Published in final edited form as:

J Inorg Biochem. 2007 November ; 101(11-12): 1748–1751.

Extending the motif of the [FeFe]-hydrogenase active site models: Protonation of $\text{Fe}_2(\text{NR})_2(\text{CO})_{6-x}\text{L}_x$ species

Phillip I. Volkers and Thomas B. Rauchfuss*

Department of Chemistry, University of Illinois, 601 S. Goodwin Ave., Urbana, IL 61801, USA

Abstract

Studies on diiron dithiolato complexes have proven fruitful for modeling the active site of the [FeFe]-hydrogenases. Here we present a departure from the classical Fe_2S_2 motif by examining the viability of Fe_2N_2 butterfly compounds as functional models for the diiron active site of [FeFe]-hydrogenases. Derivatization of $\text{Fe}_2(\text{BC})(\text{CO})_6$ (**1**, BC = benzo-[c]-cinnoline) with PMe_3 affords $\text{Fe}_2(\text{BC})(\text{CO})_4(\text{PMe}_3)_2$, which subsequently undergoes protonation at the Fe–Fe bond. The hydride $[(\mu\text{-H})\text{Fe}_2(\text{BC})(\text{CO})_4(\text{PMe}_3)_2]\text{PF}_6$ was characterized crystallographically as the C_{2v} isomer. It represents a rare example of a hydrido diiron complex that exists as observable isomers, depending on the location of the phosphine ligands – diapical and apical–basal. This hydride catalyzes the electrochemical reduction of protons.

Keywords

Fe complexes; Metal hydride; Hydrogenase; Electrocatalysis

In recent years, many compounds of the type $\text{Fe}_2(\text{S-R})_2(\text{CO})_4\text{L}_2$ have been prepared and examined as structural and functional models for the active site of [FeFe]-hydrogenases. Particular emphasis has been placed on variations of L, especially tertiary phosphines [1–3], but also isocyanides [4,5], *N*-heterocyclic carbenes [6–9], and cyanide [10–13]. While much effort has focused on functionalizing the dithiolate ligand [14–20], relatively little work has examined the possibility of replacing the thiolates with other bridging groups [21]. Best and coworkers demonstrated that the corresponding phosphides $\text{Fe}_2(\text{PR}_2)_2(\text{CO})_6$ and $[\text{Fe}_2(\text{PR}_2)_2(\text{CO})_6\text{H}]^-$ are effective catalysts for hydrogen evolution [22].

Incentives for broadening the range of bridging ligands include changing the steric profile of the catalysts, altering the susceptibility of the bridge toward electrophilic attack (important since these catalysts function in acidic media), incorporating functionality, and manipulating the electronic character (basicity, $E_{1/2}$) of the metals. Naturally, a fundamental motivation for investigating new bridging ligands is to elucidate the elementary design rules that will lead to greater mechanistic insight and, ultimately, a deeper understanding of hydrogenogenesis.

Approximately 15 nitrogenous bridges are known to link pairs of iron centers, giving complexes of the general formula $\text{Fe}_2(\text{NR}_{1,2})_2(\text{CO})_6$ (Scheme 1). Many of the complexes were first reported in the 1960s and 1970s in an era where the interactions of nitrene-forming reagents and metal carbonyls were first systematized. We selected one representative of this series, $\text{Fe}_2(\text{BC})(\text{CO})_6$ [23–26] (**1**, where BC = benzo-[c]-cinnoline, $\text{N}_2\text{C}_{12}\text{H}_8$, Scheme 1) to examine as a candidate for a new model class for [FeFe]-hydrogenases. In a structural sense, **1** differs significantly from the well-studied $\text{Fe}_2(\text{SR})_2(\text{CO})_6$ motif. For this reason we felt that its

*Corresponding author. E-mail address: rauchfuz@uiuc.edu (T.B. Rauchfuss).

properties would test most demandingly the scope of the hydrogenase behavior of the $\text{Fe}_2(\mu\text{-X})_2\text{L}_n$ systems ($\text{L} = \text{CO}$, donor ligands). This report summarizes these results, which indeed demonstrate the prospect that many nitrogenous bridging ligands could be applied to the modeling of hydrogenases.

Compound **1** was prepared using the original method, using $\text{Fe}_3(\text{CO})_{12}$ in place of $\text{Fe}(\text{CO})_5$ [27]. As for other donor ligands [26,28], PMe_3 displaced two of the CO ligands in **1** to afford the red-colored $\text{Fe}_2(\text{BC})(\text{CO})_4(\text{PMe}_3)_2$ (**2**) (Eq. (1)).¹ **1** is noticeably more electrophilic than analogous diiron dithiolates; disubstitution of the dithiolate system requires more demanding conditions (e.g. 80 °C for 9 h vs. 25 °C for 1.5 h). The BC ligand is apparently robustly attached since it was not displaced by the highly nucleophilic PMe_3 ligand.

Encouraged by the stability of the BC ligand towards nucleophiles, we examined cyanide derivatives. Treatment of **1** with two equiv. Et_4NCN indeed afforded the dicyanide complex $[\text{Fe}_2(\text{BC})(\text{CO})_4(\text{CN})_2]^{2-}$ as indicated by IR spectroscopy (MeOH: $\nu_{\text{CN}} = 2106$; $\nu_{\text{CO}} = 2039$, 2020, 1998, 1968, 1938, 1879, 1814 cm^{-1}). The appearance of numerous carbonyl bands is attributed to the presence of multiple isomers in solution, as also observed in phosphine derivatives discussed below. The dicyanide product proved to be unstable, even in the solid state. A stable monocyano derivative was prepared via the reaction of **1** with $\text{KN}(\text{SiMe}_3)_2$ [11]. Similarly, treatment of **1** with Me_3NO gave the MeCN complex $\text{Fe}_2(\text{BC})(\text{CO})_5(\text{MeCN})$ ($\nu_{\text{CO}} = 2043$, 2030, 1976, 1964, 1913 cm^{-1}) [29], which was found to react with Et_4NCN to afford $\text{Et}_4\text{N}[\text{Fe}_2(\text{BC})(\text{CO})_5(\text{CN})]$, as indicated by IR spectroscopy and ESI-MS.²

It was of interest to determine if the diiron azo system **2** could be protonated at the Fe–Fe bond and, if so, would the resulting hydride electrocatalyze proton reduction, analogous to the reactivity observed in $\text{Fe}_2(\text{SR})_2$ systems [29–31]. Indeed, we found that HCl effected protonation at the Fe–Fe bond of **2**, thereby forming a rare example of a (μ -hydrido)diiron azo system, $[\text{2H}]^+$.³ The complex was isolated as its PF_6^- salt from $\text{H}_2\text{O}/\text{MeOH}$ solution [32]. Interestingly, protonation of **2** afforded *two* solution isomers (Scheme 2), as indicated by doublet-of-doublet (unsymmetrical isomer) and triplet (symmetrical isomer) ^1H NMR signals for the hydride, in a ratio of 1.0:1.8, respectively. In contrast, protonation of $\text{Fe}_2(\text{S}_2\text{C}_2\text{H}_4)$

¹ $\text{Fe}_2(\text{N}_2\text{C}_{12}\text{H}_8)(\text{CO})_4(\text{PMe}_3)_2$, **2**. A red solution of 500 mg (1.09 mmol) of **1** in 25 mL of toluene was treated with approximately 700 μL (6.76 mmol) of PMe_3 . IR measurements indicated that the reaction was complete within 1.5 h at room temperature. The resulting deeper red solution was filtered through a plug of Celite and evaporated in vacuo. The product was precipitated twice from a toluene solution by addition of hexanes at 0 °C, washed twice with 5 mL of hexanes at 0 °C, and dried in vacuo. Yield: 317 mg (52%). ^1H NMR (500 MHz, CD_3CN): δ 7.757–7.739, 7.166–7.133, 7.068–7.050 (m, m, m, 8H, $\text{N}_2\text{C}_{12}\text{H}_8$), 1.065–1.049 (d, 18H, $\text{P}(\text{CH}_3)_3$). ^{31}P NMR (202 MHz, CD_3CN): δ 13.725 (s). IR (toluene): $\nu_{\text{CO}} = 1984$ (vs), 1976 (m), 1938 (s), 1915 (vs), 1900 (m), 1887 (w) cm^{-1} . FD-MS: $m/z = 556.0$ (100%, M^+). Anal. Calcd. for $\text{C}_{22}\text{H}_{26}\text{Fe}_2\text{N}_2\text{O}_4\text{P}_2$: C, 47.52; H, 4.71; N, 5.04. Found: C, 47.37; H, 4.64; N, 5.03.

² $\text{Et}_4\text{N}[\text{Fe}_2(\text{N}_2\text{C}_{12}\text{H}_8)(\text{CO})_5(\text{CN})]$. A slurry of 150 mg (0.326 mmol) of **1** in 10 mL of MeCN was treated with a solution of 24 mg (0.326 mmol) of Me_3NO in 5 mL of MeCN. A hazy, deep red solution formed within 5 min. Treatment of the $\text{Fe}_2(\text{N}_2\text{C}_{12}\text{H}_8)(\text{CO})_5(\text{MeCN})$ solution ($\nu_{\text{CO}} = 2043$, 2030, 1976, 1964, 1913 cm^{-1}) with a solution of 51 mg (0.326 mmol) of Et_4NCN in 3 mL of MeCN resulted in a deepening of the red color. After 1 h, solvent was removed in vacuo. The product was purified by precipitation from concentrated THF solutions by addition of hexanes. The resulting oil solidified upon trituration with hexanes. Yield: 132 mg (69%). IR (MeCN): $\nu_{\text{CN}} = 2093$ (w), $\nu_{\text{CN}} = 2025$ (vs), 1960 (vs), 1945 (vs), 1902 (m) cm^{-1} .

³ $[(\mu\text{-H})\text{Fe}_2(\text{N}_2\text{C}_{12}\text{H}_8)(\text{CO})_4(\text{PMe}_3)_2]\text{PF}_6$, $[\text{2H}]\text{PF}_6$. A slurry of 113 mg (0.203 mmol) of **2** in 2 mL of MeOH was treated with 1.5 mL of concentrated HCl to afford an orange–red solution within 5 min. After 1 h, the solution was treated with 2 mL of saturated aqueous NH_4PF_6 , which precipitated an orange solid. The solid was washed with H_2O , dried in vacuo, and washed with Et_2O (3×5 mL). The product was recrystallized three times from CH_2Cl_2 solution by addition of hexane, washed with C_6H_{14} , and dried in vacuo. Yield: 98 mg (69%). Single crystals were grown from $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$. Anal. Calcd. for $\text{C}_{22}\text{H}_{27}\text{F}_6\text{Fe}_2\text{N}_2\text{O}_4\text{P}_3$: C, 37.64; H, 3.88; N, 3.99. Found: C, 37.42; H, 3.97; N, 3.94. ^1H NMR (500 MHz, CD_3CN): δ 8.061–8.042, 7.520–7.468, 7.306–7.287 (m, m, m, 8H, $\text{N}_2\text{C}_{12}\text{H}_8$), 1.637 (d, 2H, $\text{J}_{\text{PH}} = 10.5$ Hz, unsym $\text{P}(\text{CH}_3)_3$), 1.059 (d, 2H, $\text{J}_{\text{PH}} = 10.9$ Hz, unsym $\text{P}(\text{CH}_3)_3$), 1.014 (d, 18H, $\text{J}_{\text{PH}} = 10.5$ Hz, sym $\text{P}(\text{CH}_3)_3$), –15.479 (dd, 0.09H, $\text{J}_{\text{PH}} = 8$ Hz, $\text{J}_{\text{P'H}} = 26.5$ Hz, unsym ($\mu\text{-H}$) Fe_2), –15.621 (t, 0.73H, $\text{J}_{\text{PH}} = 9$ Hz, sym ($\mu\text{-H}$) Fe_2). ^{31}P NMR (162 MHz, CD_3CN): δ 26.636 (d, 1P, unsym PMe_3), 23.805 (s, 4P, sym PMe_3), 20.299 (s, 1P, unsym PMe_3). IR (MeCN): $\nu_{\text{CO}} = 2048$ (s), 2024 (m), 1985 (s) cm^{-1} . ESI-MS: $m/z = 557.2$ (100%, M^+), 529 (3%, $\text{M}^+ - \text{CO}$), 501 (2%, $\text{M}^+ - 2\text{CO}$).

$(\text{CO})_4(\text{PMe}_3)_2$ and $\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_4(\text{PMe}_3)_2$ gives only a trans-dibasal isomer, even at low temperatures [32]. Also, $(\mu\text{-H})\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_4(\text{CN})(\text{PMe}_3)$ exists as only one predominant isomer [1]. The only case where multiple isomers have been detected was in $[(\mu\text{-H})\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_4(\text{CN})_2]^-$, which was not isolated but characterized in solution [32].

The structure of the major (symmetrical) isomer was confirmed crystallographically (Fig. 1). Both PMe_3 ligands were found to be in the apical position, *i.e.* trans to the hydride. For comparison, diiron dithiolate bis(phosphine) complexes rarely adopt a diapical structure, *e.g.* $\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_4(\text{PMe}_2\text{Ph})_2$ [3], and examples are not known of protonated (*i.e.* $\mu\text{-hydride}$) species exhibiting diapical phosphine ligands.

Selected parameters derived from crystallographic measurements of $[\text{2H}]\text{PF}_6$ and Darensbourg's $[(\mu\text{-H})\text{Fe}_2(\text{S}_2\text{C}_2\text{H}_4)(\text{CO})_4(\text{PMe}_3)_2]\text{PF}_6$ [2], featuring trans-dibasal phosphine ligands, are listed in Table 1. Comparing these data, significant differences are observed only for the Fe–E (where E = N or S) distances and angles. Similar to other diiron azo complexes, $[\text{2H}]^+$ exhibits shorter distances to iron than do thiolate ligands. The most striking difference between the Fe_2N_2 and Fe_2S_2 butterfly cores is the E–Fe–E angle, wherein the N–Fe–N angle is $\sim 40^\circ$ more acute than the S–Fe–S angle. The short Fe–N distances and the small N–Fe–N angles are compensated by expanded Fe–N–Fe angles, thereby minimizing any effect on the Fe–Fe distance. Indeed, all Fe–ligand distances are virtually identical for the azo- and dithiolato-bridged systems. Thus, the structural similarities between the azo and dithiolate systems indicate the promise of a still wider range of bridging ligands in catalysts that effect hydrogenogenesis.

We confirmed that $[\text{2H}]^+$ catalyzes hydrogen evolution from *p*-toluenesulfonic acid (HOTs) via experiments conducted electrochemically. The cathodic current at ~ -1.1 V vs. Ag/AgCl grew proportionally with additional equivalents of HOTs until *ca.* 4 equiv., at which stage $[\text{2H}]^+$ decomposes (Fig. 2). The overpotential of electrocatalysis is virtually identical to that observed for diiron dithiolate systems under the same reaction conditions.

The substitutional behavior of the diiron azo complexes bears both similarities and differences with the more commonly studied dithiolate complexes. Both the azo- and thiolato-bridged species undergo a maximum of disubstitution with conventional unidentate ligands. The Fe_2N_2 system differs significantly from the well-studied $\text{Fe}_2(\text{SR})_2$ system in terms of the rates of substitution and the isomeric content. As shown by Ellgen, the activation enthalpies for substitution of $\text{Fe}_2(\text{BC})(\text{CO})_6$ are *ca.* 2 kcal/mol more favorable relative to the corresponding dithiolato complexes [26,33]. It is significant that $[(\mu\text{-H})\text{Fe}_2(\text{S}_2\text{C}_n\text{H}_{2n})(\text{CO})_4(\text{PMe}_3)_2]^+$ exists as only one isomer, but the BC analogue also features the diapical isomer. This difference highlights the significant influence of the steric properties of the bridging ligands on the apical coordination sites trans with respect to the Fe–Fe bond. This steric interaction is greater when the two iron centers are bridged by three ligands, as in complexes of the type $[\text{Fe}_2(\text{SR})_2(\mu\text{-X})\text{L}_6]^z$ (X = CO, H).

Taking advantage of the fact that $[\text{2H}]\text{PF}_6$ crystallizes as a single isomer, we dissolved crystals of this compound in CD_3CN at 0°C to obtain the spectrum of this isomer. Indeed the solution exhibited one triplet in the hydride region of the ^1H NMR spectrum. Over a period of minutes, this symmetrical complex isomerized via a 1st order process to an equilibrium mixture of symmetrical and unsymmetrical isomers. The stability of multiple isomers is consistent with the minimal steric pressure exerted by the planar BC ligand on the ligands that occupy the apical sites. As we have discussed previously, protonation narrows the distance between apical ligands and the bridging ligand, which usually destabilizes large apical ligands [34]. Another case where multiple isomers of a substituted $\mu\text{-hydride}$ have been observed is $[(\mu\text{-H})\text{Fe}_2(\text{S}_2\text{C}_3\text{H}_6)(\text{CO})_4(\text{CN})_2]^-$, which features the small cyanide ligands in the apical position.

In summary, a new class of [FeFe]-hydrogenase active site models, based on a Fe₂N₂ butterfly core, has been established. These diiron azo compounds catalyze the electrochemical reduction of protons to H₂. Although the catalysts based on BC are less robust than the dithiolate complexes, there is considerable scope for improvement. A wide range of azo-bridged diiron complexes is known [24,27,35–37], including ligands such as chloro-substituted BC [27], the sterically imposing 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) [26,38], and PhN(X)NPh (where X = CO, SO₂) [39–41].

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

This work was supported by the United States National Institutes of Health.

References

1. Gloaguen F, Lawrence JD, Rauchfuss TB, Bénard M, Rohmer MM. *Inorg Chem* 2002;41:6573–6582. [PubMed: 12470052]
2. Zhao X, Georgakaki IP, Miller ML, Mejia-Rodriguez R, Chiang CY, Darensbourg MY. *Inorg Chem* 2002;41:3917–3928. [PubMed: 12132916]
3. Li P, Wang M, He C, Li G, Liu X, Chen C, Åkermark B, Sun L. *Eur J Inorg Chem* 2005:2506–2513.
4. Lawrence JD, Rauchfuss TB, Wilson SR. *Inorg Chem* 2002;41:6193–6195. [PubMed: 12444758]
5. Boyke CA, Rauchfuss TB, Wilson SR, Rohmer MM, Benard M. *J Am Chem Soc* 2004;126:15151–15160. [PubMed: 15548012]
6. Tye JW, Lee J, Wang HW, Mejia-Rodriguez R, Reibenspies JH, Hall MB, Darensbourg MY. *Inorg Chem* 2005;44:5550–5552. [PubMed: 16060601]
7. Capon J-F, El Hassnaoui S, Gloaguen F, Schollhammer P, Talarmin J. *Organometallics* 2005;24:2020–2022.
8. Duan L, Wang M, Li P, Na Y, Wang N, Sun L. *Dalton Trans* 2007:1277–1283. [PubMed: 17372642]
9. Morvan D, Capon J-F, Gloaguen F, Le Go A, Marchivie M, Michaud F, Schollhammer P, Talarmin J, Yaouanc J-J, Pichon R, Kervarec N. *Organometallics* 2007;26:2042–2052.
10. Schmidt M, Contakes SM, Rauchfuss TB. *J Am Chem Soc* 1999;121:9736–9737.
11. Lyon EJ, Georgakaki IP, Reibenspies JH, Darensbourg MY. *Angew Chem, Int Ed Engl* 1999;38:3178–3180. [PubMed: 10556894]
12. Le Cloirec A, Davies SC, Evans DJ, Hughes DL, Pickett CJ, Best SP, Borg S. *Chem Commun* 1999:2285–2286.
13. Razavet M, Borg SJ, George SJ, Best SP, Fairhurst SA, Pickett CJ. *Chem Commun* 2002:700–701.
14. Li H, Rauchfuss TB. *J Am Chem Soc* 2002;124:726–727. [PubMed: 11817928]
15. Lawrence JD, Li H, Rauchfuss TB. *Chem Commun* 2001:1482–1483.
16. Lawrence JD, Li H, Rauchfuss TB, Benard M, Rohmer M-M. *Angew Chem, Int Ed Engl* 2001;40:1768–1771. [PubMed: 11353506]
17. Jiang S, Liu J, Shi Y, Wang Z, Åkermark B, Sun L. *Dalton Trans* 2007:896–902. [PubMed: 17297518]
18. Song L-C, Tang M-Y, Su F-H, Hu Q-M. *Angew Chem, Int Ed* 2006;45:1130–1133.
19. Volkers PI, Rauchfuss TB, Wilson SR. *Eur J Inorg Chem* 2006:4793–4799.
20. Stanley JL, Rauchfuss TB, Wilson SR. *Organometallics* 2007;26:1907–1911.
21. Das P, Capon JF, Gloaguen F, Pétillon FY, Schollhammer P, Talarmin J, Muir KW. *Inorg Chem* 2004;43:8203–8205. [PubMed: 15606156]
22. Cheah MH, Borg SJ, Bondin MI, Best SP. *Inorg Chem* 2004;43:5635–5644. [PubMed: 15332815]
23. Herberhold M, Leonhard K. *J Organomet Chem* 1974;78:253–263.
24. Herberhold M, Leonhard K, Wagner U, Wagner FE, Danon J. *J Chem Soc, Dalton Trans* 1979:654–657.

25. Doedens RJ. *Inorg Chem* 1970;9:429–436.
26. Ellgen PC, Gerlach JN. *Inorg Chem* 1974;13:1944–1947.
27. Bennett RP. *Inorg Chem* 1970;9:2184–2186.
28. Ellgen PC, McMullin SL. *Inorg Chem* 1973;12:2004–2007.
29. Gloaguen F, Lawrence JD, Schmidt M, Wilson SR, Rauchfuss TB. *J Am Chem Soc* 2001;123:12518–12527. [PubMed: 11741415]
30. Gloaguen F, Lawrence JD, Rauchfuss TB. *J Am Chem Soc* 2001;123:9476–9477. [PubMed: 11562244]
31. Chong D, Georgakaki IP, Mejia-Rodriguez R, Sanabria-Chinchilla J, Soriaga MP, Darensbourg MY. *Dalton Trans* 2003:4158–4163.
32. Zhao X, Georgakaki IP, Miller ML, Yarbrough JC, Darensbourg MY. *J Am Chem Soc* 2001;123:9710–9711. [PubMed: 11572707]
33. Ellgen PC, Gerlach JN. *Inorg Chem* 1973;12:2526–2532.
34. Justice AK, Linck RC, Rauchfuss TB. *Inorg Chem* 2006;45:2406–2412. [PubMed: 16529459]
35. Bjorsvik HR, Gonzalez RR, Liguori L. *J Org Chem* 2004;69:7720–7727. [PubMed: 15498002]
36. Aime S, Gervasio G, Milone L, Rossetti R, Stanghellini PL. *J Chem Soc, Dalton Trans* 1978:534–540.
37. Dahl LF, Costello WR, King RB. *J Am Chem Soc* 1968;90:5422–5429.
38. Little RG, Doedens RJ. *Inorg Chem* 1972;11:1392–1397.
39. Hansert B, Vahrenkamp H. *J Organomet Chem* 1993;459:265–269.
40. Kabir SE, Ruf M, Vahrenkamp H. *J Organomet Chem* 1996;512:261–263.
41. Kabir SE, Ruf M, Vahrenkamp H. *J Organomet Chem* 1998;571:91–96.

Fig. 1. Two views of the structure of the cation in $[(\mu\text{-H})\text{Fe}_2(\text{N}_2\text{C}_{12}\text{H}_8)(\text{CO})_4(\text{PMe}_3)_2]\text{PF}_6$ with thermal ellipsoids set at the 50% probability level.

Fig. 2.
Cyclic voltammograms vs. Ag/AgCl of **2** + x HOTs, $x = 0-3$ equiv., in MeCN with Bu₄NPF₆.

Scheme 1.

Generalized structures of azodiiron carbonyl complexes and the structure of **1**.

Scheme 2.

Protonation reaction of **2** to form [2H]⁺.

Table 1Selected distances (Å) and angles (deg) for [2H]PF₆ and [(μ-H)Fe₂(S₂C₂H₄)(CO)₄(PMe₃)₂]PF₆

[2H]PF ₆		[(μ-H)Fe ₂ (S ₂ C ₂ H ₄)(CO) ₄ (PMe ₃) ₂]PF ₆	
Fe–Fe	2.5599(8)	2.5742(13)	Fe–Fe
Fe–H	1.62(3)	1.69(6)	Fe–H
Fe–P _{apical}	2.2362(12)	2.2392(16)	Fe–P _{basal}
Fe–C	1.774(4)	1.770(6)	Fe–C
Fe–N	1.927(5)	2.2562(6)	Fe–S
N–N	1.399(4)	2.924	S–S
Fe–N–Fe	82.99(11)	69.57(5)	Fe–S–Fe
N–Fe–N	42.53(11)	80.78(6)	S–Fe–S
C–Fe–P	90.46(15)	94.8(4)	C–Fe–P