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Article

CO-Migration in the Ligand Substitution Process of the Chelating Diphosphite Diiron Complex $(\mu\text{-pdt})[Fe(CO)_3][Fe(CO)\{(EtO)_2PN(Me)P(OEt)_2\}]$

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Selective synthetic routes to isomeric diiron dithiolate complexes containing the $(EtO)_2PN(Me)P(OEt)_2$ (PNP) ligand in an unsymmetrical chelating role, for example, $(\mu\text{-pdt})[Fe(CO)_3][Fe(CO)(\kappa^2\text{-PNP})]$ (**3**) and as a symmetrically bridging ligand in $(\mu\text{-pdt})(\mu\text{-PNP})[Fe(CO)_2]_2$ (**4**), have been developed. **3** was converted to **4** in 75% yield after extensive reflux in toluene. The reactions of **3** with PMe_3 and $P(OEt)_3$ afforded bis-monodentate P-donor complexes $(\mu\text{-pdt})[Fe(CO)_2PR_3][Fe(CO)_2(PNP)]$ ($PR_3 = PMe_3$, **5**; $P(OEt)_3$, **7**), respectively, which are formed via an associative PMe_3 coordination reaction followed by an intramolecular CO-migration process from the $Fe(CO)_3$ to the Fe(CO)(PNP) unit with concomitant opening of the Fe−PNP chelate ring. The PNP−monodentate complexes **5** and **7** were converted to a trisubstituted diiron complex $(\mu\text{-pdt})(\mu\text{-PNP})[Fe(CO)PR_3][Fe(CO)_2]$ ($PR_3 = PMe_3$, **6**; $P(OEt)_3$, **8**) on release of 1 equiv CO when refluxing in toluene. Variable-temperature ^{31}P NMR spectra show that trisubstituted diiron complexes each exist as two configuration isomers in solution. All diiron dithiolate complexes obtained were characterized by MS, IR, NMR spectroscopy, elemental analysis, and X-ray diffraction studies.

Introduction

The synthesis and reactivity of diiron dithiolate carbonyl complexes have been a current highlight in the field of bioinorganic chemistry due to the resemblance of their simple structures to the active site of [FeFe]-hydrogenases.[1,2] The readily accessible edt (ethane-1,2-dithiolato), pdt (propane-1,3-dithiolato), and adt (2-aza-propane-1,3-dithiolato) -bridged all-CO diiron complexes have been extensively studied. To adjust the electron density and the protophilicity of the iron centers, strong donor ligands, such as CN^-,[3–5] PR_3,[6–9] CNR,[10,11] and N-heterocyclic carbene (NHC) ligands,[12–15] were introduced to the diiron centers by CO-displacement. All of the disubstituted diiron complexes derived from all-CO complexes have general formulas of $[(\mu\text{-S})_2R][Fe(CO)_2L]_2$ ($R = CH_2CH_2$, $CH_2CH_2CH_2$, $CH_2NR'CH_2$) and $[(\mu\text{-S})_2R][Fe(CO)_2L][Fe(CO)_2L']$, where the two non-CO ligands are separately coordinated to the two vicinal iron atoms of the model complex.[3–12] Limited examples concerning diiron dithiolate complexes coordinated by chelating bidentate ligands were reported before 2007.[16,17] Density functional theory (DFT) calculations by Hall et al. suggest that unsymmetric substitution of diiron model complexes might facilitate the formation of a rotated structure similar to that of the active site in the reduced state of the enzyme.[18] In support of this prediction were several subsequent publications concerning unsymmetrically disubstituted [2Fe2S] model complexes $(\mu\text{-pdt})[Fe(CO)_3][Fe(CO)(L{-}L)]$ ($L{-}L = NHC_{MePy}$ (1-methyl-3-(2-pyridyl)imidazol-2-ylidene), NHC_{diPic} (1,3-bis(2-picolyl)imidazol-2-ylidene),[14] $I_{Me}{-}CH_2{-}I_{Me}$ (I_{Me} = 1-methylimidazol-2-ylidene),[15] 1,10-phenanthroline,[19] dppe ($Ph_2PCH_2CH_2PPh_2$),[20] dppv (*cis*-$Ph_2PCH{=}$

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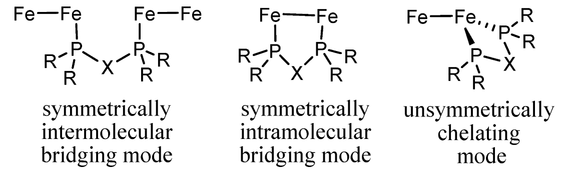

Figure 1. Three possible coordination modes for CO displacement of diiron complexes by bidentate R_2PXPR_2; other ligands are omitted for clarity.

$CHPPh_2$),[21,22] dppm ($Ph_2PCH_2PPh_2$), dppp ($Ph_2P(CH_2)_3$-PPh_2), $Ph_2PCH_2C(CH_3)(CH_2PPh_2)CH_2PPh_2$, *o*-$(PPh_2)_2C_6H_4$,[23] and $RN(PPh_2)_2$),[24] which indeed display some characteristics in electrochemistry and protonation and that contrast to symmetrically disubstituted diiron complexes.

As described in the literature, there are three possible coordination modes for diphosphine or diphosphite R_2PXPR_2 acting as bidentate ligands in diiron complexes. They are shown in Figure 1 as (i) a symmetrically intermolecular bridging (spanning) mode,[17,25,26] (ii) a symmetrical intramolecular bridging mode,[16,26,27] and (iii) an unsymmetrical chelating mode (to a single iron) (Figure 1).[16,17,19–24] Selective preparation of these coordination isomers and the chemistry of unsymmetric diphosphine diiron complexes are of particular interest as these unsymmetric [2Fe2S] complexes might become attractive functional models of the [FeFe]−hydrogenase active site.

For some time, we have investigated the CO displacement of [(μ-pdt)$Fe_2(CO)_6$] with a diphosphite ligand $(EtO)_2$-$PN(Me)P(OEt)_2$ (PNP). The N-bridged diphosphine and phosphite ligands are particularly interesting as they feature chelating ability with hydrophilic and basic sites deemed to be valuable for functional modes of $H_2 \leftrightarrow 2H^+ + 2e$.[28–30]

Here, we describe the selective preparation of two isomeric diiron dithiolate complexes, an unsymmetrically chelating complex (μ-pdt)[Fe(CO)$_3$][Fe(CO)(κ^2-PNP)] (**3**), and a symmetrically bridging complex (μ-pdt)(μ-PNP)[Fe(CO)$_2$]$_2$ (**4**). An interesting result is the swift migration of a CO ligand from the Fe(CO)$_3$ to the Fe(CO)(κ^2-PNP) unit in the reactions of **3** and monodentate phosphine and phosphite ligands, to afford bis-monodentate complexes (μ-pdt)[Fe(CO)$_2$-PR_3][Fe(CO)$_2$(PNP)] (PR_3 = PMe_3, **5**; P(OEt)$_3$, **7**), which are further converted to trisubstituted diiron complexes (μ-pdt)(μ-PNP)[Fe(CO)PR_3][Fe(CO)$_2$] (PR_3 = PMe_3, **6**; P(OEt)$_3$, **8**) after refluxing in toluene for 72 h. During the course of our preparation for this manuscript, a paper appeared in *Inorganic Chemistry*[31] describing a similar CO migration of unsymmetrically substituted diiron dithiolate complexes to the corresponding symmetric isomers in the electrochemical reduction process. The CO migration reported herein is simply promoted by PMe_3- and P(OEt)$_3$-coordination, and the diphosphite-monodentate diiron complexes **5** and **7**, supposed as intermediates in the isomerization of unsymmetrically to symmetrically diphosphite-substituted complexes, were successfully isolated and structurally characterized.

Results and Discussion

Selective Preparation of 3 and 4. Diiron dithiolate complexes (μ-SR)$_2$[Fe(CO)$_3$][Fe(CO){κ^2-$Ph_2PN(Et)PPh_2$}] (R = Me, Et) and (μ-SR)$_2${μ-$Ph_2PN(Et)PPh_2$}[Fe(CO)$_2$]$_2$ were prepared and identified by IR and ^{1}H NMR spectroscopies more than 30 years ago.[16] The pdt-bridged diiron dithiolate complexes (μ-pdt)[Fe(CO)$_3$][Fe(CO){$Ph_2PN(R)$-PPh_2}] (R = *i*Pr, allyl) were recently reported.[24] In addition to the inherent features of diphosphines such as the rigidity and steric effect of the backbone, the reaction temperature and the initial stoichiometry of the diphosphine can influence the coordination mode of the diphosphine ligand in the substitution reaction. De Beer et al. reported the reaction of (μ-SR)$_2Fe_2(CO)_6$ (R = Me, Et) and the ligand $Ph_2PN(Et)PPh_2$ gave unsymmetrically chelating diiron complexes (μ-SR)$_2$[Fe(CO)$_3$][Fe(CO){κ^2-$Ph_2PN(Et)PPh_2$}] as sole products.[16] Despite attempts to ensure the same conditions, in

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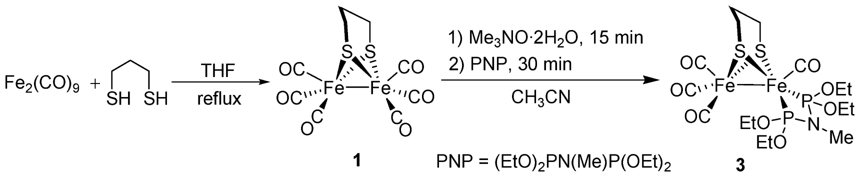
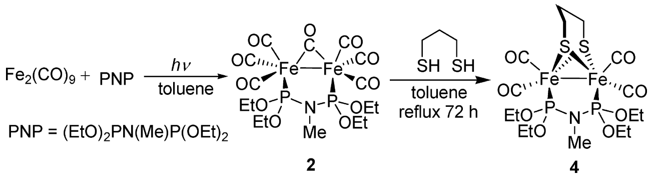
Scheme 1



Scheme 2



our studies the reaction of (μ-pdt)$Fe_2(CO)_6$ and PNP yielded a mixture of isomers **3** and **4**. Therefore, alternate synthetic routes were followed in attempts to optimize yields of each product. Unsymmetrically PNP-chelating diiron complex **3** and the symmetrically PNP-bridged isomer **4** can be prepared by introducing μ-pdt and PNP ligands to the iron carbonyl complex $Fe_2(CO)_9$ in different orders. **3** was prepared in a satisfactory yield by treating (μ-pdt)$Fe_2(CO)_6$ with PNP in the presence of the CO-removing reagent $Me_3NO \cdot 2H_2O$ in CH_3CN at room temperature (Scheme 1). The structural isomer of **3**, for example, the PNP-bridged diiron complex **4**, was not detected in the IR spectrum of the mother solution. **4** was prepared exclusively in a good yield according to the synthetic route of Scheme 2 from a known PNP-bridged diiron complex **2**.[32] Complexes **3** and **4** are air stable in the solid state and stable in solution under an N_2 atmosphere at room temperature; however, at elevated temperature, **3** converts to **4**.

Substitution of 3 by L (L = PMe_3, $P(OEt)_3$). As revealed by X-ray analysis, the active site of the [FeFe] hydrogenases has a diiron tricarbonyl unit that can be described as [(μ-$SCH_2)_2X$][$Fe_2(CO)_3L_2LH_n$] ($n = 0, 1$).[1,2] Although a number of disubstituted diiron(I) dithiolate complexes are known,[3–10,13–27,34–36] only a few trisubstituted [2Fe2S] complexes have been reported. The usual preparation is via irradiation of a benzene solution of (μ-SR)$_2Fe_2(CO)_6$ in the presence of an excess of phosphine ligand.[16] In general, the symmetrically disubstituted diiron(I) complexes are inert toward further substitution under mild conditions. To the best of our knowledge, the complexes (μ-edt)[Fe(CO)$_2$L][Fe(CO)(κ^2-dppv)]$^{n-}$ (dppv = *cis*-$Ph_2PCH{=}CHPPh_2$, $n = 0$, $L = PMe_3$; $n = 1$, L = CN^-), reported by Rauchfuss and co-workers very recently,[21,22] are the only crystallographically characterized trisubstituted diiron(I) dithiolate complexes with the exception of a diiron complex with a triphosphine chelating ligand.[33]

To develop hydrogenase active site mimics of trisubstituted diiron(I) dithiolate complexes with the general formula (μ-pdt)$Fe_2(CO)_3$(L^L)(L′), we tried to introduce another PR_3 ligand to **3**. The reaction of **3** with 1 equiv of PMe_3 in CH_3CN or in toluene was finished in a few minutes at room temperature to give an unexpected PNP−monodentate complex (μ-pdt)[Fe(CO)$_2$PMe$_3$][Fe(CO)$_2$(PNP)] (**5**). The observed high yield of this reaction implied quantitative transfer of one CO ligand from the Fe(CO)$_3$ in **3** to the Fe(CO)(κ^2-PNP) unit. The attack of the incoming ligand PMe_3 exclusively takes place at the Fe(CO)$_3$ unit of **3**, and one phosphorus donor of the chelating PNP ligand, rather than the CO ligand in the Fe(CO)$_3$, dissociates from the other iron center. Such CO migration in diiron complexes has been previously observed in the CN^-/CO substitution of [$Fe_2(CO)_5\{CH_3SCH_2C(CH_3)(CH_2S)_2\}$] and in the electrochemical reduction of [(μ-$SCH_2)_2X$][Fe(CO)$_3$][Fe(CO)(κ^2-dppe)] (X = CH_2, NR).[31,34] The rate of this reaction contrasts to that reported for the dppv unsymmetrically disubstituted diiron complex (μ-edt)[Fe(CO)$_3$][Fe(CO)(dppv)],[21] where one of the CO ligands acts as leaving ligand and complete substitution requires more than 10 h. When the PMe_3 reaction with **3** was carried out in refluxing toluene, the ν(CO) IR monitor showed that **3** first converted to **5** and then to the trisubstituted complex **6** (μ-pdt)(μ-PNP)[Fe(CO)PMe$_3$][Fe(CO)$_2$] after 72 h. The pendant terminal (P(OEt)$_2$) of the PNP in **5** is recoordinated to the other iron atom to form **6** with an intramolecular PNP bridge (Scheme 3). **6** could not be obtained by the CO-displacement of **4** with PMe_3 at room temperature or in refluxing toluene.

The poorer nucleophile, $P(OEt)_3$ resulted in slower CO displacement on reaction with **3**, and emphasized the need for more stringent conditions. A moderate yield (77%) of (μ-pdt)[Fe(CO)$_2$P(OEt)$_3$][Fe(CO)$_2$(PNP)] (**7**) was obtained after 3 h in refluxing CH_3CN. Subsequently, trisubstituted complex **8** was obtained after refluxing **7** in toluene for 72 h (Scheme 3).

For the conversion of **3** to **5** in CH_3CN, the IR monitor showed that the further substitution of **3** by PMe_3 took place in an almost identical rate under N_2 or CO atmosphere. This result indicates that the first step of the reaction does not occur via a CO-dissociation mechanism, consistent with earlier studies that established a bimolecular kinetic rate expression for such substitution.[35–37] DFT calculations suggest that the presence of a chelating ligand in an unsymmetrically substituted diiron dithiolate complex could lower the barrier to the rotation of the Fe(CO)$_3$ unit.[18,21] According to the results obtained and the conclusion of DFT

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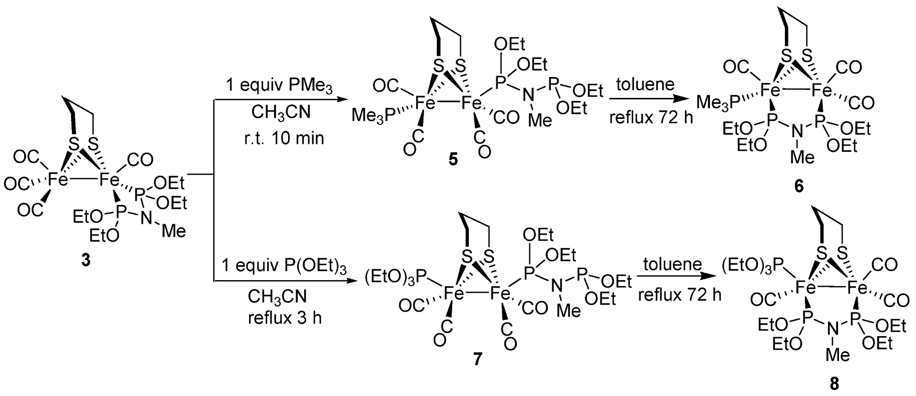
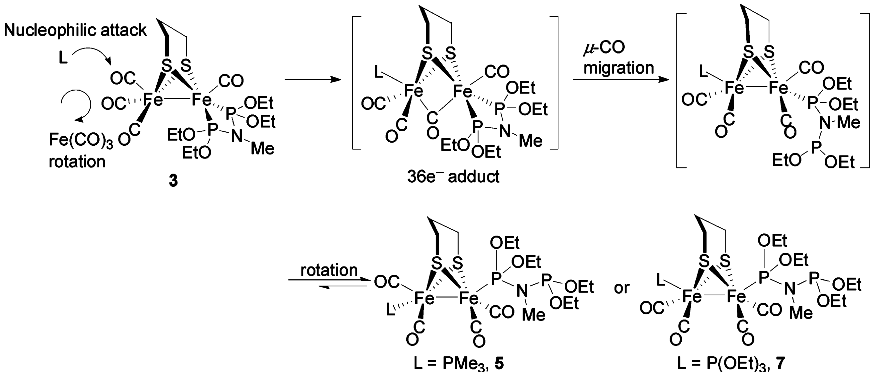
Scheme 3



Scheme 4. Nucleophilic Attack/CO Rotation Coupled Mechanism



calculations, a reasonable mechanism for the CO migration during the substitution of **3** by phosphine and phosphite ligands is proposed in Scheme 4. A concerted process of the turnstile rotation of the Fe(CO)$_3$ subunit and the PR$_3$ coordination is involved in the first step, namely, flexibility of the pseudo square pyramidal S$_2$Fe(CO)$_3$ site permits easy access to a conformation that accommodates the incoming ligand, concomitant with formation of a μ-CO bridge or semibridge.[34,37] The following step in the mechanism is similar to that suggested for the substitution of (μ-edt)[Fe(CO)$_3$][Fe(CO)(dppv)], that is, loss of CO from the 36 e$^-$ adduct affords the normal CO-displacement product. In the proposed mechanism given in Scheme 4, the hemilability of the chelating PNP ligand results in disassociation of one phosphorus donor from the Fe(CO)(κ^2-PNP) unit, permitting transfer of CO from one iron to the second via a bridging CO intermediate. Presumably, relief of the strained four-membered FePNP ring in the electron rich 36e$^-$ adduct accounts for this hemilability and the capture of the open site by the migrating μ-CO conversion results in the observed product. Concomitantly, the Fe−Fe bond is fully reformed, and the molecule reaches its stable configuration by a subsequent turnstile rotation of each Fe(CO)$_2$L unit.

Attempts to observe a transient μ-CO species by in situ (REACTIR) monitoring (−40 and −78 °C) were unsuccessful, presumably due to the short lifetime of the μ-CO intermediate caused by the steric interaction between the bridging CO ligand and the chelating PNP ligand in the 36e$^-$ intermediate. The in situ IR spectra of the reaction solution of **3** and PMe$_3$ display only the ν_{CO} bands of the starting **3** and product **5** (Figure S1 in the Supporting Information). The substitution reaction of **3** by PMe$_3$ was also explored under a ^{13}CO atmosphere to further distinguish whether a dissociative or associative mode is operative in the reaction. The IR monitor revealed exclusive formation of **5**, and no ^{13}CO labeled species was detected. The result is consistent with the much greater nucleophilicity of PMe$_3$ than exogenous CO and indicates that phosphine coordination and CO migratory substitution take place in a coupled mechanism. It should be noted that the open site generated by CO or phosphite dissociation through thermal or photochemical means could be trapped by ^{13}CO to produce detectable ^{13}CO labeled species (Experimental Section).

Table 1. Comparison of ν_{CO} Bands of **3**−**8** and Related Diiron Complexes[a]

complex	ligand(s)	ν_{CO} (cm^{-1})
3	κ^2-PNP	2019, 1939, 1908
4	μ-PNP	2000, 1966, 1930
5	PNP, PMe$_3$	1985, 1946, 1920, 1899
6	μ-PNP, PMe$_3$	1965, 1905, 1878
7	PNP, P(OEt)$_3$	2001, 1960, 1940, 1921
8	μ-PNP, P(OEt)$_3$	1970, 1916
9[b]	P(OEt)$_3$	2046, 1989, 1936
10[c]	P(OEt)$_3$, PMe$_3$	1991, 1949, 1907
11[b]	2 P(OEt)$_3$	2002, 1960, 1935

[a] In CH$_3$CN solution. [b] Ref. 8. [c] Ref. 9.

Spectroscopic Characterization of 3−8. Complexes **3**−**8** were characterized by IR, MS, ^{1}H and ^{31}P NMR spectroscopy, and elemental analysis. The IR data of the ν_{CO} bands for **3**−**8** are listed in Table 1 together with the ν_{CO} data of (μ-pdt)[Fe(CO)$_2$P(OEt)$_3$][Fe(CO)$_2$L] (L = CO, **9**; PMe$_3$, **10**; P(OEt)$_3$, **11**).[8,9] The low-energy absorption at 1908 cm^{-1} for

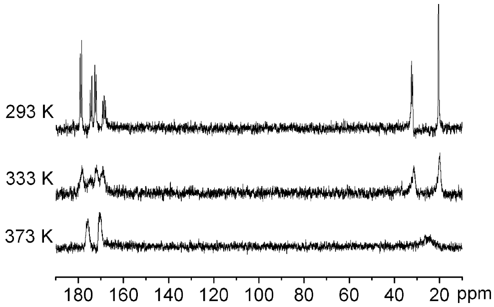
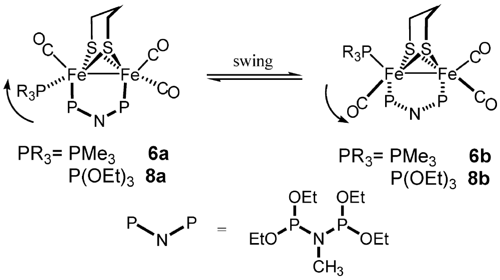


Figure 2. ^{31}P NMR spectra of **6** in DMSO at 293 (top), 333 (middle), and 373 K (bottom).

Scheme 5



3 is attributed to the single CO ligand in the Fe(CO)(κ^2-PNP) unit. A comparison of the ν_{CO} data of **3** with those of **4**, **7**, and **11** shows that the highest energy ν_{CO} band for **3** is higher than the corresponding bands displayed by the symmetrically disubstituted diiron complexes, whereas both frequencies of the second and the third ν_{CO} bands of **3** are apparently lower than the corresponding ν_{CO} frequencies of **4**, **7**, and **11**. Further interpretation of these spectroscopic results require computations, which are at this time unavailable.

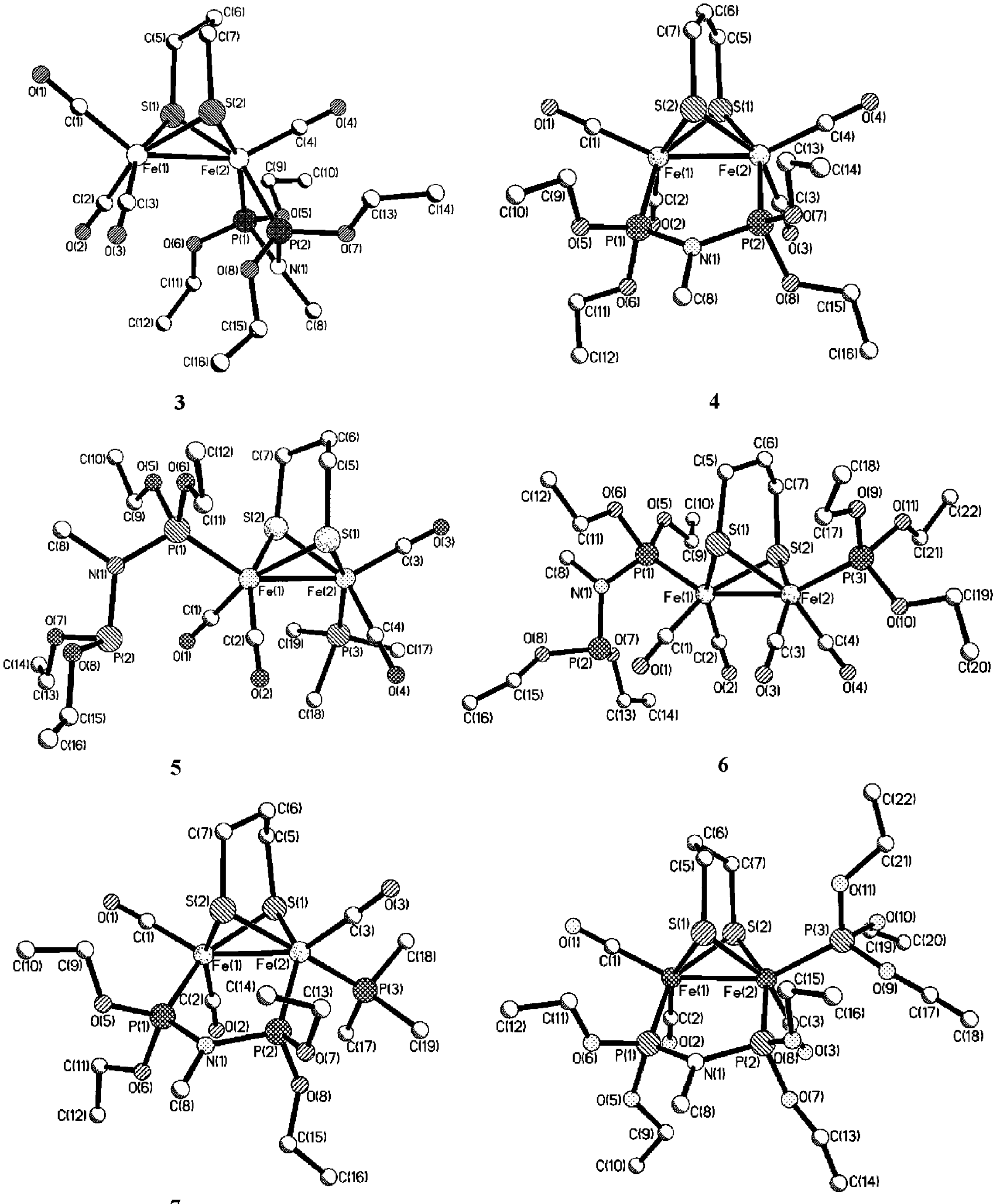
At 293 K in $CDCl_3$ solution, **3** and **4** display a single ^{31}P NMR resonance at δ 139.5 and δ 172.6, respectively. The observation of a single resonance of **4** indicates that the irondithiolatohexane-like (FeS_2C_3) ring is rapidly interconverting on the NMR time scale. **5** displays three signals, a singlet at δ 26.9 for PMe_3, a doublet at δ 144.4 for the uncoordinated $P(OEt)_2$ terminal, and another doublet at 179.5 for the coordinated $P(OEt)_2$ terminal. The analogous **7** shows a doublet at δ 144.4 and a doublet of doublets at δ 179.8 for the monodentate PNP ligand with almost identical chemical shifts as for **5**, along with a doublet at δ 175.8 for $P(OEt)_3$.

6 displays six ^{31}P signals at 293 K, two doublets at δ 32.3 and 20.1 for PMe_3, a doublet of doublet at δ 168.6, and three doublets at δ 180.0, 176.3, and 175.3 for PNP (Figure 2, 293 K). As the $Fe_2S_2C_3$ ring flip is rapid at 293 K for **4**, we assume the same applies to **6**. Therefore, the additional resonances are indicative of two configuration isomers (Scheme 5) for the trisubstituted complex in an approximate ratio of 1.7:1. There are six doublets in the ^{31}P NMR spectrum of **8** (Figure S2 in the Supporting Information) at 293 K, giving a further support for existence of two configuration isomers for such triphosphine-substituted diiron complexes. The four doublets in the region of δ 181.2−177.7 are attributed to the bridging PNP ligand, and the other two doublets at δ 175.5 and 174.8 are assigned to the $P(OEt)_3$ ligand. The approximate ratio of two configuration isomers is 1.5:1.

Variable-temperature ^{31}P NMR spectra of **6** measured in the range of 293−373 K in DMSO show that the line shape and the number of the ^{31}P signals are temperature dependent (Figure 2). The six ^{31}P signals of **6** change to two broad signals at δ 175.6 and 170.3 for the μ-PNP and a bump at δ 24.0 for PMe_3 as the measuring temperature increases from 293 to 373 K. The result provides a further proof for existence of two isomers in the solution of **6**. Although the bridging coordination of the PNP in **6** limits the turnstile rotation of the three nonsulfur ligands on the iron atom, the bridging PNP can swing between two basal positions, leading to the interconversion of the axial and basal positions for the PMe_3 ligand. The swing of the PNP in **6** is slow at 293 K relative to the NMR time scale with an increase in rate upon increasing temperature. It could be deduced that the analogous complex **8** also exist as two isomers in solution.

Molecular Structures of 2−8. The molecular structures of **3**−**8** displayed in Figure 3 as ball and stick drawings are determined by X-ray diffraction studies of single crystals. The parent compound **2** was previously reported in literature without crystallographic characterization.[32] It was therefore also subjected to X-ray analysis (Figure S5 and Table S1 in the Supporting Information). Selected bond lengths and angles for **3**−**8** are listed in Table 2. The central 2Fe2S structures of six diiron dithiolate complexes are all in the butterfly conformation, and each iron atom is coordinated with a pseudosquare−pyramidal geometry as in previously reported models.[3−15,19−24] During the preparation of this article, the molecular structures of unsymmetric disubstituted diiron complexes (μ-pdt)[Fe(CO)$_3$][Fe(CO){Ph$_2$PN(R)PPh$_2$}] (R = *i*Pr, allyl) were reported,[24] which are quite similar with that of **3** containing a chelating PNP ligand. The PNP lies in the basal positions in **3**, consistent with the solution ^{31}P NMR spectrum, which shows two equivalent phosphorus atoms. The coordination mode of the diphosphite plays an apparent influence on the Fe−Fe distance, which is 2.5624(10) Å in the PNP-chelating **3** and 2.4776(8) Å in the PNP-bridging **4**. The distances of the Fe−P bonds in **3** and **4** are quite similar. Somewhat unsymmetric thiolate bridges to the two iron centers are found for **3**. The Fe−S bonds related to the Fe(CO)(κ^2-PNP) unit are around 0.04 and 0.02 Å shorter than the corresponding Fe−S bonds involved in the Fe(CO)$_3$ unit. The Fe(2)−C(4) bond length of 1.754(5) Å in **3** is notably shorter than three Fe(1)−C bonds at an average of 1.784 Å. Accordingly, the C(4)−O(4) distance of 1.150(5) Å is longer than the C−O distances ($C-O_{av}$ = 1.141 Å) in the Fe(CO)$_3$ unit. The reasonable explanation is that the higher electron density of the Fe(2) atom leads to the stronger electron back-donation to the C(4)O(4) as compared to the back-donation from the Fe(1) center to the CO ligands. The structural results are consistent with the IR spectroscopic findings for **3**, which show a low energy absorption at 1908 cm^{-1} for the Fe(CO)(κ^2-PNP) unit and the absorptions at 2019 and 1939 cm^{-1} for the Fe(CO)$_3$unit.

5 possesses an apical (monodentate PNP)/basal (PMe_3) coordination geometry in the solid state, whereas the



7 **8**

Figure 3. Molecular structures of **3**−**8** as ball and stick drawings. Hydrogen atoms have been omitted for clarity.

analogous complex **7** features an apical/apical conformation as found in diiron dithiolate complexes containing two bulky ligands.[8,9] Although the ^{31}P NMR spectra show that trisubstituted complexes **6** and **8** each exist as two isomers in solution at room temperature, only the isomer with all-basal coordination geometry is observed in the crystalline state of **6**. This complex is labeled as **6a** in Scheme 5, whereas an apical (P(OEt)$_3$)/basal−basal (μ-PNP) orientation is found for **8**, which is labeled as **8b**. The lengths of the two Fe−P (μ-PNP) bonds in **6** differ from each other by ca. 0.03 Å. The coordination of the PMe$_3$ results in lengthening of the Fe−P (μ-PNP) bond on the same iron atom.

Conclusion

Unsymmetrical **3** with chelating PNP ligand on a single iron of (μ-pdt)Fe$_2$(CO)$_6$ and the symmetrically PNP bridging isomer **4** can be prepared selectively according to the order of addition of μ-pdt and PNP ligands to the iron carbonyl complex Fe$_2$(CO)$_9$. To our knowledge, the approach to **4** is unprecedented. Via thermal isomerization, **3** converts to **4**, indicating that **4** lies at a lower energy minimum than that of **3**.

Both the electrophilicity of the Fe(CO)$_3$ unit in **3** and its low barrier to Fe(CO)$_3$ rotation contribute to the lower

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for **3**−**8**

	3	**4**	**5**	**6**	**7**	**8**
Fe(1)−Fe(2)	2.5624(10)	2.4776(8)	2.5470(8)	2.5504(8)	2.5044(14)	2.4691(16)
Fe(1)−S(1)	2.2788(12)	2.2683(12)	2.2686(11)	2.2553(13)	2.257(2)	2.2692(17)
Fe(1)−S(2)	2.2582(13)	2.2507(11)	2.2604(10)	2.2708(12)	2.2670(19)	2.2612(19)
Fe(2)−S(1)	2.2374(12)	2.2633(13)	2.2632(12)	2.2529(12)	2.266(2)	2.2508(19)
Fe(2)−S(2)	2.2355(12)	2.2566(12)	2.2495(12)	2.2314(11)	2.257(2)	2.2445(18)
Fe−P_{PNP}	2.1508(12) 2.1681(12)	2.1663(12) 2.1567(13)	2.1844(11)	2.1443(12) 2.1735(12)	2.175(2)	2.158(2) 2.1472(19)
Fe−P_{PR3}			2.156(3)	2.2142(13)	2.162(2)	2.141(2)
Fe(1)−C_{av}	1.784	1.759		1.766	1.759	1.756
Fe(2)−C_{av}	1.754(5)	1.758	1.742	1.741(5)	1.753	1.728(8)
Fe−S−Fe	69.33	66.49	68.58	68.96	67.23	66.35
S−Fe−S	86.35	84.60	84.23	84.79	83.92	84.55
P−Fe−P	70.92(5)			93.85(5)		102.22(7)
Fe−Fe−P(1)	109.25(5)	93.90(4)	148.18(3)	99.52(3)	150.89(7)	93.81(6)
Fe−Fe−P(2)	106.90(4)	96.85(4)		87.86(3)		97.14(5)
Fe−Fe−P(3)			104.33(9)	117.14(4)	155.72(8)	152.72(7)
Fe−Fe−C_{apical}	147.23	154.18	152.72(16)	150.24		153.2(3)

Table 3. Crystallographic Data and Processing Parameters for **3**−**8**

complex	**3**	**4**	**5**	**6**	**7**	**8**
empirical formula	$C_{16}H_{29}O_8NP_2S_2Fe_2$	$C_{16}H_{29}O_8NP_2S_2Fe_2$	$C_{19}H_{36}O_8NP_3S_2Fe_2$	$C_{23}H_{28}O_4NP_2S_2Fe_2$	$C_{22}H_{44}O_{11}NP_3S_2Fe_2$	$C_{21}H_{44}O_{10}NP_3S_2Fe_2$
M_w	601.16	601.16	675.23	649.22	767.31	739.30
T (K)	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2$ (1)/n	$P2$ (1)/c	$P2$ (1)/c	$C2/c$	$P2$ (1)/n	$P2$ (1)/c
a (Å)	8.731(3)	16.4802(19)	11.103(3)	32.4145(5)	15.3850(8)	16.509(5)
b (Å)	18.031(6)	10.0459(11)	20.547(5)	9.9057(1)	9.0454(5)	9.140(5)
c (Å)	17.594(6)	16.4328(18)	16.013(3)	18.1493(2)	26.3458(13)	22.877(5)
β (deg)	104.37	99.135(2)	119.129(12)	101.527(1)	94.070(4)	89.934
V (Å^3)	2683.0(16)	2686.1(5)	3191.1(13)	5709.99(12)	3657.1(3)	3452(2)
Z	4	4	4	8	4	4
ρ_{calcd} (g cm^{-3})	1.488	1.487	1.405	1.510	1.394	1.423
cryst size (mm^3)	0.11 × 0.20 × 0.28	0.04 × 0.30 × 0.44	0.20 × 0.21 × 0.45	0.08 × 0.12 × 0.12	0.08 × 0.10 × 0.32	0.05 × 0.13 × 0.33
$\theta_{min/max}$ (deg)	1.64/26.12	2.38/26.08	1.76/26.13	2.15/25.00	1.58/27.53	1.78/27.67
reflns collected/ unique	14 299/5295	14 680/5306	17 670/6275	17 633/4702	22 083/8353	13 926/6480
params refined	280	280	345	298	370	353
GOF on F^2	1.027	1.015	1.025	1.074	0.914	0.863
R1 [$I > 2\sigma(I)$]	0.0460	0.0488	0.0481	0.0458	0.0662	0.0559
wR2	0.1193	0.1223	0.1238	0.1311	0.1809	0.1021
residual electron density (e Å^{-3})	0.652, −0.413	0.471, −0.477	0.470, −0.270	1.793, −0.578	0.530, −0.521	0.386, −0.285

activation energy for addition of the phosphorus-donor nucleophiles (i.e., PMe_3 and $P(OEt)_3$) with subsequent intramolecular CO transfer and Fe−PNP bond cleavage. The dppv ligand used by Rauchfuss et al.[21] as well as the PNP ligand of this study possess rigidity conducive to binding to the (μ-pdt)Fe_2 derivatives rather than facile spanning[17,25,26] and the generation of tetrairon complexes. The PNP ligand is evidently more prone to serve as a bidentate bridging ligand than is the dppv ligand.

The present study and previous reports[21,31] suggest the nature and coordination modes of chelating P^P ligands (P^P = diphosphine and diphosphite) have great influence on reactivity and stability of modified complexes as exemplified by **3**, **4**, and **5**. In the context of the design of biomimetics for [FeFe]−H_2ase, the present study enriches the coordination chemistry of diiron carbonyls and is instructive for synthetic design involving ligand substitution processes.

Experimental Section

General Procedures. All reactions and operations related to organometallic complexes were carried out under dry, oxygen-free dinitrogen with standard Schlenk techniques. Solvents were dried and distilled prior to use according to the standard methods. Commercially available chemicals, 1,3-propanedithiol, $Fe(CO)_5$, PCl_3, $P(OEt)_3$, and $Me_3NO\cdot 2H_2O$ were reagent grade and used as received. Infrared spectra were recorded on JASCO FT/IR 430 spectrometer. ^{1}H and ^{31}P NMR spectra were collected with a Varian INOVA 400 NMR instrument. Mass spectra were recorded on an HP1100 MSD mass spectrometer. Elemental analyses were performed with a Thermoquest-Flash EA 1112 elemental analyzer.

Preparation of the Diphosphite Ligand and Starting Iron Carbonyl Complexes. Compounds MeN{$P(OEt)_2$}$_2$, $Fe_2(CO)_9$, (μ-pdt)$Fe_2(CO)_6$ (**1**), and (μ-CO)(μ-PNP)$Fe_2(CO)_6$ (**2**) were prepared according to literature methods.[38–41]

(μ-pdt)[Fe(CO)$_3$][Fe(CO)(κ^2-PNP)] (3). The CO-removing reagent $Me_3NO\cdot 2H_2O$ (0.12 g, 1.1 mmol) was added to a solution of **1** (0.38 g, 1 mmol) in CH_3CN (20 mL). The red solution was stirred for 15 min, and the color turned dark red. The PNP ligand (0.30 g, 1.1 mmol) was added to the solution. After the mixture was stirred for 30 min, the solvent was removed under reduced

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pressure. The residue was purified by chromatography on an alumina column with hexane/CH_2Cl_2 (5:1, v/v) as eluent. A red powder was obtained from the collected red band after removal of solvent. Yield: 0.43 g (72%). ^{1}H NMR ($CDCl_3$): δ 4.22, 3.99 (2s br, 8H, OCH_2), 2.68 (s, 3H, NCH_3), 2.17, 1.86 (2s br, 6H, SCH_2CH_2CH_2S), 1.44, 1.23 (2s br, 12H, CH_3). ^{31}P NMR ($CDCl_3$): δ 139.5 (s). IR (KBr): ν_{CO} 2019, 1939, 1908 cm^{-1}. ESI-MS: *m/z* 623.8 [M+Na]$^+$. Anal. Calcd for $C_{16}H_{29}Fe_2NO_8P_2S_2$ (found): C, 31.97 (32.17); H, 4.86 (4.87); N, 2.33 (2.31).

(μ-pdt)(μ-PNP)[Fe(CO)$_2$]$_2$ (4). Propane-1,3-dithiol (0.54 g, 5.0 mmol) was added to a solution of **2** (0.38 g, 1.0 mmol) in THF (30 mL), and the mixture was refluxed for 72 h. The resulting solution was evaporated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel with hexane/CH_2Cl_2 (5:1, v/v) as eluent. An orange solid was obtained from the collected red band after removal of solvent. Yield: 0.45 g (75%). ^{1}H NMR ($CDCl_3$): δ 4.20, 3.98 (2s br, 8H, OCH_2), 2.49 (s, 3H, NCH_3), 2.07, 1.82 (2s, 6H, SCH_2CH_2CH_2S), 1.32 (s, 12H, CH_3). ^{31}P NMR ($CDCl_3$): δ 172.6 (s). IR (KBr): ν_{CO} 1998, 1965, 1928 cm^{-1}. ESI-MS: *m/z* 623.8 [M+Na]$^+$. Anal. Calcd for $C_{16}H_{29}Fe_2NO_8P_2S_2$ (found): C, 31.97 (31.98); H, 4.86 (4.90); N, 2.33 (2.35).

(μ-pdt)[Fe(CO)$_2$PMe$_3$][Fe(CO)$_2$(PNP)] (5). Phosphine ligand PMe_3 (0.08 g, 1.0 mmol) was added to a solution of **3** (0.60 g, 1.0 mmol) in CH_3CN (20 mL). The red solution was stirred for 10 min at room temperature. The solvent was removed under reduced pressure, and the residue was chromatographed on an alumina column with hexane/CH_2Cl_2 (5:1, v/v) as eluent. A dark-red crystalline solid was obtained from the collected red band after removal of solvent. Yield: 0.58 mg (85%). ^{1}H NMR ($CDCl_3$): δ 4.16, 3.89 (2s br, 8H, OCH_2), 2.79 (s br, 3H, NCH_3), 2.08, 1.85 (2s br, 6H, SCH_2CH_2CH_2S), 1.47−1.30 (2s br, 21H, CH_3). ^{31}P NMR ($CDCl_3$): δ 179.5 (d, $J_{p\text{-}p}$ = 137.3 Hz), 144.4 (d, $J_{p\text{-}p}$ = 136.9 Hz), 26.9 (s). IR (KBr): ν_{CO} 1985, 1946, 1920, 1899 cm^{-1}. ESI-Ms: *m/z* 678.0 [M+H]$^+$. Anal. Calcd for $C_{16}H_{33}Fe_2NO_8P_2S_2$ (found): C, 33.65 (33.67); H, 5.70 (5.63); N, 2.07 (2.14).

The reactivity of (μ-pdt)[Fe(CO)$_3$][Fe(CO)$_2$(PNP)] (3) with PMe$_3$ under ^{13}CO. A 20 mg portion of **3** was dissolved in 10 mL CH_3CN, and an initial IR spectrum was recorded for the starting material. The solution was then frozen with liquid N_2 and backfilled with ^{13}CO to ca. 0.40 atm. After the solution was returned to room temperature, 1 equiv of PMe_3 was added. At 10 m later, a second IR spectrum was recorded, which indicated the complete digestion of the starting material and the exclusive formation of **5**. No ^{13}CO labeled species was detected.

(μ-pdt)(μ-PNP)[Fe(CO)PMe$_3$][Fe(CO)$_2$] (6). Ligand PMe_3 (0.08 g, 1.0 mmol) was added to a solution of **3** (0.60 g, 1.0 mmol) in toluene (20 mL). The mixture was refluxed for 72 h. The resulting solution was evaporated to dryness under vacuum, and the residue was chromatographed on an alumina column with hexane/CH_2Cl_2 (3:1, v/v) as eluent. A dark-red crystalline solid was obtained from the collected red band after removal of solvent. Yield: 0.52 g (80%). ^{1}H NMR (DMSO-d_6, 80 °C): δ 4.10−3.85 (m, 8H, OCH_2), 2.48 (s, 3H, NCH_3), 2.05−1.70 (3s, 6H, SCH_2CH_2CH_2S), 1.52 (s, 9H, CH_3), 1.28−1.20 (m, 12H, CH_3). ^{31}P NMR ($CDCl_3$, 20 °C): δ 180.0 (d, $J_{p\text{-}p}$ = 111.6 Hz), 176.3 (d, $J_{p\text{-}p}$ = 117.6 Hz), 175.3 (d, $J_{p\text{-}p}$ = 112.3 Hz), 168.6 (dd, $J_{p\text{-}p}$ = 109.9, 85.6 Hz), 32.3 (d, $J_{p\text{-}p}$ = 78.7 Hz), 20.1 (d, $J_{p\text{-}p}$ = 19.3 Hz). IR (KBr): ν_{CO} 1965, 1905, 1878 cm^{-1}. ESI-MS: *m/z* 672.1 [M+Na]$^+$. Anal. Calcd for $C_{15}H_{32}Fe_2NO_7P_3S_2$ (found): C, 33.30 (33.51); H, 5.90 (5.92); N, 2.16 (2.20).

(μ-pdt)[Fe(CO)$_2$P(OEt)$_3$][Fe(CO)$_2$(PNP)] (7). The $P(OEt)_3$ ligand (0.17 g, 1.0 mmol) was added to a solution of **3** (0.60 g, 1.0 mmol) in CH_3CN (20 mL). The solution was refluxed for 3 h. The resulting solution was evaporated to dryness under vacuum, and the residue was purified by column chromatography on an alumina column with hexane/CH_2Cl_2 (7:1, v/v) as eluent. A red powder was obtained from the collected red band after removal of solvent. Yield: 0.59 g (77%). ^{1}H NMR ($CDCl_3$): δ 4.14−4.07 (m, 8H, OCH_2), 3.90−3.79 (m, 6H, OCH_2), 2.75 (d, J_{P-H} = 7.2 Hz, 3H, NCH_3), 1.96−1.71 (m, 6H, SCH_2CH_2CH_2S), 1.31, 1.24 (2t, 21H, CH_3). ^{31}P NMR ($CDCl_3$): δ 179.8 (dd, $J_{p\text{-}p}$ = 132.9, 11.7 Hz), 175.8 (d, $J_{p\text{-}p}$ = 11.2 Hz), 144.4 (d, $J_{p\text{-}p}$ = 132.9 Hz). IR (KBr): ν_{CO} 2001, 1960, 1940, 1921 cm^{-1}. ESI-MS: *m/z* 790.3 [M+Na]$^+$. Anal. Calcd for $C_{22}H_{44}Fe_2NO_{11}P_3S_2$ (found): C, 34.44 (34.67); H, 5.78 (5.90); N, 1.83 (1.91).

(μ-pdt)(μ-PNP)[Fe(CO)P(OEt)$_3$][Fe(CO)$_2$] (8). An equiv of $P(OEt)_3$ (0.17 g, 1.0 mmol) was added to a solution of **3** (0.60 g, 1.0 mmol) in toluene (20 mL). The mixture was refluxed for 72 h. The resulting solution was evaporated to dryness under vacuum, and the residue was chromatographed on an alumina column with hexane/CH_2Cl_2 (5:1, v/v) as eluent. A red crystalline solid was obtained from the collected red band after removal of solvent. Yield: 0.55 g (76%). ^{1}H NMR ($CDCl_3$, 20 °C): δ 4.42−3.75 (m, 14H, OCH_2), 2.45 (s br, 3H, NCH_3), 2.10−1.50 (m, 6H, SCH_2CH_2CH_2S), 1.35−1.23 (m, 21H, CH_3). ^{31}P NMR ($CDCl_3$, 20 °C): δ 181.2 (d, $J_{p\text{-}p}$ = 17.9 Hz), 181.0 (d, $J_{p\text{-}p}$ = 17.6 Hz), 178.4 (d, $J_{p\text{-}p}$ = 16.0 Hz), 177.7 (d, $J_{p\text{-}p}$ = 16.0 Hz), 175.5 (d, $J_{p\text{-}p}$ = 22.8 Hz), 174.8 (d, $J_{p\text{-}p}$ = 23.9 Hz). IR (KBr): ν_{CO} 1970, 1916 cm^{-1}. ESI-MS: *m/z* 761.9 [M+Na]$^+$. Anal. Calcd for $C_{21}H_{44}Fe_2NO_{10}P_3S_2$ (found): C, 34.12 (34.21); H, 6.00 (6.12); N, 1.89 (1.94).

Crystal Structure Determination of 2−8. Single crystals of **2**−**8** were all obtained from dichloromethane/hexane solution. Crystallographic data were collected on a Bruker Smart Apex II CCD diffractometer with graphite monochromated Mo−Kα radiation (λ = 0.71073 Å) at 295 K using the $\omega-2\theta$ scan mode. Data processing was accomplished with the *SAINT* processing program. Intensity data were corrected for absorption by the *SADABS* program. The structures were solved by direct methods and refined on F^2 against full-matrix least-squares methods using the *SHELX-97* program package.[42] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by geometrical calculation, but their positions and thermal parameters were fixed during the structure refinement. Crystal data and parameters for data collections and refinements of **3**−**8** are listed in Table 3 (for **2**, see Table S2 in the Supporting Information).

Acknowledgment. We are grateful to the Chinese National Natural Science Foundation (Grant no. 20633020), the Swedish Energy Agency, the Swedish Research Council, and K & A Wallenberg Foundation for financial support of this work. The financial support from the National Science Foundation (CHE-0616695 to MYD) and the R.A. Welch Foundation (A-0924 to MYD) is greatly appreciated.

Supporting Information Available: X-ray crystallographic data for **2**−**8**, React-IR spectra of **3** with 1 equiv of PMe_3 at −78 °C, ^{31}P NMR spectrum of **8**, molecular structure of **2**, and crystallographic data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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