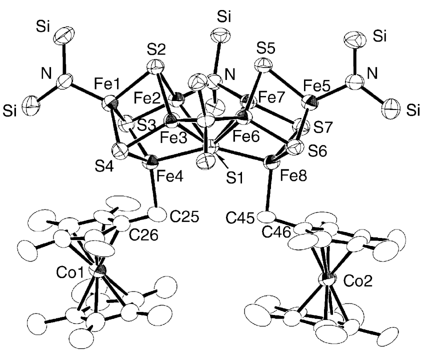
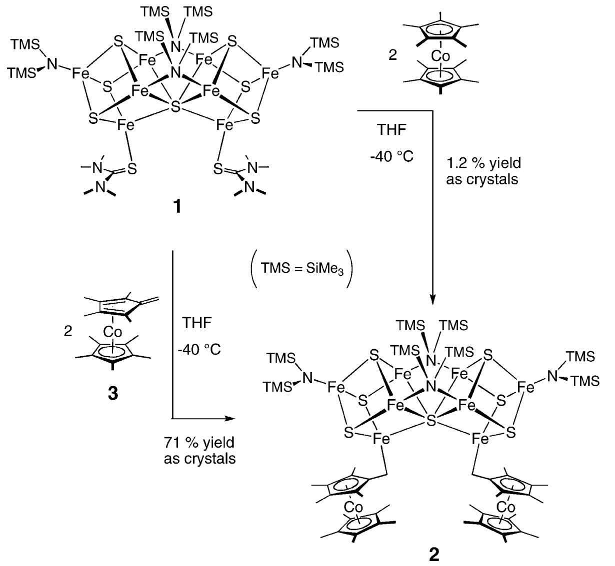


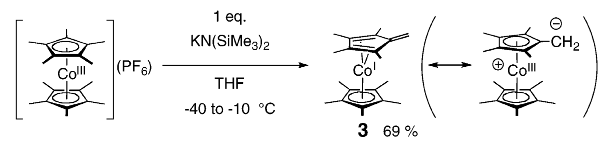
Figure 1. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. The methyl groups of $N(SiMe_3)_2$ are omitted for clarity.

Scheme 1



2·3THF was determined by X-ray crystallography (Figure 1). A striking aspect of the structure is that two decamethylcobaltocenyl groups are directly bound to the $[Fe_8S_7]$ skeleton via Fe−C bonds, as shown in Figure 1. The yield of crystalline **2** is low (1.2%), and sometimes separation of crystals from a black powder is difficult when crystals are small. Nevertheless, isolation of **2** provides the first example of C−H bond cleavage mediated by a biologically relevant Fe/S cluster. The $[Fe_8S_7]$ core geometry of **2** is very similar to that of **1**, while two decamethylcobaltocenyls replace the tetramethylthiourea $[SC(NMe_2)_2]$ ligands of **1** at Fe4 and Fe8. There are six ferrous and two ferric sites in the $[Fe_8S_7]$ core of **1**. If these oxidation states of the Fe atoms are to be retained in **2**, and then each decamethylcobaltocenyl is regarded as a neutral zwitterionic ligand, where the anionic center resides at the methylene carbon attached to iron with the cationic center at Co^{III}. The average distance from the Co atoms to the ring C atoms of the remote Cp* ligands is 2.047(16) Å, typical of that observed for structures of $Cp^*_2Co^{III+}$.[8] C−C distances in the Cp* ring that is bound to Fe show some fulvene character with bond distances of C25−C26 = 1.457(11) Å and C45−C46 = 1.457(12) Å. Within the $[Fe_8S_7]$ core, the mean Fe−Fe distance of **2** (2.719 Å) is slightly shorter than that of **1** (2.738 Å), while the mean Fe−S bond length, excluding the Fe−(μ_6-S) bonds, is comparable between **2** [2.284(2) Å] and **1** [2.2854(11) Å]. In contrast, the Fe−(μ_6-S) bonds of Fe4−S1 = 2.383(2) Å and Fe8−S1 = 2.396(2) Å are notably longer compared with the corresponding distance in **1** [2.348(2) Å], consistent with decamethylcobaltocenyl being a stronger donor than $SC(NMe_2)_2$. The Fe−CH_2 distances [2.110(8) and 2.127(7) Å] are longer than those in $FeCH_2Ar$ complexes [2.0414(18)−2.0683(17) Å][9] and are comparable to those in the fuluvene-bridged dinuclear iron complexes [$FeCH_2(\eta^5\text{-}C_5H_4)Fe$, 2.124−2.133(11) Å].[10] Elongation of the Fe−S1 bonds is accompanied by opening up of the Fe4−S1−Fe8 angle, 150.67(9)° (**2**) vs 143.61(6)° (**1**), and shortening of the Fe3−Fe6 and Fe2−Fe7 distances by 0.051−0.052 Å.

Scheme 2



Deprotonation of $[Cp^*CoCp]^+$ (Cp = η^5-C_5H_5) with $KN(SiMe_3)_2$ was reported to generate the tetramethylfulvene complex (η^4-$C_5Me_4CH_2$)CoCp as a thermally unstable product, which was characterized by ^1H and ^{13}C NMR.[11] Following this procedure, we synthesized an analogous tetramethylfulvene complex (η^4-$C_5Me_4CH_2$)CoCp* (**3**) by the reaction of $[Cp^*_2Co](PF_6)$ with $KN(SiMe_3)_2$, and **3** was isolated as a dark-green powder in 69% yield (Scheme 2). Like (η^4-$C_5Me_4CH_2$)CoCp, complex **3** was found to decompose gradually in solution at room temperature.

With the preformed tetramethylfulvene complex (**3**) in hand, we examined the reaction of **3** with $^1/_2$ equiv of **1** in THF. The thiourea ligands in **1** were readily replaced by **3**, and cluster **2** was isolated in 71% yield (Scheme 1). This result indicates that **3** may also be generated in the reaction of **1** with Cp^*_2Co, prior to the formation of **2**. On the basis of this assumption, we envisage the following mechanism for the C−H bond activation of Cp^*_2Co by **1**. The initial stage of the reaction probably involves the electron transfer from Cp^*_2Co to **1**, giving rise to $[Cp^*_2Co]^+$ and a “reduced cluster” such as $[\mathbf{1}]^-$, which we have not been able to isolate. Because **1** does not react with $[Cp^*_2Co]^+$ in THF, the abstraction of a proton from $[Cp^*_2Co]^+$ must be carried out by the more basic “reduced cluster”, presumably by an amide nitrogen or a thiolate/sulfide sulfur. Subsequently, thiourea of unreacted **1** is substituted by the resulting **3** to generate

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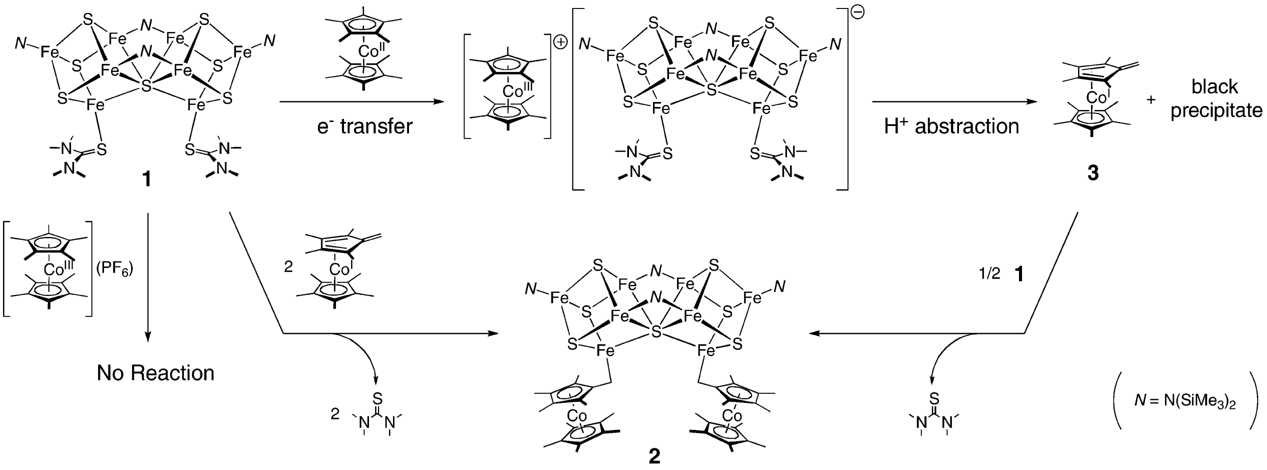
Scheme 3. Possible Mechanism for the Formation of **2**



2, while the reduced form of the Fe/S cluster degrades into an insoluble black powder after proton abstraction. The proposed reaction sequences are summarized in Scheme 3.

In summary, a C−H bond of Cp^*_2Co was cleaved by a $[Fe_8S_7]$ cluster model of the P-cluster core of nitrogenase. This is the first example of C−H bond activation mediated by a biologically relevant Fe/S cluster. The reaction mechanism probably consists of electron transfer from Cp^*_2Co to the $[Fe_8S_7]$ cluster and the subsequent proton abstraction by the reduced form of the cluster. Coupled electron/proton-transfer processes have been thought to be important in the biological function of metal−sulfur clusters, and our finding demonstrates that these cluster active sites of metalloenzymes may, in fact, activate substrates by such a mechanism.

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Supporting Information Available: Synthesis and spectroscopic data for **2** and **3** and a CIF file of the X-ray crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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