

Influence of Tertiary Phosphanes on the Coordination Configurations and Electrochemical Properties of Iron Hydrogenase Model Complexes: Crystal Structures of $[(\mu\text{-S}_2\text{C}_3\text{H}_6)\text{Fe}_2(\text{CO})_{6-n}\text{L}_n]$ ($\text{L} = \text{PMe}_2\text{Ph}$, $n = 1, 2$; PPh_3 , P(OEt)_3 , $n = 1$)

Ping Li,^[a] Mei Wang,^{*[a]} Chengjiang He,^[a] Guanghua Li,^[b] Xiaoyang Liu,^[a,b] Changneng Chen,^[c] Björn Åkermark,^[d] and Licheng Sun^{*[a,e]}

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A series of mono- and disubstituted diiron complexes $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_5\text{L}]$ [pdt = 1,3-propanedithiolato; $\text{L} = \text{PMe}_3$ (**2**), PMe_2Ph (**3**), PPh_3 (**4**), P(OEt)_3 (**5**)] and $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_4\text{L}_2]$ [$\text{L} = \text{PMe}_2\text{Ph}$ (**6**), PPh_3 (**7**), P(OEt)_3 (**8**)] were prepared as Fe-only hydrogenase-active-site models by controllable CO displacement of $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_6]$ by tertiary phosphanes. The coordination configurations of **3–6** were characterized by X-ray crystallography. Disubstituted diiron complex **6** features an

apical/apical coordination mode, instead of the typical *transoid* basal/basal configuration. The electrochemistry of **2–6** and **8** was studied by cyclic voltammetry to evaluate the effects of different tertiary phosphane ligands on the redox properties of the iron atoms of model complexes.

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Introduction

The Fe-only hydrogenases, which can effectively catalyze the reduction of protons to dihydrogen in numerous microorganisms,^[1,2] are of significance to the economical production of H_2 . The composition and the structure of the active site of Fe-only hydrogenases have been established by high-resolution X-ray crystallographic and spectroscopic studies of Fe-only hydrogenases isolated from *Desulfovibrio desulfuricans* and *Clostridium pasteurianum*.^[3,4] These achievements in molecular biology and protein crystallography provide an opportunity for chemists to chemically mimic the structure and function of the Fe-only hydrogenase-active site and to explore cheap and efficient catalyst candidates for proton reduction.

The propanedithiolato-bridged dinuclear complex $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_6]$ (**1**) bears remarkable structural similarities

with the active site of Fe-only hydrogenase. The introduction of good donor ligands, such as cyanide, tertiary phosphanes and isonitriles, in the $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_6]$ complex renders the iron atoms more electron-rich and more protophilic. In recent years, there have been numerous reports regarding the CO displacement of $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_6]$ by CN^- ,^[5–9] PR_3 ,^[10–13] and CNR ,^[14,15] as well as the protonation and electrochemistry of the CN^- - and PR_3 -substituted derivatives.^[16–19] Tertiary phosphane ligands are preferably used in many model complexes of the Fe-only hydrogenase-active site for the following reasons: 1) The electronic characteristics of tertiary phosphane ligands towards the Fe atom are similar to those of CN^- ligands. 2) The steric and electronic properties of PR_3 are tunable by changing the R groups. 3) The replacement of CN^- by PR_3 can avoid the complications of protonation on the cyanide nitrogen atom. Although CO-displacement reactions of $[(\mu\text{-SR})_2\text{Fe}_2(\text{CO})_6]$ with tertiary phosphanes have been extensively studied since the 1970s,^[19–23] to the best of our knowledge, only a limited number of structurally characterized PR_3 -monosubstituted derivatives of diiron dithiolate complexes have been reported in the literature.^[11–13] In addition to the crystal structures of PMe_3 -disubstituted complexes $[(\mu\text{-SR})_2\text{Fe}_2(\text{CO})_4(\text{PMe}_3)_2]$ ($\text{R} = \text{Me}, \text{Et}$)^[17,24] and $[(\mu\text{-SRS})\text{Fe}_2(\text{CO})_4(\text{PMe}_3)_2]$ ($\text{R} = \text{CH}_2\text{CH}_2, \text{CH}_2\text{CH}_2\text{CH}_2$),^[10,17] the coordination configurations of other PR_3 -disubstituted complexes, $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_4\text{L}_2]$ ($\text{L} = \text{PMe}_2\text{Ph}, \text{PPh}_3$), are still not known. Albeit complex $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_4(\text{PMe}_2\text{Ph})_2]$ was reported recently^[17] and the PPh_3 -disubstituted complexes $[(\mu\text{-SR})\text{Fe}_2(\text{CO})_4(\text{PPh}_3)_2]$ ($\text{R} = \text{Me}, \text{Ph}$) were pre-

[a] State Key Laboratory of Fine Chemicals, Dalian University of Technology, Zhongshan Road 158–46, Dalian 116012, China
E-mail: symbuono@vip.sina.com

[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, China

[c] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou 350002, China

[d] Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, 10691 Stockholm, Sweden

[e] KTH Chemistry, Organic Chemistry, Royal Institute of Technology, 10044 Stockholm, Sweden

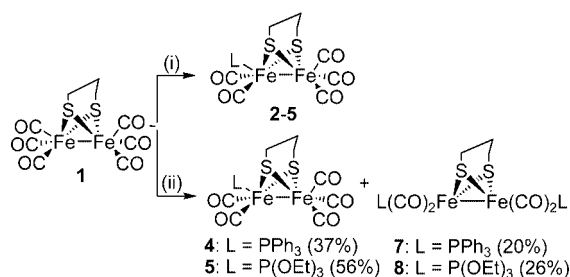
pared in the early 1970s,^[25–27] the coordination positions of PMe_2Ph and PPh_3 in these diiron complexes are hitherto unknown. A series of PR_3 -substituted diiron complexes, $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_5\text{L}]$ [$\text{L} = \text{PMe}_3$ (**2**), PMe_2Ph (**3**), PPh_3 (**4**), $\text{P}(\text{OEt})_3$ (**5**)] and $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_4\text{L}_2]$ [$\text{L} = \text{PMe}_2\text{Ph}$ (**6**), PPh_3 (**7**), $\text{P}(\text{OEt})_3$ (**8**)], were prepared for a systematic study of the influence of phosphane ligands on the coordination structures and the redox potentials. Here we describe the preparation, spectroscopic characterization and the coordination configurations of complexes **2–8**, as well as the electrochemical properties of complexes **2–6** and **8**. The X-ray crystallographic study shows that the PMe_2Ph ligands on the Fe atoms of **6** are in an apical/apical coordination mode, which is in contrast with the *transoid* basal/basal configuration of $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_4(\text{PMe}_3)_2]^{[10]}$ and the recently reported complex $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_4(\text{PTA})_2]$ (PTA = 1,3,5-tri-*a*-7-phosphaadamantane).^[12]

Results and Discussion

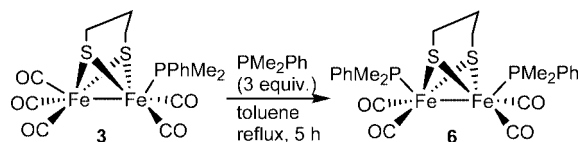
Preparation and Spectroscopic Characterization of Complexes **2–8**

Monosubstituted complexes $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_5\text{L}]$ (**2–5**) were readily prepared in moderate to good yields by treating **1** with PR_3 , according to literature procedures (see Scheme 1).^[20,26] Different solvents, namely, hexane, benzene and toluene, were used for the individual reactions in the light of the solubility of the tertiary phosphanes. The reaction of **1** with 1 equiv. of a less bulky tertiary phosphane ($\text{L} = \text{PMe}_3$, PMe_2Ph) can be controlled at the monosubstituted stage at room temp. Complex **5** was obtained by treating **1** with 1 equiv. of $\text{P}(\text{OEt})_3$ in refluxing toluene. PPh_3 (2 equiv.) is required to obtain **4** in good yield for the displacement of CO in **1** by PPh_3 in refluxing toluene. The PMe_2Ph -disubstituted complex **6** was obtained in satisfactory yield either by treatment of the monosubstituted complex **3** with an additional equiv. of PMe_2Ph in refluxing toluene (see Scheme 2) or by a straightforward reaction of the all-CO complex **1** with 4 equiv. of PMe_2Ph . The formation of PPh_3 -disubstituted complex **7** is more difficult than that of the PMe_3 -^[10] and PMe_2Ph -disubstituted derivatives,^[17] presumably due to the large bulk of the PPh_3 ligand. The reaction of **1** with PPh_3 in a molar ratio of 1:4 ($1/\text{PPh}_3$) in refluxing toluene for 5 h afforded the PPh_3 -monosubstituted complex **4** as a major product together with a low yield of the PPh_3 -disubstituted complex **7**. With the PPh_3 -monosubstituted complex **4** as a starting reactant, the reaction also gave **7** in low yield after 10 h of reflux in toluene but the major part of **4** did not react, even in excess PPh_3 . A similar behaviour to PPh_3 was found for the double CO-displacement of **1** by $\text{P}(\text{OEt})_3$. The reaction of **1** with 4 equiv. of $\text{P}(\text{OEt})_3$ in refluxing toluene gave **5** as the major product and the $\text{P}(\text{OEt})_3$ -disubstituted complex **8** in low yield. All complexes (**2–8**) are relatively thermo- and air-stable in the solid state. The PPh_3 derivatives, **4** and **7**, are less stable in solution than their analogous PMe_3 -, PMe_2Ph - and $\text{P}(\text{OEt})_3$ -substituted diiron complexes. In toluene at room temp., dissociation of

the PPh_3 ligand in **4** and **7** was indicated by ^{31}P NMR spectral studies.



Scheme 1. Reagents and conditions: (i) for **2**, $\text{L} = \text{PMe}_3$ (1 equiv.), hexane, room temp., 5 h; for **3**, $\text{L} = \text{PMe}_2\text{Ph}$ (1 equiv.), benzene, room temp., 10 h; for **4**, $\text{L} = \text{PPh}_3$ (2 equiv.), toluene, reflux, 6 h; for **5**, $\text{L} = \text{P}(\text{OEt})_3$ (1 equiv.), toluene, reflux, 3 h; (ii) $\text{L} = \text{PPh}_3$, $\text{P}(\text{OEt})_3$ (4 equiv.), toluene, reflux, 6 h.



Scheme 2.

The products obtained were characterized by IR, ^1H and ^{31}P NMR spectroscopy and elemental analysis. The results of the elemental analyses for all products are in good agreement with the supposed compositions. Complexes **2–8** each show three or four infrared bands in the $\nu(\text{CO})$ stretching region ($1900\text{--}2050\text{ cm}^{-1}$). The IR data of $\nu(\text{CO})$ for **2–8** are listed in Table 1 for a comparison, together with the $\nu(\text{CO})$ data of $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_6]$ and $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_4\text{L}_2]$ [$\text{L} = \text{PMe}_3$ (**9**)].^[10,28,29] The $\nu(\text{CO})$ bands are considered as a useful indicator for detecting the variation in the electron density of the Fe atoms in the model complexes of the Fe-only hydrogenase-active site. A comparison of the $\nu(\text{CO})$ bands for the four subsets of mono- and disubstituted homologues in Table 1 (**2** vs. **9**, **3** vs. **6**, **4** vs. **7** and **5** vs. **8**) indicates that the introduction of a phosphane ligand has a considerable effect on the $\nu(\text{CO})$ bands, while the difference in phosphane ligands appears to have a smaller influence on the shift values of the $\nu(\text{CO})$ bands of **2–8**. The red shifts of $44\text{--}58\text{ cm}^{-1}$ for the first $\nu(\text{CO})$ bands and of $29\text{--}38\text{ cm}^{-1}$ for the second ones are observed (see Table 1) as the monosubstituted complexes **2–5** are converted into their disubstituted homologues **6–9**. Compared with the all-carbonyl complex **1**, the average values of the three strong $\nu(\text{CO})$ bands for the PR_3 -disubstituted complexes are lowered by about 95, 89, 75, and 69 cm^{-1} for **9**, **6**, **7**, and **8**, respectively. The order of the red-shift values of the $\nu(\text{CO})$ bands for **6–9** is consistent with the electron-donating capabilities of different phosphane ligands, which exhibit a clear ranking of $\text{PMe}_3 > \text{PMe}_2\text{Ph} > \text{PPh}_3 > \text{P}(\text{OEt})_3$.

Table 1. Comparison of $\nu(\text{CO})$ bands in PR_3 -mono- and -disubstituted complexes of **1**.^[a]

Complex	$\nu(\text{CO})$ [cm^{-1}]	$\Delta\nu$ ^[b] [cm^{-1}]		Note
		$\Delta\nu$ of 1st $\nu(\text{CO})$	$\Delta\nu$ of 2nd $\nu(\text{CO})$	
1	2074(m), 2036(s), 1995(s)	—	—	ref. ^[29]
2	2037(s), 1980(s), 1919(m)	−37	−56	this work
3	2040(s), 1980(s), 1921(m)	−34	−56	this work
4	2044(s), 1984(s), 1931(m)	−30	−52	this work
5	2046(s), 1989(s), 1936(m)	−28	−47	this work
6	1982(s), 1946(s), 1910(s)	−58	−34	this work
7 ^[c]	1997(s), 1951(s), 1933(s)	−47	−33	this work
8	2002(s), 1960(s), 1935(s)	−44	−29	this work
9	1979(s), 1942(s), 1898(s)	−58	−38	ref. ^[10]

[a] The spectra were measured in CH_3CN unless stated otherwise. [b] For the PR_3 -monosubstituted complexes **2–5**: $\Delta\nu = \nu(\text{CO})_{\text{mono}} - \nu(\text{CO})_{\text{allCO}}$ and for the PR_3 -disubstituted complexes **6–9**: $\Delta\nu = \nu(\text{CO})_{\text{di}} - \nu(\text{CO})_{\text{mono}}$. [c] The spectrum was measured in CHCl_3 .

Molecular Structures of Complexes 3–6

Complexes **4** and **6** were previously prepared according to the same reactions,^[11,17] but until now their coordination configurations had not been structurally characterized. As the coordination positions of the phosphane ligands in the diiron complexes cannot be determined solely by the spectroscopic data, X-ray diffraction studies were undertaken for **3–6**. The molecular structures of **3–6** are displayed in Figure 1 and selected bond lengths and angles are listed in Tables 2 and 3. The central $2\text{Fe}2\text{S}$ structures of four com-

plexes are all in the butterfly conformation as in previously reported models,^[9–17] and each iron atom is coordinated with a pseudo-square-pyramidal geometry. The CO displacement by one or two molecules of tertiary phosphane ligands has only a small effect on the Fe–Fe distances [2.5048(10) Å in **3**, 2.5247(6) Å in **4**, 2.5142(9) Å in **5** and 2.5198(13) Å in **6**] as compared to that of $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_6]$ [2.5103(11) Å].^[28]

The coordination configurations of the monosubstituted complexes **3**, **4** and **5** are essentially identical with that of

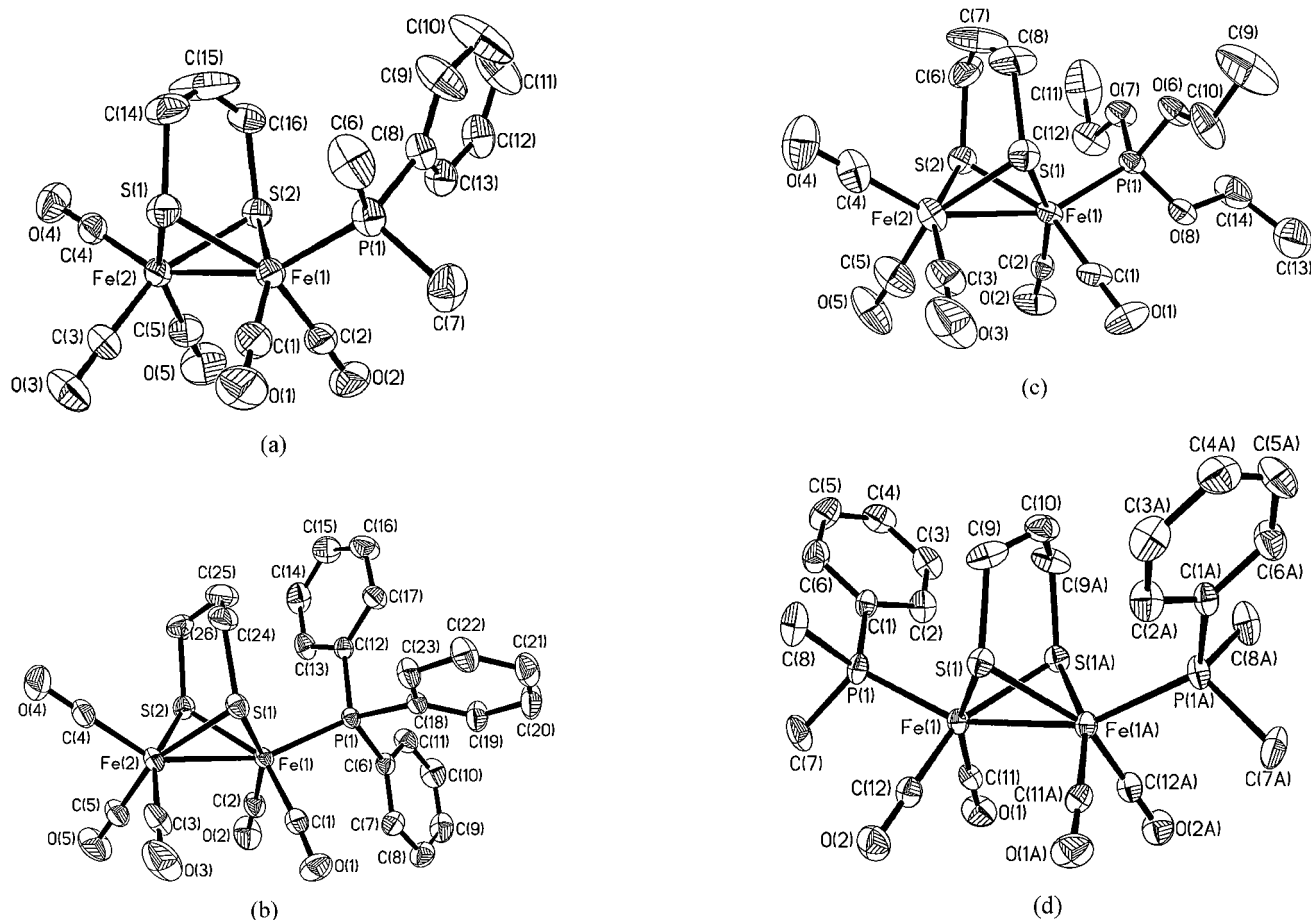
Figure 1. Molecular structures of **3** (a), **4** (b), **5** (c) and **6** (d).

Table 2. Selected bond lengths [Å] and angles [°] for complexes **3**–**5**.

Complex	3	4	5
Bond lengths			
Fe(1)–Fe(2)	2.5048(10)	2.5247(6)	2.5142(9)
Fe(1)–S(2)	2.2653(14)	2.2639(10)	2.253(4)
Fe(1)–S(1)	2.2617(13)	2.2700(9)	2.267(4)
Fe(2)–S(1)	2.2653(14)	2.2598(9)	2.276(4)
Fe(2)–S(2)	2.2707(13)	2.2629(10)	2.259(4)
Fe(1)–P(1)	2.2222(15)	2.2566(9)	2.1696(12)
Fe(1)–C(1)	1.791(5)	1.759(4)	1.771(14)
Fe(1)–C(2)	1.772(5)	1.756(4)	1.779(15)
Fe(2)–C(3)	1.776(6)	1.786(4)	1.785(12)
Fe(2)–C(4)	1.788(6)	1.797(4)	1.800(7)
Fe(2)–C(5)	1.797(6)	1.771(5)	1.770(19)
Bond angles			
P(1)–Fe(1)–S(1)	107.04(6)	107.13(3)	104.86(15)
P(1)–Fe(1)–S(2)	105.45(5)	111.79(4)	105.42(14)
P(1)–Fe(1)–C(1)	93.1(2)	97.15(12)	98.0(5)
P(1)–Fe(1)–C(2)	97.61(19)	94.94(13)	94.9(4)
S(1)–Fe(1)–C(1)	87.72(18)	89.37(12)	87.7(5)
S(1)–Fe(1)–C(2)	155.34(19)	157.80(13)	160.2(4)
S(2)–Fe(1)–C(1)	161.3(2)	150.99(12)	156.5(5)
S(2)–Fe(1)–C(2)	88.31(18)	85.34(13)	88.5(4)
S(1)–Fe(1)–Fe(2)	56.47(4)	55.94(3)	56.56(11)
S(2)–Fe(1)–Fe(2)	56.59(4)	56.08(3)	56.24(11)
S(1)–Fe(2)–C(3)	88.2(2)	86.70(13)	83.0(5)
S(1)–Fe(2)–C(4)	105.37(16)	101.93(12)	103.7(5)
S(1)–Fe(2)–C(5)	155.3(2)	157.88(14)	155.8(6)
S(2)–Fe(2)–C(3)	154.8(2)	158.12(16)	154.2(5)
S(2)–Fe(2)–C(4)	104.59(17)	101.73(14)	106.3(5)
S(2)–Fe(2)–C(5)	85.4(2)	87.53(14)	89.4(5)

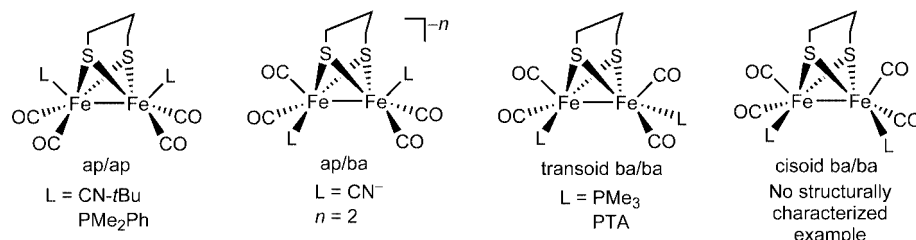
Table 3. Selected bond lengths [Å] and angles [°] for complex **6**.

Complex	6
Bond lengths	
Fe(1)–Fe(1A)	2.5198(13)
Fe(1)–S(1)	2.2750(14)
Fe(1)–S(1A)	2.2691(14)
Fe(1)–P(1)	2.2286(13)
Fe(1)–C(11)	1.757(5)
Fe(1)–C(12)	1.724(5)
Bond angles	
P(1)–Fe(1)–S(1)	103.81(5)
P(1)–Fe(1)–S(1A)	110.50(5)
P(1)–Fe(1)–C(11)	96.54(18)
P(1)–Fe(1)–C(12)	93.24(17)
S(1)–Fe(1)–C(11)	159.64(17)
S(1)–Fe(1)–C(12)	88.53(18)
S(1A)–Fe(1)–C(11)	87.96(16)
S(1A)–Fe(1)–C(12)	156.21(17)
S(1)–Fe(1)–Fe(1A)	56.43(4)
S(1A)–Fe(1)–Fe(1A)	56.21(4)

their analogues [$\{\mu\text{-S}(\text{C}_6\text{H}_3\text{-}m\text{-CH}_3)\text{S}\}\text{Fe}_2(\text{CO})_5(\text{PPh}_3)\text{S}\}$]^[11] [$\{\mu\text{-pdt}\}\text{Fe}_2(\text{CO})_5(\text{PTA})\text{S}\}$]^[12] and [$\{\mu\text{-SCH}_2\text{N}(\text{C}_6\text{H}_4\text{-}4\text{-Br})\}\text{-Fe}_2(\text{CO})_5(\text{PPh}_3)\text{S}\}$]^[13] Tertiary phosphane ligands PMe_2Ph , PPh_3 and $\text{P}(\text{OEt})_3$ are coordinated to an apical site on Fe(1) and roughly *trans* to the Fe–Fe bond. Both ^{31}P NMR and X-ray crystallographic analyses of **3**–**5** suggest that one CO displacement by tertiary phosphane in [$\{\mu\text{-pdt}\}\text{Fe}_2(\text{CO})_6\}$] affords only an apical isomer, as shown in Figure 1(a–c). One of the phenyl groups of the apical PPh_3 ligand in **4** and the sole phenyl group of the apical PMe_2Ph ligand in **3** are

approximately facing the six-membered ring of the propanedithiolate. The angles of C(14)S(1)Fe(1) [114.9(2)°] and C(16)S(2)Fe(1) [114.04(18)°] in **3** are a bit wider than the corresponding angles of C(14)S(1)Fe(2) [110.7(2)°] and C(16)S(2)Fe(2) [111.93(19)°]. Compared with **3**, even larger differences between the counterpart angles C(24)S(1)Fe(1) [116.29(15)°] vs. C(24)S(1)Fe(2) [108.84(15)°] and C(26)S(2)–Fe(1) [116.62(15)°] vs. C(26)S(2)Fe(2) [109.71(15)°] are observed for the structure of **4**. It shows that the six-membered ring of the propanedithiolate in **3** and **4** is pushed away from the site occupied by an apical PMe_2Ph or PPh_3 ligand, leading to the tilt of the propanedithiolate ring towards the $\text{Fe}(\text{CO})_3$ site. The P(1)Fe(1)Fe(2) angle is 10.17(17)° larger than the C(4)Fe(2)Fe(1) angle in **4**, while the difference between two angles is only 1.99(34) and 0.57(21)° for **3** and **5**, respectively. The PR_3 ligands used in the present work display the steric effects on the coordination structures in the order $\text{PPh}_3 \gg \text{PMe}_2\text{Ph} > \text{P}(\text{OEt})_3$. The Fe(1)–P(1) bond lengths of 2.2222(15) Å in **3**, 2.2566(9) Å in **4** and 2.1696(12) Å in **5** are similar to the values of Fe–P bond lengths reported for PR_3 -coordinating diiron complexes.^[9–13,17–19] The average Fe(2)–C(CO) bonds, 1.785–1.787 Å for **3**–**5**, are slightly shorter than in [$\{\mu\text{-pdt}\}\text{Fe}_2(\text{CO})_6\}$] [av. 1.800(3) Å],^[28] and the average Fe(1)–C(CO) distance [1.757(9) Å] of **4** is considerably shortened by coordination of PPh_3 to Fe(1).

Theoretically, there are four possible coordination configurations for double-CO displacement by two identical non-carbonyl ligands on each iron atom of [$\{\mu\text{-pdt}\}\text{Fe}_2(\text{CO})_6\}$], that is, ap/ap, ap/ba, *transoid* and *cisoid* ba/ba configurations (see Scheme 3).^[17] The first three possible configurations can each be related to one or two well-characterized examples, reported in recent years as biomimetic models of the Fe-only hydrogenase-active site.^[5,10,12,15] The structurally characterized diiron propanedithiolate with an Fe–Fe bond for the *cisoid* ba/ba configuration model has not yet been reported. Only a protonated diiron complex with double-CO displacement by PMe_3 and CN^- on two iron atoms was found in a *cisoid* ba/ba configuration.^[18] The X-ray single-crystal analysis shows that the PMe_2Ph -disubstituted complex **6** possesses an ap/ap coordination configuration, which is identical to the coordination mode of the large isocyanide ligand *t*BuNC,^[15] but in contrast with the *transoid* ba/ba configuration of [$\{\mu\text{-pdt}\}\text{Fe}_2(\text{CO})_4(\text{PMe}_3)_2\text{S}\}$] and [$\{\mu\text{-pdt}\}\text{Fe}_2(\text{CO})_4(\text{PTA})_2\text{S}\}$]^[10,12] presumably due to the steric requirement of PMe_2Ph . It could be predicted that for tertiary phosphane ligands of large volume an ap/ap configuration should be sterically less crowded than a ba/ba and an ap/ba configuration. It is noteworthy that the complex [$\{\mu\text{-pdt}\}\text{Fe}_2(\text{CO})_4(\text{CN})_2\text{S}\}]^{2-}$ with two small CN^- ligands on each iron atom features an ap/ba configuration,^[5] implying that not only the steric requirement but also the electronic effects of a ligand can influence the coordination configurations of diiron propanedithiolates. Another noticeable fact is that although the protonated species [$\{\mu\text{-H}\}\text{Fe}_2(\text{CO})_4(\text{PMe}_2\text{Ph})_2\text{S}\}]$ is in a *transoid* ba/ba configuration in the crystalline state,^[17] the coordination structure of its parent complex [$\{\mu\text{-pdt}\}\text{Fe}_2(\text{CO})_4(\text{PMe}_2\text{Ph})_2\text{S}\}]$ is in an



Scheme 3. Four possible coordination configurations resulting from the L orientation.

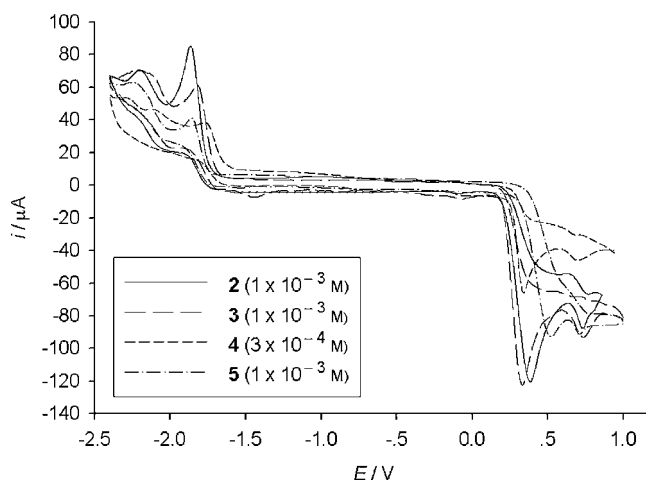
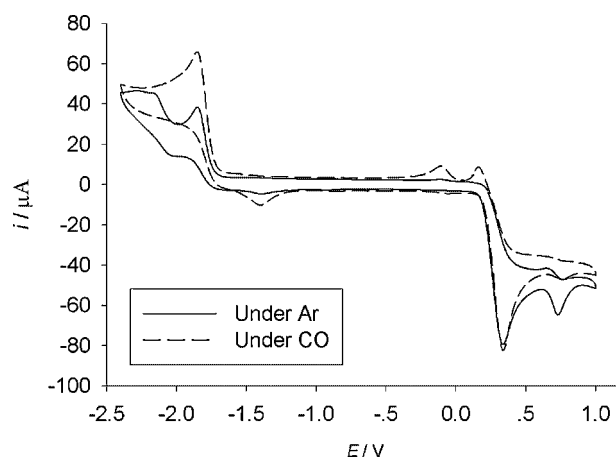
ap/ap geometry in the crystalline state. In solution, the coordination configurations of the PR₃-substituted diiron complexes might be mobile structural forms.^[12] It is unambiguous that there exists a rotation of CO and PMe₂Ph ligands during the protonation process of iron atoms in **6**, just as in the very recently reported isomerization in the protonation process of diruthenium propanedithiolate.^[30]

The phenyl groups of the apical PMe₂Ph ligands in **6** both face the inner top side of the molecule, framing a glider-shape conformation with a C₂ symmetry. The dihedral angle between the S(1)C(9)C(9A)S(1A) and S(1A)-Fe(1)S(1) planes and the counterpart angle between the planes of S(1A)C(9)C(9A)S(1) and S(1A)Fe(1A)S(1) are found to have the same value (131.5°) for **6**. The average Fe–C(CO) bond of 1.741 Å in **6** is shortened, and meanwhile the average C–O bond [1.163(1) Å in **6**] is elongated by coordination of the PMe₂Ph ligands to the iron atoms, as compared with [(μ-pdt)Fe₂(CO)₆] [Fe–C(CO)_{av} 1.800(3) Å and C–O_{av} 1.136(1) Å].^[28] The CO displacement by the better donating tertiary phosphane ligands enhances electron accumulation on the iron centers of a diiron dithiolate model, resulting in stronger back-bonding from the metal atoms to the CO ligands and at the same time weakening the CO triple bonds.

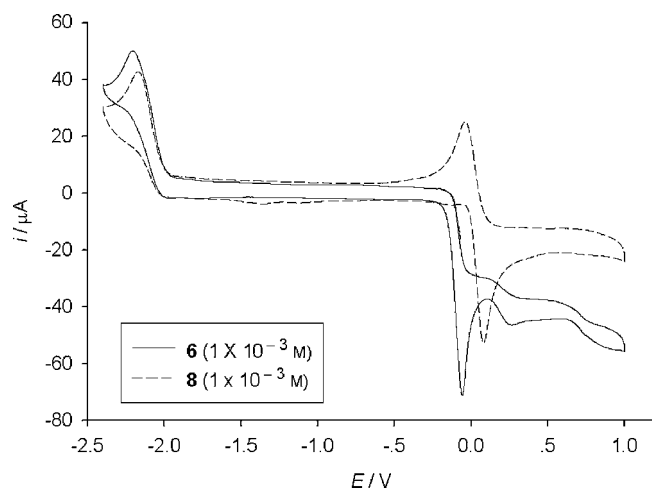
Cyclic Voltammograms of Complexes 2–6 and 8

The redox properties of model complexes are one of the interesting features in the structural and functional mimics of the Fe-only hydrogenase-active site. The cyclic voltammograms (CV) of complexes **2–6** and **8** were studied to evaluate the effects of different phosphane ligands on the redox properties of the central iron atoms. The CV measurements were carried out in CH₃CN and scanned in the cathodic direction as indicated in Figures 2, 3 and 4. The redox potentials of **2–6** and **8**, as well as their parent complex [(μ-pdt)Fe₂(CO)₆], are given in Table 4. A good CV of the PPh₃-disubstituted complex **7** was not obtained because of the poor solubility of **7** in CH₃CN.

Each phosphane-monosubstituted diiron complex displays four irreversible peaks, two oxidative and two reductive peaks. Compared with the electrochemical data of the all-carbonyl diiron complex **1** and other analogues,^[9,29,31,32] the peaks at 0.33–0.52 V are assigned to the one-electron oxidation process of Fe^IFe^I to Fe^{II}Fe^I, and the more anodic peaks at 0.70–0.74 V are proposed to be the response of the further oxidation process of Fe^{II}Fe^I to

Figure 2. Cyclic voltammograms of complexes **2–5**.Figure 3. Cyclic voltammograms of **3** (1 × 10⁻³ M) under Ar and CO.

Fe^{II}Fe^{II}. Complexes **2–5** exhibit the first reductive peaks at –1.86, –1.82, –1.76 and –1.73 V, respectively, which are attributed to the reduction process of Fe^IFe^I to Fe⁰Fe^I (*E*₁). The second reductive peaks for **2–5** in the range of –2.06 to –2.19 V, detected under Ar, were not observed when the CV measurement was carried out under CO (Figure 3). The CV control studies of **2–5** suggest that the more negative peaks at –2.06 to –2.19 V might be raised by the one-electron reduction process of Fe^IFe^I/Fe^IFe⁰ for a CH₃CN-substituted species, [(μ-pdt)[Fe(CO)₂(PR₃)]₂[Fe(CO)₂(NCCH₃)].^[12] The assignment of the third irreversible reductive peak for complex **4** at ca. –2.29 V is not clear. The first reduction potential is shifted in a cathodic direction

Figure 4. Cyclic voltammograms of complexes **6** and **8**.Table 4. Redox potentials of complexes **1–6** and **8**.^[a]

Complex	$E_{\text{pa}} [\text{V}]$ $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{II}}$	$E_{\text{pa}} [\text{V}]$ $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{I}}$	$E_{\text{pc}} [\text{V}]$ $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}/\text{Fe}^0\text{Fe}^{\text{I}}$
1	+0.84	–	–1.57
2	+0.73	+0.39	–1.86
3	+0.74	+0.33	–1.82
4	+0.70	+0.34	–1.76
5	+0.71	+0.52	–1.73
6	+0.28	–0.06	–2.22
8	–	+0.08	–2.19

[a] $n\text{Bu}_4\text{NPF}_6$ (0.1 M) in CH_3CN ; scan rate: 0.1 V s^{-1} ; working electrode: glassy carbon electrode of diameter 3 mm; reference electrode: non-aqueous Ag/Ag^+ electrode (0.01 M AgNO_3 in CH_3CN); counter electrode: platinum wire.

by ca. 290, 250, 190 and 160 mV for **2–5**, respectively, as compared to that of the all-carbonyl parent complex.^[31] The better donor character of PMe_3 and PMe_2Ph renders the reduction of the iron core more difficult. Complexes **4** and **5**, with either a PPh_3 or a $\text{P}(\text{OEt})_3$ ligand, display smaller cathodic shifts in CV relative to **2** and **3**. The reduction potential (E_1) for **5** is obviously less cathodic than that for complex **2** by 130 mV, indicative of a considerable influence of different phosphane ligands on the redox properties of the iron atoms of Fe-only hydrogenase-active-site model complexes.

As for previously reported CVs of PMe_3 -disubstituted derivatives,^[29] **6** and **8** each show only one reductive peak at ca. -2.2 V , which is attributed to the reduction process of $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ to $\text{Fe}^0\text{Fe}^{\text{I}}$. The second reductive peaks of **6** and **8** are not accessible within the solvent window in Figure 4. The first reductive peaks of **6** and **8** apparently move to more negative potentials by 400 and 460 mV, respectively, as compared with that of the corresponding monosubstituted homologues **3** and **5**. It suggests that the introduction of the second tertiary phosphane ligand exerts a stronger influence on the redox potentials of diiron complexes than the introduction of the first one. With the conversion of mono- to disubstituted derivatives, the anodic peak, assigned to the oxidation of $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ to $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$, shifts from

+0.33 to -0.06 V for the conversion of **3** to **6** and from +0.52 to +0.08 V for **5** to **8**. Another oxidative peak at +0.28 V for **6**, with a cathodic shift of 460 mV compared with the corresponding peak of **3**, is tentatively ascribed to the oxidation process of $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$ to $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$.

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, $[\text{Fe}(\text{CO})_5]$ and all tertiary phosphanes and phosphite, were reagent grade and used as received. The starting compound $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_6]$ (**1**) was prepared according to the literature.^[28,33] Infrared spectra were recorded from KBr pellets with a JASCO FT/IR 430 spectrophotometer. ^1H and ^{31}P NMR spectra were collected with a Varian INOVA 400 NMR spectrometer. Elemental analyses were performed with a Thermoquest-Flash EA 1112 elemental analyzer.

Synthesis of $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_5\text{L}]$ [$\text{L} = \text{PMe}_3$ (2**), PMe_2Ph (**3**):** Trimethylphosphane (46 mg, 0.6 mmol) was added to a solution of hexacarbonyldiiron dithiolate **1** (240 mg, 0.6 mmol) in hexane (30 mL). The red solution was stirred for 5 h and the color turned dark red. After the solution was concentrated by solvent evaporation in vacuo, the crude product was purified by flash column chromatography on silica gel, first with hexane and then with hexane/ CH_2Cl_2 (6:1) as eluents. Product **2** was obtained by cooling the concentrated hexane solution to -20°C . Yield: 0.16 g (61%). $\text{C}_{11}\text{H}_{15}\text{O}_5\text{PS}_2\text{Fe}_2$ (434.0): calcd. C 30.44, H 3.48; found C 31.28, H 3.57. IR (KBr, ν_{CO}): $\tilde{\nu} = 2037, 1980, 1919 \text{ cm}^{-1}$. ^1H NMR (CDCl_3): $\delta = 1.95$ (m, 4 H, SCH_2), 1.71 (m, 2 H, CCH_2C), 1.48 (d, $J_{\text{P-H}} = 9.19 \text{ Hz}$, 9 H, CH_3) ppm. ^{31}P NMR (CDCl_3): $\delta = 24.96$ (PMe_3) ppm. Complex **3** was prepared by a procedure similar to that of **2**. The reaction of **1** (3.0 g, 7.8 mmol) with PMe_2Ph (1.07 g, 7.8 mmol) was carried out in benzene (100 mL). Analytically pure complex **3** was obtained by column chromatography on silica gel, with hexane and then hexane/ CH_2Cl_2 (3:1) as eluents. Yield: 2.8 g (72%). $\text{C}_{16}\text{H}_{17}\text{Fe}_2\text{O}_5\text{PS}_2$ (496.1): calcd. C 38.74, H 3.45; found C 38.90, H 3.51. IR (KBr, ν_{CO}): $\tilde{\nu} = 2040, 1980, 1921 \text{ cm}^{-1}$. ^1H NMR (CDCl_3): $\delta = 7.57, 7.41$ (2 s, br., 5 H, Ph), 1.94 (m, 4 H, SCH_2), 1.80 (s, br., 6 H, CH_3), 1.66 (m, 2 H, CCH_2C) ppm. ^{31}P NMR (CDCl_3): $\delta = 32.66$ (PMe_2Ph) ppm.

Synthesis of $[(\mu\text{-pdt})\text{Fe}_2(\text{CO})_5\text{L}]$ [$\text{L} = \text{PPh}_3$ (4**), $\text{P}(\text{OEt})_3$ (**5**):** Triphenylphosphane (2.0 g, 6.5 mmol) was added to a solution of **1** (1.3 g, 3.2 mmol) in toluene (100 mL). The solution was refluxed for 6 h and the color turned purple-red. After the solution was concentrated by solvent evaporation in vacuo, the crude product was purified by flash column chromatography on silica gel with CH_2Cl_2 as eluent. Purple crystals of **4** were obtained by recrystallization in hexane/ CH_2Cl_2 . Yield: 1.2 g (64%). $\text{C}_{26}\text{H}_{21}\text{O}_5\text{PS}_2\text{Fe}_2$ (620.2): calcd. C 50.35, H 3.41; found C 50.29, H 3.45. IR (KBr, ν_{CO}): $\tilde{\nu} = 2044, 1984, 1931 \text{ cm}^{-1}$. ^1H NMR (CDCl_3): $\delta = 7.69, 7.43$ (2 s, 15 H, Ph), 1.73 (m, 4 H, SCH_2), 1.54 (m, 2 H, CCH_2C) ppm. ^{31}P NMR (CDCl_3): $\delta = 65.74$ (PPh_3) ppm. Complex **5** was prepared by a procedure similar to that for **4**. The reaction of **1** (386 mg, 1.0 mmol) with $\text{P}(\text{OEt})_3$ (0.17 mL, 1.0 mmol) was carried out in toluene (20 mL) for 3 h. Analytically pure complex **5** was obtained by recrystallization of the product in hexane/ CH_2Cl_2 at -20°C . Yield: 0.158 g (33%). $\text{C}_{14}\text{H}_{21}\text{Fe}_2\text{O}_8\text{PS}_2$ (524.1): calcd. C 32.08, H 4.04; found C 32.04, H 4.04. IR (KBr, ν_{CO}): $\tilde{\nu} = 2046,$

Table 5. Crystallographic data and processing parameters for complexes 3–6.

Complex	3	4	5	6
Empirical formula	C ₁₆ H ₁₇ Fe ₂ O ₅ PS ₂	C ₂₆ H ₂₁ Fe ₂ O ₅ PS ₂	C ₁₄ H ₂₁ Fe ₂ O ₈ PS ₂	C ₂₃ H ₂₈ Fe ₂ O ₄ P ₂ S ₂
<i>M_w</i>	496.09	620.22	524.10	606.21
<i>T</i> [K]	293(2)	293(2)	293(2)	293(2)
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>c</i>	<i>C</i> 2	<i>Fdd</i> 2
<i>a</i> [Å]	9.061(2)	9.2533(4)	20.5038(8)	25.633(5)
<i>b</i> [Å]	9.155	17.5257(6)	13.8441(7)	27.503(6)
<i>c</i> [Å]	14.067(4)	16.8340(6)	8.4154(5)	7.7193(15)
α [°]	106.5720(10)	90.00	90.00	90.00
β [°]	96.578(2)	102.7620(10)	103.953(4)	90.00
γ [°]	108.048(2)	90.00	90.00	90.00
<i>V</i> [Å ³]	1036.81(4)	2662.54(17)	2318.3(2)	5441.8(19)
<i>Z</i>	2	4	4	8
$\rho_{\text{calcd.}}$ [g cm ^{−3}]	1.589	1.547	1.502	1.480
<i>F</i> (000)	504	1264	1072	2496
Crystal size [mm]	0.09 × 0.10 × 0.28	0.07 × 0.15 × 0.20	0.05 × 0.08 × 0.13	0.18 × 0.25 × 0.34
$\theta_{\text{min/max}}$ [°]	1.55/25.04	1.70/25.06	1.79/28.30	3.18/27.48
Reflections collected/unique	5375/3607	7906/4204	8384/ 5091	11919/2893
Parameters refined	235	325	244	154
Goodness-of-fit on <i>F</i> ²	1.019	1.036	0.920	1.050
Final <i>R</i> ₁ [<i>I</i> > $\sigma(I)$]	0.0461	0.0386	0.0447	0.0500
Final <i>wR</i> ₂	0.1268	0.0931	0.0981	0.1038
Residual electron density [e Å ^{−3}]	0.524, −0.416	0.621, −0.344	0.581, −0.356	0.481, −0.514

1989, 1936 cm^{−1}. ¹H NMR (CDCl₃): δ = 4.13 (s, 6 H, OCH₂), 2.05 (m, 4 H, SCH₂), 1.76 (m, 2 H, CCH₂C), 1.37 (s, 9 H, CH₃) ppm. ³¹P NMR (CDCl₃): δ = 171.09 [P(OEt)₃] ppm.

Synthesis of [(μ-pdt)Fe₂(CO)₄(PMe₂Ph)₂] (6): Product **6** can be prepared directly from [(μ-pdt)Fe₂(CO)₆] in one pot according to the reported protocol^[17] or by a stepwise CO displacement with **3** as a starting compound. The crystal suitable for X-ray analysis was obtained from a solution of hexane at −20 °C.

Synthesis of [(μ-pdt)Fe₂(CO)₄L₂] [L = PPh₃ (7), P(OEt)₃ (8)]: Compound **1** (2.5 g, 6.5 mmol) was dissolved in toluene (150 mL) and then an excess of PPh₃ (6.8 g, 26.0 mmol) was added. The red solution was refluxed for 6 h and the color turned dark red. The solution was concentrated by solvent evaporation in vacuo. Mono- and disubstituted complexes **4** and **6** were separated by column chromatography on silica gel with hexane/CH₂Cl₂ (2:1) and then CH₂Cl₂ as eluents. Product **4** was obtained from the first band (1.5 g, 37%) and **7** from the second band (1.1 g, 20%). C₄₃H₃₆Fe₂O₄P₂S₂ (854.5): calcd. C 60.44, H 4.25; found C 60.27, H 4.28. IR (KBr, νCO): $\tilde{\nu}$ = 1997, 1951, 1933 cm^{−1}. ¹H NMR (CDCl₃): δ = 7.69, 7.34 (2s, 30 H, Ph), 1.85 (m, 4 H, SCH₂), 1.56 (m, 2 H, CCH₂C) ppm. ³¹P NMR (CDCl₃): δ = 62.79 (PPh₃) ppm. Essentially the same procedure as for **7** was applied for the preparation of **8**, by refluxing a toluene solution (35 mL) of **1** (1.3 g, 3.4 mmol) and P(OEt)₃ (2.0 mL, 11.6 mmol) for 6 h. Product **5** was obtained from the first band (1.0 g, 56%) and **8** from the second band (0.57 g, 26%). C₁₉H₃₆Fe₂O₁₀P₂S₂ (662.3): calcd. C 34.46, H 5.48; found C 34.64, H, 5.63. IR (KBr, νCO): $\tilde{\nu}$ = 2002, 1960, 1935 cm^{−1}. ¹H NMR (CDCl₃): δ = 4.15 (s, 12 H, OCH₂), 1.95 (m, 4 H, SCH₂), 1.70 (m, 2 H, CCH₂C), 1.36 (s, 18 H, CH₃) ppm. ³¹P NMR (CDCl₃): δ = 175.43 [P(OEt)₃] ppm.

Crystal Structure Determination of Complexes 3, 4 and 6: The single-crystal X-ray diffraction data were collected with a Siemens SMART CCD diffractometer for **3** and **4** and with an AFE5R Rigaku diffractometer for **5** and **6** with graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å) at 293 K using the ω -2 θ scan mode. Data processing was accomplished with the SAINT processing program.^[34] Intensity data were corrected for absorption by

the SADABS program.^[35] The structure was solved by direct methods and refined on *F*² against full-matrix least-squares methods by using the SHELXTL97 program package.^[36] 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 complexes **3–6** are listed in Table 5. CCDC-218501 (**3**), -228422 (**4**), -255204 (**5**) and -253139 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemistry Studies of Complexes 2–6 and 8: Acetonitrile (Aldrich, spectroscopy grade) used for electrochemical measurements was dried with molecular sieves and then freshly distilled from CaH₂ under N₂. A solution of 0.1 M *n*Bu₄NPF₆ (Fluka, electrochemical grade) in CH₃CN was used as electrolyte, which was degassed by bubbling with dry argon for 10 min before measurement. Electrochemical measurements were recorded using a BAS-100W electrochemical potentiostat at a scan rate of 200 mV/s. Cyclic voltammograms were obtained in a three-electrode cell under argon. The working electrode was a glassy carbon disc (diameter 3 mm) successively polished with 3- and 1-μm diamond pastes and sonicated in ion-free water for 10 min. The reference electrode was a non-aqueous Ag/Ag⁺ electrode (0.01 M AgNO₃ in CH₃CN) and the auxiliary electrode was a platinum wire.

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