Published in final edited form as:

Organometallics. 2017 June 12; 36(11): 2054–2057. doi:10.1021/acs.organomet.7b00236.

Characterization of a Borane σ Complex of a Diiron Dithiolate: Model for an Elusive Dihydrogen Adduct

Noémie Lalaoui[†], Toby Woods[†], Thomas B. Rauchfuss^{*,†}, and Giuseppe Zampella[‡]

[†]School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801, United States

[‡]Department of Biotechnology and Biosciences, University of Milano-Bicocca, Piazza della Scienza 2, 20126-Milan, Italy

Abstract

The azadithiolate complex $\text{Fe}_2[(\text{SCH}_2)_2\text{NMe}](\text{CO})_6$ reacts with borane to give an initial 1:1 adduct, which spontaneously decarbonylates to give $\text{Fe}_2[(\text{SCH}_2)_2\text{NMeBH}_3](\text{CO})_5$. Featuring a Fe–H–B three-center, two-electron interaction, the pentacarbonyl complex is a structural model for H_2 complexes invoked in the [FeFe]-hydrogenases. The pentacarbonyl compound is a “ σ complex”, where a B–H σ bond serves as a ligand for iron. The structure of this σ complex was characterized by variable-temperature NMR spectroscopy and X-ray crystallography. Complementary to the 1:1 borane adduct is the quaternary ammonium complex $[\text{Fe}_2](\text{SCH}_2)_2\text{NMe}_2(\text{CO})_6^+$, which was also characterized. It represents a kinetically robust analogue of the N-protonated amine cofactor, as indicated by its mild reduction potential.

The production and oxidation of dihydrogen by the hydrogenase enzymes has attracted the attention of many researchers.^{1,3} Major efforts are aimed at elucidating the mechanisms of these processes by both the biophysical² and organometallic communities.^{3,4} Such studies obviously benefit from knowledge of the structure of catalyst with bound substrate. For the hydrogenases, the substrates are H^+ (bound as H^- , according to the usual organometallic formalism) and H_2 . The binding of hydride has been observed directly for the [NiFe]- H_2 ases^{2,5} and recently⁶ in the [FeFe]- H_2 ases.⁷

The binding of H_2 is assumed and invoked in all three hydrogenases ([FeFe], [NiFe], and [Fe]; Figure 1). Such enzyme–substrate intermediates have, however, never been observed. Although dihydrogen adducts have not been observed, we suggest that high rates of catalysis are achieved because weak substrate binding is compensated by rapid processing via PCET

*Corresponding Author: for T.B.R.: rauchfuz@illinois.edu.

Supporting Information: The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00236.

Notes: The authors declare no competing financial interest.

pathways uniquely available to protic substrates. Years of attempts^{3,8} in our and presumably other laboratories have failed to reveal dihydrogen adducts for any biomimetic active site model. We now describe the characterization of an approximate replica of these delicate species. It must be admitted at the outset that while this report focuses on derivatives of $\text{Fe}_2[(\text{SCH}_2)_2\text{NR}](\text{CO})_6$, the diiron site in the enzyme is much more complex, featuring two cyanide ligands, an attached [4Fe-4S] cluster and an unusual geometry at the substrate-binding (“distal”) Fe center.²

Our approach exploits reactivity inherent in the azadithiolate cofactor, which is known to be relatively basic and to participate in activation and production of H_2 . Since the amine in adt cofactor undergoes protonation,⁹ logically it should form adducts with boranes. Once formed, such adducts should convert to the σ complex with a B–H group occupying the apical site on the diiron complex, analogous to the behavior proposed for H_2 . We tested this idea by examining the reaction of a CH_2Cl_2 solution of $\text{Fe}_2[(\text{SCH}_2)_2\text{NH}](\text{CO})_6$ (**1**^H) with $\text{BH}_3\cdot\text{THF}$. Combining the borane and diiron reagents in an approximately 1:1 ratio resulted in a subtle lightening of the solution color. N-protonation also causes a slight bleaching.¹⁰ In the FT-IR spectrum, the ν_{CO} pattern remains constant, and the frequencies shift only ca. 10 cm^{-1} to higher energy. In contrast, protonation of **1**^H induces shifts of ν_{CO} bands more dramatically, by ca. 40 cm^{-1} .¹⁰ The small shifts induced by borane binding are consistent with the diminished Lewis acidity of BH_3 vs H^+ .¹¹ The ^{13}C NMR spectrum indicates that the CH_2 groups are shifted toward lower field (more deshielding), and the signal for the CO ligands is split, consistent with a desymmetrized structure (Figures S1 and S8 in the Supporting Information). The ^1H NMR chemical shifts are reminiscent of those for $\text{Me}_2\text{NH}\cdot\text{BH}_3$.¹² The structure of this adduct was confirmed crystallographically. The N-bonded BH_3 group occupies the equatorial site on the bicyclic $\text{Fe}_2(\text{SCH}_2)_2\text{NH}$ core, projecting away from the diiron center (Figure 2).

Addition of $\text{BH}_3\cdot\text{THF}$ to a solution of the tertiary amine $\text{Fe}_2[(\text{SCH}_2)_2\text{NMe}](\text{CO})_6$ (**1**^{Me}) proceeded similarly to the reaction of **1**^H. Upon standing for a few minutes, however, solutions of **1**^{Me} BH_3 darken, concomitant with a significant change in the IR spectrum (Figure 1). The contrasting lability of **1**^{Me} BH_3 vs **1**^H BH_3 is attributed to Thorpe–Ingold or gemdimethyl effects: i.e., larger substituents favor ring closure/chelation (Scheme 1).

Single-crystal X-ray diffraction shows that the compound derived from **1**^{Me} BH_3 is indeed the result of decarbonylation (Figure 3). The product is $\text{Fe}_2[(\text{SCH}_2)_2\text{NMe}\cdot\text{BH}_3](\text{CO})_5$ (**2**^{Me} BH_3). The molecule has crystallographically imposed Cs symmetry. One of the two apical CO ligands in **1**^{Me} BH_3 has been displaced by the borane. The Fe–CO and C–O distances indicate that the B–H ligand is an electron donor. Thus, the $(\text{Fe}–\text{CO})_{\text{avg}}$ distances are noticeably longer on the $\text{Fe}(\text{CO})_3$ site ($1.807(13)\text{ \AA}$) vs the $\text{Fe}(\text{CO})_2(\text{BH})$ site ($1.7661(10)\text{ \AA}$), and the $(\text{C}–\text{O})_{\text{avg}}$ distances ($1.1379(13)$ vs $1.1467(13)\text{ \AA}$) anti-correlate with these $(\text{Fe}–\text{C})_{\text{avg}}$ distances. Because the crystals were of exceptional quality, it is easy to discern that the coordinated B–H bond ($1.22(2)\text{ \AA}$) is $0.15\text{ \AA}$ longer than the two uncoordinated B–H bonds. This difference is consistent with a three-center, two-electron bond: i.e., **2**^{Me} BH_3 is a σ complex. The structure of **2**^{Me} BH_3 was also reproduced by DFT calculations with only small differences in bond lengths. The HOMO is localized on the Fe–

Fe bonding region. Although numerous organoiron complexes are active catalysts for the dehydrogenation of amine–boranes,^{11,13–19} no intermediates in such processes appear to have been isolated, much less characterized crystallographically. Several studies have examined distortions from the idealized C_{2v} core characteristic of $Fe_2(SR)_2(CO)_{6-x}L_x$ complexes.²⁰ Such distortions can be induced through the use of bulky dithiolate ligands of the type $[(SCH_2)_2CR_2]^{2-}$, where $R = Me, Et, etc.$ ^{21–25} Since $[(SCH_2)_2NMe \cdot BH_3]^{2-}$ and $[(SCH_2)_2CMe_2]^{2-}$ are nearly isostructural, the formation of $2^{Me}BH_3$ is proposed to arise via such a rotated intermediate (eq 1).

(1)

It is also instructive to contrast the Fe–H interactions in $2^{Me}BH_3$ with those seen in these same crowded diiron(I) dithiolates.^{21–25} In the latter complexes one apical coordination site on one Fe center is occupied weakly by one C–H substituent provided by the bulky dithiolate. In contrast to $2^{Me}BH_3$, these bulky compounds have semibridging CO ligands. In such bulky complexes, the Fe–H interaction is anagostic (electrostatic), whereas the Fe–H interaction in $2^{Me}BH_3$ is agostic-like.²⁶

The variable-temperature 1H NMR spectra of $2^{Me}BH_3$ proved informative (Figures S12 and S14 in the Supporting Information). The CH_2 signals remain diastereotopic up to 80 °C, indicating that the borane is not readily dissociating. In contrast the CH_2 signals in the amine 1^{Me} appear equivalent by 1H NMR spectroscopy at all temperatures. At –40 °C, the BH signals in $2^{Me}BH_3$ are resolved into 2:1 broadened singlets at δ 2.05 and –17.9, respectively. These signals are assigned to the uncoordinated and coordinated BH centers. The dynamic process that interchanges these sites is depicted in eq 2. The BH signals coalesce at 40 °C, consistent with the dynamic process in eq 2 with an activation energy near 13.6 kcal/mol.

(2)

Isostructural and isoelectronic with $1^{Me}BH_3$ is the quaternary ammonium complex $[Fe_2[(SCH_2)_2NMe_2](CO)_6]^+$ ($[1^{Me2}]^+$). The triflate salt of this cation was obtained in good yield by treatment of 1^{Me} with MeOTf (eq 3).

(3)

Isolated as an orange microcrystalline salt, this compound is the first quaternized adt derivative to be purified. The cation is of interest as a model for the N-protonated adt complexes. Whereas 2^{Me}BH_3 simulates aspects of H_2 activation, $[\mathbf{1}^{\text{Me}_2}]^+$ provides insight into the influence of N protonation on reduction. The quaternary ammonium ligand is a kinetically well-behaved analogue of the ammonium-containing adt cofactor. Cyclic voltammetry reveals that the redox properties of $[\mathbf{1}^{\text{Me}_2}]^+$ and $[\mathbf{1}^{\text{Me},\text{H}}]^+$ differ (Figure 4). These differences are attributed to the lability of the N-H bond in the tertiary ammonium salt.²⁷

In summary, the results presented here reveal new manifestations of amine-based reactivity in the azadithiolate diiron complexes. The species $[\text{Fe}_2[(\text{SCH}_2)_2\text{NMe}_2](\text{CO})_6]^+$ behaves as an aprotic analogue of the protonated adt complex, whereas $\text{Fe}_2[(\text{SCH}_2)_2\text{NMe}(\text{BH}_3)](\text{CO})_5$ is a model for the elusive H_2 adduct. Derivatives of the quaternary ammonium cation $[\mathbf{1}^{\text{Me}_2}]^+$ represent possible models for ammonium-containing intermediates,^{6,7} without the complication of the acidity of the N-H centers.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This project was supported by the National Institutes of Health through grant GM061153.

References

1. Cammack, R., Frey, M., Robson, R. *Hydrogen as a Fuel: Learning from Nature*. Taylor & Francis; London: 2001.
2. Lubitz W, Ogata H, Rüdiger O, Reijerse E. *Chem Rev*. 2014; 114:4081–4148. [PubMed: 24655035]
3. Schilter D, Camara JM, Huynh MT, Hammes-Schiffer S, Rauchfuss TB. *Chem Rev*. 2016; 116:8693–8749. [PubMed: 27353631]
4. Schollhammer, P., Weigand, W., editors. *Bioinspired Catalysis*. Wiley-VCH; Weinheim Germany: 2015.
5. Ogata H, Nishikawa K, Lubitz W. *Nature*. 2015; 520:571–574. [PubMed: 25624102]
6. Reijerse EJ, Pham CC, Pelmenschikov V, Gilbert-Wilson R, Adamska-Venkatesh A, Siebel JF, Gee LB, Yoda Y, Tamasaku K, Lubitz W, Rauchfuss TB, Cramer SP. *J Am Chem Soc*. 2017; 139:4306–4309.
7. Mulder DW, Guo Y, Ratzloff MW, King PW. *J Am Chem Soc*. 2017; 139:83–86. [PubMed: 27973768]
8. Tard C, Pickett CJ. *Chem Rev*. 2009; 109:2245–2274. [PubMed: 19438209]
9. Rauchfuss TB. *Acc Chem Res*. 2015; 48:2107–2116. [PubMed: 26079848]

10. Lawrence JD, Li H, Rauchfuss TB, Benard M, Rohmer MM. *Angew Chem Int Ed*. 2001; 40:1768–1771.
11. Staubitz A, Robertson APM, Sloan ME, Manners I. *Chem Rev*. 2010; 110:4023–4078. [PubMed: 20672859]
12. Nainan KC, Ryschkewitsch GE. *Inorg Synth*. 2007; 15:122–125.
13. Glueer A, Foerster M, Celinski VR, Schmedt auf der Guenne J, Holthausen MC, Schneider S. *ACS Catal*. 2015; 5:7214–7217.
14. Bhattacharya P, Krause JA, Guan H. *J Am Chem Soc*. 2014; 136:11153–11161. [PubMed: 25036653]
15. Vance JR, Robertson APM, Lee K, Manners I. *Chem - Eur J*. 2011; 17:4099–4103. [PubMed: 21387434]
16. Baker RT, Gordon JC, Hamilton CW, Henson NJ, Lin PH, Maguire S, Murugesu M, Scott BL, Smythe NC. *J Am Chem Soc*. 2012; 134:5598–5609. [PubMed: 22428955]
17. Lunsford AM, Blank JH, Moncho S, Haas SC, Muhammad S, Brothers EN, Darensbourg MY, Bengali AA. *Inorg Chem*. 2016; 55:964–973. [PubMed: 26716767]
18. Vance JR, Schafer A, Robertson APM, Lee K, Turner J, Whittell GR, Manners I. *J Am Chem Soc*. 2014; 136:3048–3064. [PubMed: 24527706]
19. Staubitz A, Robertson APM, Manners I. *Chem Rev*. 2010; 110:4079–4124. [PubMed: 20672860]
20. Filippi G, Arrigoni F, Bertini L, De Gioia L, Zampella G. *Inorg Chem*. 2015; 54:9529–9542. [PubMed: 26359661]
21. Jablonskyt A, Webster LR, Simmons TR, Wright JA, Pickett CJ. *J Am Chem Soc*. 2014; 136:13038–13044. [PubMed: 25116589]
22. Singleton ML, Bhuvanesh N, Reibenspies JH, Darensbourg MY. *Angew Chem Int Ed*. 2008; 47:9492–9495.
23. Hsieh CH, Erdem ÖF, Harman SD, Singleton ML, Reijerse E, Lubitz W, Popescu CV, Reibenspies JH, Brothers SM, Hall MB, Darensbourg MY. *Am Chem Soc*. 2012; 134:13089–13102.
24. Goy R, Bertini L, Görls H, De Gioia L, Talarmin J, Zampella G, Schollhammer P, Weigand W. *Chem - Eur J*. 2015; 21:5061–5073. [PubMed: 25689265]
25. Goy R, Bertini L, Elleouet C, Görls H, Zampella G, Talarmin J, De Gioia L, Schollhammer P, Apfel UP, Weigand W. *Dalton Trans*. 2015; 44:1690–1699. [PubMed: 25436832]
26. Brookhart M, Green MLH, Parkin G. *Proc Natl Acad Sci U S A*. 2007; 104:6908–6914. [PubMed: 17442749]
27. Bourrez M, Steinmetz R, Gloaguen F. *Inorg Chem*. 2014; 53:10667–10673. [PubMed: 25219687]

Scheme 1. Binding and Complexation of Borane in Diiron Azadithiolate Complexes

Figure 1. Proposed structures of H₂ adducts of the three hydrogenases

Figure 2.

Structure of $\text{Fe}_2[(\text{SCH}_2)_2\text{NH}\cdot\text{BH}_3](\text{CO})_6$ (1^{H}BH_3). Selected distances ($\text{\AA}$): Fe–Fe, 2.5033(7); (Fe1–S) $_{\text{avg}}$, 2.2520(9); (Fe2–S) $_{\text{avg}}$, 2.2554(10); S–C3, 1.822(4), N–CH₂, 1.479(4); N–B, 1.638(5); B–H ($\times 3$), 1.10(4)–1.19(4).

Figure 3.

(left) Structure of $\text{Fe}_2[(\text{SCH}_2)_2\text{NMe}\cdot\text{BH}_3](\text{CO})_5$ (2^{Me}BH_3). Selected distances ($\text{\AA}$): Fe–Fe, 2.5169(3); Fe1–S, 2.2514(3); Fe2–S, 2.2518(3); S–C3, 1.8097(10); N–C, 1.4948(12) - 1.5104(18); N–B, 1.619(2); B–H1a, 1.22(2); B–H (uncoordinated), 1.058(14), Fe(2)–H1a, 1.639(19) (right) HOMO (B3LYP) of 2^{Me}BH_3 .

Figure 4. Cyclic voltammetry of 3.7 mM of $\mathbf{1}^{\text{Me}}$ (black), $[\mathbf{1}^{\text{MeH}}]\text{BF}_4$ (red), and $[\mathbf{1}^{\text{Me}_2}]\text{OTf}$ (blue) in MeCN with 0.125 M Bu_4NPF_6 electrolyte (100 mV s^{-1} scan rate).