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C–S, C–H, and N–H bond cleavage of heterocycles by a zero-valent iron complex, $Fe(N_2)(depe)_2$ [depe = 1,2-bis(diethylphosphino)ethane]

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Abstract

Treatment of $Fe(N_2)(depe)_2$ [depe = 1,2-bis(diethylphosphino)ethane] (**1**) with benzo[*b*]thiophene at room temperature results in the regioselective C–S and C–H bond cleavages giving $Fe(SC_6H_4CH{=}CH)(depe)_2$ (**2a**) and *trans*-$FeH(C{=}CHC_6H_4S)(depe)_2$ (**3a**) in 72 and 19% yields, respectively. Complex **1** also reacts with thiophene, 2- and 3-acetylthiophenes and 2- and 3-methylthiophenes to give both C–S and C–H bond oxidative addition products: $Fe(SCH{=}CHCH{=}CH)(depe)_2$ (**2b**) and *trans*-$FeH(C{=}CHCH{=}CHS)(depe)_2$ (**3b**), $Fe[SC(COMe){=}CHCH{=}CH](depe)_2$ (**2c**) and *trans*-$FeH[C{=}CHCH{=}C(COMe)S](depe)_2$ (**3c**), $Fe[SC(Me){=}CHCH{=}CH](depe)_2$ (**2d**) and *trans*-$FeH[C{=}CHCH{=}C(Me)S](depe)_2$ (**3d**), and $Fe[SCH{=}C(Me)CH{=}CH](depe)_2$ (**2e**) and *trans*-$FeH[C{=}CHC(Me){=}CHS](depe)_2$ (**3e**), respectively. On the other hand, only C–H bond cleavage takes place in the reactions of **1** with furans such as furan, benzo[*b*]furan, and 2,3-dihydrofuran to give *trans*-$FeH(C{=}CHCH{=}CHO)(depe)_2$ (**4a**), $FeH(C{=}CHC_6H_4O)(depe)_2$ (**4b**) and *trans*-$FeH(C{=}CHOCH_2CH_2)(depe)_2$ (**4c**) and N–H bond is exclusively cleaved by the reaction of **1** with pyrroles such as pyrrole, indole and 2-acetylpyrrole to give *trans*-$FeH(NCH{=}CHCH{=}CH)(depe)_2$ (**5a**), *trans*- and *cis*-$FeH(NCH{=}CHC_6H_4)(depe)_2$ (**5b**) and $FeH[NC(COMe){=}CHCH{=}CH](\eta^2\text{-depe})(\eta^1\text{-depe})$ (**6**). Treatment of **2a** with MeI results in the Fe–S bond cleavage of the thiaferracycle giving *trans*-$FeI[(E)\text{-}CH{=}CHC_6H_4\text{-}2\text{-}SMe](depe)_2$ (**7**) whose structure is unequivocally characterized by X-ray analysis. In contrast, hydrogenolysis of **2a** with H_2 (50 atm) leads to the cleavage of the Fe–C bond of the thiaferracycle to yield *cis*- and *trans*-$FeH(SC_6H_4\text{-}2\text{-}Et)(depe)_2$ (**8**). © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Iron complexes; Diphosphine complexes; Sulfur ligand complexes; Activation of heterocycles

1. Introduction

Activation of heterocyclic compounds is an intriguing field of organometallic chemistry because of its potential applications in catalysis and organic synthesis. Particularly, much attention has been focused on the activation of thiophenes in the viewpoint of mechanisms for catalytic hydrodesulfurization (HDS) [1–5]. Although many examples using Ni, Pt, Co, Rh, Ir, Ru and Mo complexes have been reported as models for HDS [1–5], such activation of heterocyclic compounds with Fe complexes is still less explored, except for the photochemical C–S and C–H bond activation of thiophene and methylthiophene by $FeH_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] by Field and co-workers [6]. We recently reported the isolation of a dinitrogen complex of iron(0), $Fe(N_2)(depe)_2$ [depe = 1,2-bis(diethylphosphino)ethane] (**1**), which showed a variety of reactivities toward H_2, CO, CO_2, CS_2, C_2H_4, 2,6-xylyl isocyanide and styrenes accompanied by smooth release of a dinitrogen molecule at room temperature (r.t.) without irradiation of light [7,8]. Such lability of **1** is considered to arise from the easy liberation of the dinitrogen ligand. Herein we wish to report the C–H and C–S bond activation of heterocyclic

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compounds such as thiophenes, furans, and pyrroles with **1** without photo irradiation under ambient conditions. Reactions of the resulting complexes are also described.

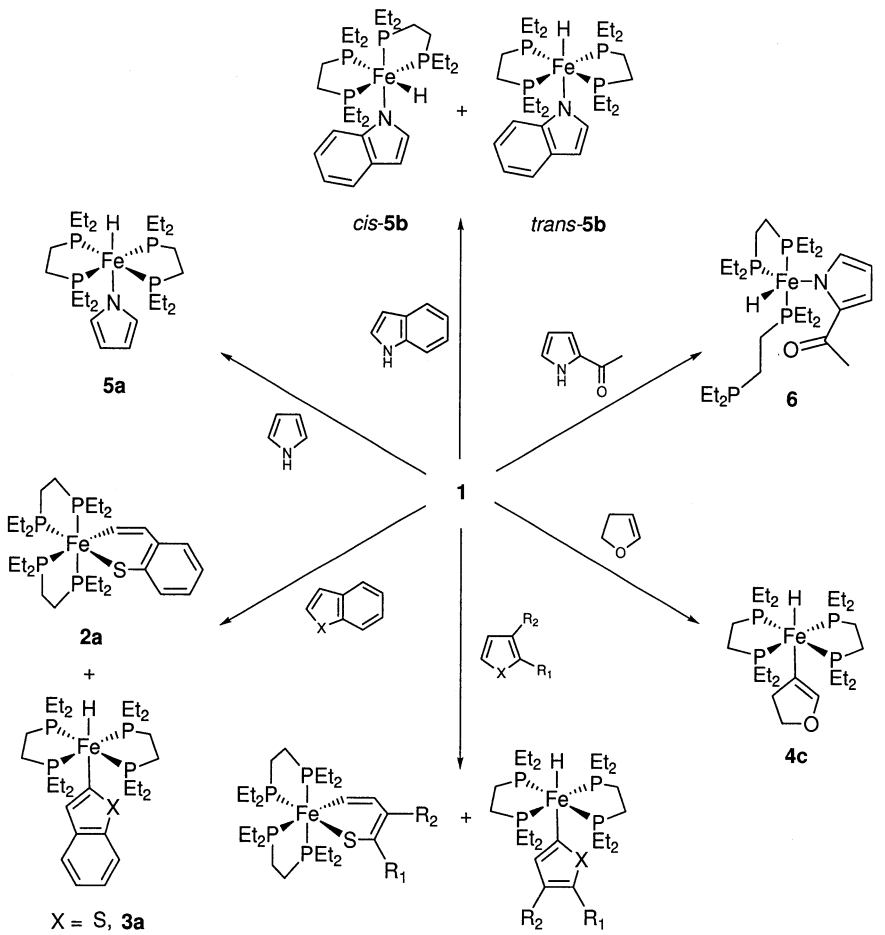
2. Results and discussion

2.1. Reactions of heterocycles with $Fe(N_2)(depe)_2$

Reactions of various heterocycles such as thiophenes, furans, and pyrroles with $Fe(N_2)(depe)_2$ [depe = 1,2-bis(diethylphosphino)ethane] (**1**) were performed and these results are summarized in Scheme 1 and Table 1. Activation of heterocycles with **1** and characterization of the products are discussed below.

2.1.1. C–S and C–H bond cleavage of thiophenes

The reaction of $Fe(N_2)(depe)_2$ [depe = 1,2-bis(diethylphosphino)ethane] (**1**) with benzo[*b*]thiophene at r.t. in THF resulted in the cleavage of both C–S and C–H bonds to give $Fe(SC_6H_4CH{=}CH)(depe)_2$ (**2a**) and *trans*-$FeH(C{=}CHC_6H_4S)(depe)_2$ (**3a**), respectively, in a 7:2 ratio (Table 1, entry 1). The former complex **2a** was isolated by the preferential crystallization from cold pentane in 41% yield as analytically pure dark red crystals. The molecular structure of **2a** was determined by NMR spectroscopy as well as by X-ray structure analysis. The $^{31}P\{^1H\}$ NMR spectrum of **2a** showed an AMNX pattern at δ 55.1, 66.6, 69.5 and 76.5 indicating *cis* configuration of **2a**. In the ^1H NMR spectrum of **2a**, the olefinic protons are observed at δ 7.91 (dd, $J = 11.7$



R_1 = H, R_2 = H, **2b**; COMe, H, **2c**; Me, H, **2d**; H, Me, **2e**

X = S, R_1 = H, R_2 = H, **3b**; S, COMe, H, **3c**; S, Me, H, **3d**; S, H, Me, **3e**; O, H, H, **4a**

Scheme 1.

Table 1
Summary of the reactions of **1** with five-membered heterocycles [a]

Entry	Heterocycles	Time (h)	Temp. (°C)	Product(s) (% yield)
1	Benzo[*b*]thiophene	168	r.t.	**2a** (72)+**3a** (19)
2	Thiophene	168	r.t.	**2b** (44)+**3b** (51)
3	2-Acetylthiophene	168	r.t.	**2c** (53)+**3c** (26)
4	2-Methylthiophene	168	r.t.	**2d** (24)+**3d** (62)
5	3-Methylthiophene	168	r.t.	**2e** (16)+**3e** (70)
6	Dibenzothiophene	48	70	n.r. [b]
7	2,5-Dimethylthiophene	48	70	n.r.
8	Tetrahydrothiophene	48	70	n.r.
9	2-Methylbenzo[*b*]thiophene	48	70	n.r.
10	2,3-Dihydrobenzo[*b*]thiophene	48	70	n.r.
11	Furan	48	r.t.	**4a** (47)
12	Benzo[*b*]furan	48	r.t.	**4b** (65)
13	2,3-Dihydrofuran	48	r.t.	**4c** (95)
14	2-Acetylfuran	48	50	n.r.
15	Dibenzofuran	48	50	n.r.
16	2,5-Dimethylfuran	48	50	n.r.
17	2,5-Dihydrofuran	48	50	n.r.
18	Tetrahydrofuran	48	50	n.r.
19	2,3-Dihydrobenzofuran	48	50	n.r.
20	Pyrrole	48	r.t.	**5a** (95)
21	Indole	48	r.t.	*cis*-**5b** (23)+*trans*-**5b** (12)
22	2-Acetylpyrrole	48	r.t.	**6** (95)
23	*N*-Methylpyrrole	48	50	n.r.
24	2,5-Dimethylpyrrole	48	r.t.	n.r.
25	Pyrrolidine	48	50	n.r.
26	2-Methylindole	48	50	n.r.

[a] Solvent: C_6D_6.
[b] n.r., no reaction.

and 6.3 Hz, 1H) and 8.27 (ddt, $J = 21.0$, 11.7 and 3.1 Hz, 1H) coupled to each other [$^3J(H-H) = 11.7$ Hz] and to phosphorus atoms [$^3J(H-P_{trans}) = 21.0$ Hz, $^3J(H-P_{cis}) = 3.1$ Hz, and $^4J(H-P_{trans}) = 6.3$ Hz]. These facts suggest that the C–S bond between the olefinic carbon and the sulfur atoms has been cleaved via oxidative addition.

The molecular structure of **2a** was also determined by the X-ray structure analysis. An ORTEP drawing of **2a** is shown in Fig. 1 and selected bond distances and angles are summarized in Table 2.

Complex **2a** is best regarded as an octahedral thiaferracycle, which is formed by oxidative addition of the C(1)–S(1) bond of benzo[*b*]thiophene to the iron(0). This is consistent with the NMR data of **2a** suggesting that the molecular structure basically remained intact in the solution state. Similar C–S oxidative addition products of benzo[*b*]thiophene such as $Ir(SC_6H_4CH{=}CH)(Cl)(PMe_3)_4$ [9], $Ir(SC_6H_4CH{=}CH)(tdpme)$ [2b], $Pt(SC_6H_4CH{=}CH)(PEt_3)_2$ [2c], and $Rh(SC_6H_4CH{=}CMe)(Cp^*)(PMe_3)$ [10] have also been reported recently.

The C–H oxidative addition product **3a** was isolated from the mother liquor after preferential crystallization of **2a** in the analytically pure form. The $^{31}P\{^1H\}$ NMR spectrum of **3a** shows a singlet at δ 92.8 suggesting two depe ligands in an equatorial plane in the octahedral iron(II) center. Consistently, in the ^1H NMR spectrum, a hydride signal is observed as a quintet at δ −18.83 [$J(H-P) = 48.2$ Hz] coupled to four magnetically equivalent phosphorus atoms. The olefinic proton of benzo-

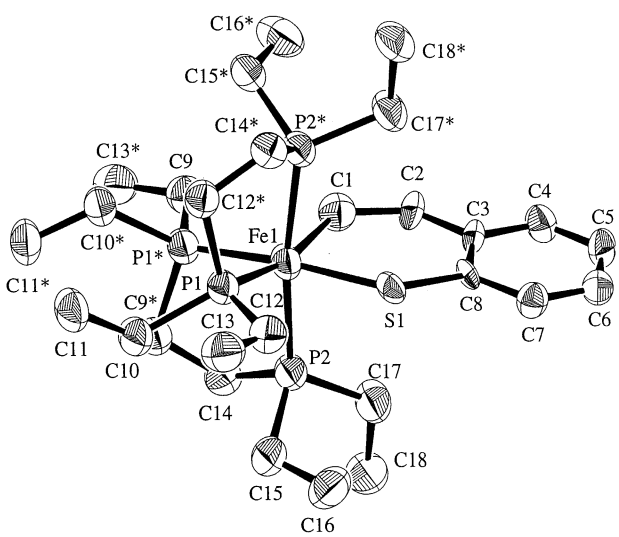


Fig. 1. ORTEP drawing of $Fe(SC_6H_4CH{=}CH)(depe)_2$ (**2a**). All hydrogen atoms are omitted for clarity. Atoms with an asterisk were generated by the symmetrical operations. Ellipsoids represent 50% probability.

Table 2
Selected bond angles (°) and lengths (Å) of Fe(SC$_6$H$_4$CH=CH)(depe)$_2$ (**2a**)

Fe(1)–S(1)	2.207(2)	Fe(1)–C(1)	2.132(6)
Fe(1)–P(1)	2.236(1)	Fe(1)–P(2)	2.233(1)
C(1)–C(2)	1.42(1)	C(2)–C(3)	1.45(1)
C(3)–C(4)	1.39(1)	C(3)–C(8)	1.38(1)
C(4)–C(5)	1.34(2)	C(5)–C(6)	1.40(2)
C(6)–C(7)	1.37(1)	C(7)–C(8)	1.42(1)
C(7)–C(8)	1.24(3)		
C(1)–Fe(1)–S(1)	91.5(2)	C(1)–Fe(1)–P(1)	166.8(2)
C(1)–Fe(1)–P(2)	82.7(2)	C(1)–Fe(1)–P(1*)	84.4(2)
C(1)–Fe(1)–P(2*)	82.7(2)	S(1)–Fe(1)–P(1)	93.69(6)
S(1)–Fe(1)–P(2)	86.52(8)	S(1)–Fe(1)–P(1*)	171.25(7)
S(1)–Fe(1)–P(2*)	86.91(8)	P(1)–Fe(1)–P(2)	100.55(5)
P(1)–Fe(1)–P(1*)	92.01(6)	P(1)–Fe(1)–P(2*)	85.52(5)
P(1*)–Fe(1)–P(2*)	100.55(5)	P(2)–Fe(1)–P(2*)	171.33(7)

thienyl ligand is observed as a singlet at δ 6.83, and the aromatic protons appear at δ 6.95 (t), 7.20 (t), 7.64 (d), and 7.81 (d). These data support the oxidative addition of one of the olefinic C–H bonds of benzo[*b*]thiophene.

Complexes **2a** and **3a** must be produced by independent reactions of **1** with benzo[*b*]thiophene, because the ratio of the isolated **2a** and **3a** remained intact even after prolonged heating at 70°C for 48 h in benzene-d_6. In addition, the isolated complexes **2a** and **3a** did not isomerize under these conditions, suggesting that these complexes are not in equilibrium. However, upon increasing the [benzo[*b*]thiophene]:[**1**] ratio from 1:1 to 30:1, the ratio of **2a**:**3a** increased from 70:30 to 85:15. These results suggest that the C–S and C–H bond cleavages took place via independent routes and the C–S bond cleavage process is more effectively enhanced with increase in the benzo[*b*]thiophene concentration. Such a concentration effect of benzo[*b*]-thiophene would be most consistent with the associative pathway for **2a** but not for **3a**. Consistently, no significant enhancement was observed for the formation of **2a** under vacuum excluding a dissociative mechanism. As we reported previously [7a], complex **1** does not liberate the dinitrogen ligand under high vacuum and Perthuisot and Jones [8] proposed an associative mechanism for the displacement of the dinitrogen ligand in **1** by H_2, CO, ethylene, and 2,6-xylyl isocyanide by kinetic studies. On the other hand, the rate determining step for the formation of **3a** would be independent of the concentration of the benzo[*b*]thiophene, though a detailed mechanism is not clear at present.

Encouraged by the above results, reactions of **1** with various thiophene derivatives were carried out (Scheme 1) and detail spectroscopic and physical data of these products are described in Section 3. Reaction of **1** with thiophene also gave a mixture of the C–S and C–H bond oxidative addition products Fe(SCH=CHCH=CH)(depe)$_2$ (**2b**) and *trans*-FeH(C=CHCH=CHS)(depe)$_2$ (**3b**) (entry 2). In this reaction, the C–H bond oxidative addition of thiophene can take place at the 2- and 3-positions. It is known that *trans*-RhCl(CO)(PMe$_3$)$_2$ can react with both the 2- and 3-positions of thiophene to give RhHCl(C=CHCH=CHS)(PMe$_3$)$_2$ and RhHCl(C=CHSCH=CH)(PMe$_3$)$_2$ [11]. The thienyl group in **3b** must bond to Fe at the 2-position, because all signals assignable to the thienyl protons show a linkage of coupling. The total yields of **2b** and **3b** were 44 and 51%, respectively (entry 2).

The treatment of **1** with 2-acetylthiophene resulted in the formation of a mixture of two iron species (Table 1, entry 3), from which *trans*-FeH[C=CHCH=C(COMe)S](depe)$_2$ (**3c**) was isolated by recrystallization from hexane, and the other species is assigned as the C–S bond oxidative addition product Fe[SC(COMe)=CHCH=CH](depe)$_2$ (**2c**). π-Electrons in the thiaferracycle are considered to be delocalized because one of the protons appeared at extremely low field (δ 8.98) which may be characteristic of the proton of alkenyl α-carbon due to the ring current effect as Bleeke et al. reported [12].

The reaction of **1** with 2-methylthiophene gave a similar mixture of two species (Table 1, entry 4). One of them is characterized as a C–S bond oxidative addition product Fe[SC(Me)=CHCH=CH](depe)$_2$ (**2d**) by NMR data (see Section 3). However, characterization of the other species is worth noting. This other species shows a singlet at δ 93.6 in the ^{31}P{^{1}H} NMR spectrum, and signals at δ −19.47, 2.59, 6.36 and 6.89 assignable to the hydrido, methyl, and aromatic protons in the ^{1}H NMR spectrum, suggesting the formation of a hydridothienyliron(II) complex. Unfortunately, the regiochemistry in the C–H bond oxidative addition of 2-methylthiophene is not clear at present, since broadening of signals of the thienyl ring in the ^{1}H NMR spectrum prevented the detail assignment of the coupling. We believe that *trans*-FeH[C=CHCH=C(Me)S](depe)$_2$ (**3d**) is the most appropriate structure because of the following reasons: (i) both thiophene and 2-acetylthiophene react with **1** at the carbon adjacent to the sulfur atom to give **3b** and **3c**; (ii) formation of Fe[SC(Me)=CHCH=CH](dmpe)$_2$ (dmpe analog of **2d**) and *trans*-FeH[C=CHCH=C(Me)S](dmpe)$_2$ (dmpe analog of **3d**) is reported in the reaction of 2-methylthiophene with FeH$_2$(dmpe)$_2$ [6].

Reaction of **1** with 3-methylthiophene also gave a mixture of the C–H and C–S bond oxidative addition products (Table 1, entry 5). The C–S bond oxidative addition product shows an AMNX pattern at δ 55.6, 65.8, 68.1 and 76.5 in the ^{31}P{^{1}H} NMR spectrum, and a singlet at δ 2.11 due to the methyl group, two broad peaks at δ 5.68 and 7.29, and a broad multiplet at δ

8.02 coupled to the phosphorus atoms in the ^{1}H NMR spectrum. Since two types of thiaferracycles, Fe[SCH=C(Me)CH=CH](depe)$_2$ and Fe[SCH=CHC(Me)=CH](depe)$_2$ are possible, 2-deuterio-3-methylthiophene (99% deuterized) was employed in this reaction to determine the regioselectivity. The ^{1}H NMR spectrum of the thiaferracycle shows that a singlet at δ 2.11 due to the methyl group, and broad peaks at δ 7.29 and 8.02 due to the thienyl ring protons. While a broad peak at δ 5.68 disappeared, a multiplet at δ 8.02 coupled to phosphorus atoms remained in the ^{1}H NMR spectrum. These results clearly show the formation of Fe[SCH=C(Me)CH=CH](depe)$_2$ (**2e**) as the C–S bond oxidative addition product. On the other hand, the C–H bond oxidative addition product shows a singlet at δ 93.4 in the ^{31}P{^{1}H} NMR spectrum. In the ^{1}H NMR spectrum, a quintet at δ −19.40 assignable to the hydride, a singlet at δ 2.38 due to the methyl group, and signals at δ 6.19 and 7.07 due to the thienyl ring protons are observed. When 2-deuterio-3-methylthiophene was employed in this reaction, a signal at δ 7.07 disappeared, but the signals at δ −19.40, 2.38 and 6.19 remained. Taking into account these results and by the analogies discussed above, the C–H bond oxidative addition product was characterized as *trans*-FeH[C=CHC(Me)=CHS](depe)$_2$ (**3e**).

As summarized in Table 1, it seems that an electron withdrawing group in thiophene enhances the activation of the C–S bond over the C–H bond. Such a trend is also reported for Rh complexes [2k]. It is also noteworthy that the iron has regioselectively attacked the less hindered C–S or C–H bond. These regioselectivities are in sharp contrast to the photochemical reactions of *cis*-FeH$_2$(dmpe)$_2$ with 3-methylthiophene which gave a mixture of the regioisomers [6]. Dibenzothiophene, 2,5-dimethylthiophene, and 2-methylbenzo[*b*]-thiophene did not react (Table 1, entries 6, 7 and 9). This is most likely due to the steric congestion around the sulfur atom, suggesting the importance of pre-coordination of the sulfur atom may be important for these bond cleavage reactions. It is interesting that both tetrahydrothiophene and 2,3-dihydrobenzo[*b*]thiophene also did not react on treatment with **1** even at 70°C.

2.1.2. C–H bond cleavage of furans

Contrary to the reactions of thiophenes, reactions of **1** with furans such as furan, benzo[*b*]furan, and 2,3-dihydrofuran exclusively lead to oxidative addition of the C–H bond to give (hydrido)(furyl)iron (II) complexes *trans*-FeH(C=CHCH=CHO)(depe)$_2$ (**4a**), *trans*-FeH(C=CHC$_6$H$_4$O)(depe)$_2$ (**4b**) and *trans*-FeH(C=CHOCH$_2$CH$_2$)(depe)$_2$ (**4c**), respectively (Scheme 1).

The ^{31}P{^{1}H} NMR spectrum of **4a** shows only one resonance at δ 96.6, which is assignable to four magnetically equivalent phosphorus atoms in the octahedral structure. The ^{1}H NMR spectrum of **4a** shows a quintet in high field (δ −18.15) assignable to the hydride group and three broad signals assignable to the furyl ligand in the aromatic region. Although furan can react with **1** at either the 2- or 3-position of furan, detailed characterization of **4a** was unsuccessful because of significant broadening of the aromatic protons. The C–H bond activation at the 2-position of furan was previously reported by Guerchais and co-workers [13], Selnau and Merola [9] and Jones et al. [14], and no examples have been reported for that at the 3-position of furan to our knowledge. Thus, this product is likely to be (hydrido)(2-furyl)iron(II) complex, *trans*-FeH(C=CHCH=CHO)(depe)$_2$ (**4a**) (Table 1, entry 11).

Treatment of **1** with benzo[*b*]furan also gave only the C–H bond oxidative addition product *trans*-FeH(C=CHC$_6$H$_4$O)(depe)$_2$ (**4b**), which was characterized by the analogy of the benzo[*b*]thiophene analog **3a** (Table 1, entry 12).

It is worth noting that 2,3-dihydrofuran quantitatively reacted with **1** at the 3-position to give *trans*-FeH(C=CHOCH$_2$CH$_2$)(depe)$_2$ (**4c**) (Table 1, entry 13). The ^{31}P{^{1}H} NMR spectrum of **4c** shows a singlet at δ 96.8 suggesting magnetically equivalent phosphorus atoms. In the ^{1}H NMR spectrum of **4c**, a quintet at δ −17.85 assignable to the hydride group is observed. Two triplets and one singlet are observed at δ 2.64 (t, J = 8.3 Hz, 2H), 4.00 (s, 1H) and 4.02 (t, J = 8.3 Hz, 2H), which are assigned to two types of aliphatic protons coupled to each other and one isolated olefinic proton on the dihydrofuranyl ring. These coupling patterns suggest the sp^2 C–H bond cleavage of 2,3-dihydrofuran at the 3-position. It is worthwhile noting that the reaction of FeH$_2$(dmpe)$_2$ with cyclopentene under UV irradiation also resulted in the sp^2 C–H bond oxidative addition to the iron center to give FeH(C=CHCH$_2$CH$_2$CH$_2$)(dmpe)$_2$ exclusively [15].

On the other hand, 2-acetylfuran, dibenzofuran, 2,5-dimethylfuran, 2,5-dihydrofuran, tetrahydrofuran and 2,3-dihydrobenzo[*b*]furan remained unreacted (Table 1, entries 14–19) even at 50°C.

2.1.3. N–H bond cleavage of pyrroles

Complex **1** reacted with pyrroles such as pyrrole, and indole in C$_6$D$_6$ at r.t. to give (hydrido)(*N*-pyrrolyl)-iron(II) complexes *trans*-FeH(NCH=CHCH=CH)-(depe)$_2$ (**5a**) and *cis*- and *trans*-FeH(NCH=CHC$_6$H$_4$)-(depe)$_2$ (**5b**) as shown in Scheme 1 (Table 1, entries 20 and 21).

A singlet at δ 91.8 in the ^{31}P{^{1}H} NMR spectrum and a quintet at δ −27.94 indicating a hydride suggest a *trans* structure of **5a**. The pyrrolyl protons appear as two broad signals with equal intensity (2H each) in the

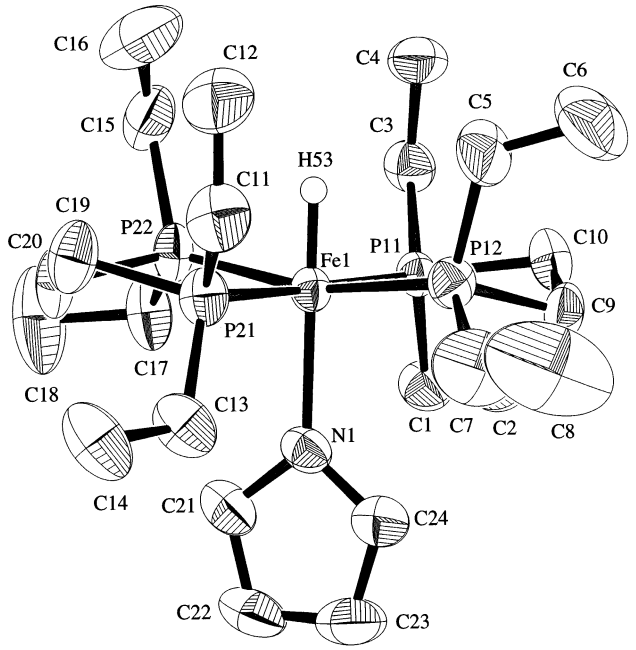


Fig. 2. ORTEP drawing of FeH(NCH=CHCH=CH)(depe)$_2$ (**5a**). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

aromatic region at δ 6.21 and 6.58. The molecular structure of **5a** was unambiguously determined by X-ray structure analysis. An ORTEP drawing of **5a** is shown in Fig. 2 and selected bond distances and angles are summarized in Table 3.

The geometry of **5a** is also regarded as an octahedron where the pyrrolyl and the hydrido ligands are located in *trans* positions. The bond distances between N(1)–C(21), C(21)–C(22), C(22)–C(23), C(23)–C(24) and C(24)–N(1) are in the range of 1.360–1.383 Å, showing extensive electron delocalization in the pyrrolyl ligand.

Table 3
Selected bond angles (°) and lengths (Å) of *trans*-FeH(NCH=CHCH=CH)(depe)$_2$ (**5a**)

Fe(1)–N(1)	2.092(3)	Fe(1)–P(11)	2.209(1)
Fe(1)–P(12)	2.220(1)	Fe(1)–P(21)	2.211(1)
Fe(1)–P(22)	2.209(1)	Fe(1)–H(53)	1.29(4)
N(1)–C(21)	1.366(5)	N(1)–C(24)	1.360(5)
C(21)–C(22)	1.368(6)	C(22)–C(23)	1.383(7)
C(23)–C(24)	1.372(6)		
P(11)–Fe(1)–P(12)	85.25(4)	P(11)–Fe(1)–P(21)	177.25(5)
P(11)–Fe(1)–P(22)	93.48(4)	P(12)–Fe(1)–P(21)	94.90(5)
P(12)–Fe(1)–P(22)	165.04(5)	P(21)–Fe(1)–P(22)	85.67(5)
N(1)–Fe(1)–H(53)	176(1)	P(11)–Fe(1)–H(53)	86(1)
P(12)–Fe(1)–H(53)	84(1)	P(21)–Fe(1)–H(53)	90(1)
P(22)–Fe(1)–H53)	80(1)	P(11)–Fe(1)–N(1)	91.00(9)
P(12)–Fe(1)–N(1)	97.4(1)	P(21)–Fe(1)–N(1)	91.70(9)
P(22)–Fe(1)–N(1)	97.5(1)	N(1)–C(21)–C(22)	111.5(4)
C(21)–C(22)–C(23)	107.0(4)	C(22)–C(23)–C(24)	150.2(4)
C(21)–N(1)–C(24)	103.6(3)		

Reaction of **1** with indole also led to the oxidative addition of the N–H bond to give **5b**. In these reactions, only the N–H bond oxidatively adds to the iron(0) to give **5** and neither the C–N nor C–H bond is cleaved under these conditions. Specific activation of the N–H bond in pyrroles may be due to the high acidity of the N–H proton in pyrroles. Among these complexes, it is interesting to note the structural feature of hydrido(pyrrolyl)iron(II) complex FeH[NC(COMe)=CHCH=CH](η^2-depe)(η^1-depe) (**6**) derived from 2-acetylpyrrole (Table 1, entry 22). The $^{31}P\{^1H\}$ NMR spectrum of **6** shows four magnetically inequivalent phosphorus atoms at δ −18.2 (d, $J = 21.8$ Hz, 1P), 48.9 (ddd, $J = 125.2$, 37.1, 21.8 Hz, 1P), 95.6 (dd, $J = 125.2$, 37.1 Hz, 1P) and 98.7 (t, $J = 37.1$ Hz, 1P). Observation of a large coupling constant ($J = 125.2$ Hz) between the above two P ligands suggests the *trans* configuration of these P atoms. The signal at δ −18.2 is assignable to the uncoordinated P atom in depe ligands providing a monodentate depe ligand. Consistently with this fact, the hydride signal appears as a doublet of doublets of doublets at δ −26.18 ($J = 63.3$, 52.8, 47.9 Hz, 1H) in the ^{1}H NMR spectrum of **6**, which is coupled to only three inequivalent phosphorus atoms. A possible *O,N*-bidentate coordination of the 2-acetylpyrrolyl ligand giving a stable 18 electron complex is excluded, since the IR spectrum of **6** shows a ν(C=O) band at 1652 cm^{-1} the value of which is almost the same as that of free 2-acetylpyrrole [ν(C=O) = 1646 cm^{-1}]. Thus, **6** may have a *tbp* structure where both the hydrido and 2-acetylpyrrolyl ligands occupy the equatorial sites. Probably, steric congestion around the iron center may force such a partial dissociation of the P ligand.

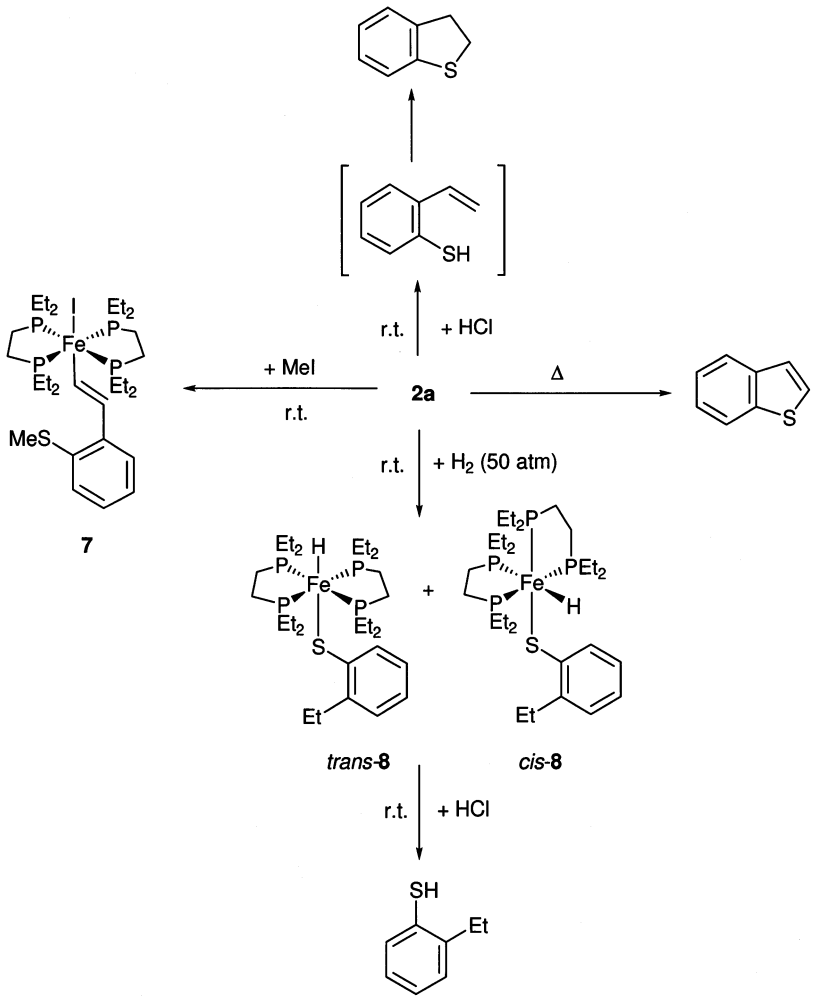
Complex **1** did not react with *N*-methylpyrrole, 2,5-dimethylpyrrole, pyrrolidine and 2-methylindol (Table 1, entries 22–26).

2.2. Reactions of the thiaferracycle complex *2a*

It is important to describe the chemical reactivity of thiaferracycle complexes, since they are regarded as one of the possible intermediates in the HDS process, as well as in the chemical transformation of heterocyclic compounds.

The thiaferracycle complex **2a** is reformed to benzo[*b*]thiophene in 58% yield by heating at 170°C in the solid state under argon (Scheme 2).

Such reductive elimination of the C–S bond is enhanced by exposure of **2a** with CO at 50°C to give benzo[*b*]thiophene in 94% yield producing Fe(CO)(depe)$_2$ (ν(C=O) = 1800 cm^{-1}) [7a,c,8,16]. Protonolysis of **2a** by an excess amount of HCl gas in THF or C_6D_6 gave 2,3-dihydrobenzo[*b*]thiophene in 53% yield with liberation of benzo[*b*]thiophene in 10% yield. It is likely that 2,3-dihydrobenzo[*b*]thiophene was



Scheme 2.

formed via 2-vinylbenzene-thiol [17] followed by the cyclization[1].

The reaction of **2a** with 10-fold amounts of MeI immediately gave *trans*-FeI[(*E*)-CH=CHC$_6$H$_4$-2-SMe](depe)$_2$ (**7**) in 52% yield. The ^{31}P{^{1}H} NMR spectrum of **7** shows a singlet at δ 70.2, suggesting four equivalent phosphorus atoms. In the ^{1}H NMR spectrum of **7**, a singlet at δ 2.05 (3H), a doublet at δ 6.43 ($J = 16.5$ Hz, 1H) and a doublet of quintets at δ 8.06 ($J = 16.5$, 6.7 Hz, 1H) were observed. The singlet at δ 2.05 is assigned to the SMe group, and the signals at δ 6.43 and 8.06 are assignable to the olefinic protons, where the large coupling constant ($J = 16.5$ Hz) indicates that those protons are mutually *trans*. The latter olefinic proton (δ 8.06) also involves further coupling to four equivalent phosphorus atoms ($J = 6.7$ Hz). Therefore, the structure of **7** is likely to be *trans*-FeI[(*E*)-CH=CHC$_6$H$_4$-2-SMe](depe)$_2$.

The X-ray structure analysis of **7** unequivocally indicated a *trans* structure. The ORTEP drawing is depicted in Fig. 3, and bond distances and angles are summarized in Table 4.

This molecular structure is consistent with that deduced by NMR spectra and demonstrates that electrophilic attack of MeI took place at the S atom, followed by Fe–S bond cleavage and rotation of the C=C double bond giving a *trans* configuration of the styryl moiety. Probably, the contribution of carbene character in **7** facilitates the rotation of the C=C double bond. Although the bond distance between Fe and C(1) (2.00(2) Å) is typical of a single bond, C(1) resonates at δ 179.7 in the ^{13}C{^{1}H} NMR spectrum, supporting a small contribution of its carbene character.

On the other hand, reaction of the thiaferracycle complex with molecular hydrogen is interesting from the mechanistic point of view of hydrodesulfurization. Treatment of **2a** with 50 atm of hydrogen at r.t. produces a mixture of *cis*- and *trans*-FeH(SC$_6$H$_4$-2-Et)-

[1] The protonolysis of **2a** with an excess amount of HCl gave paramagnetic iron species which is tentatively assigned as FeCl$_2$(depe)$_2$, because the ^{31}P{^{1}H} NMR spectrum gave a broad peak at δ 75 in C$_6$D$_6$, which is identical with that of authentic FeCl$_2$(depe)$_2$ (δ 75 (br) in C$_6$D$_6$ at r.t.) (see Ref. [7a]).

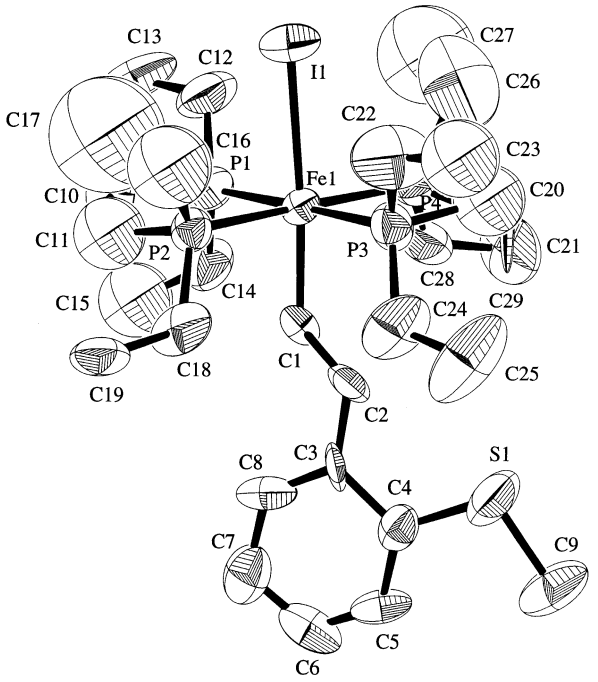


Fig. 3. ORTEP drawing of *trans*-FeI[(*E*)-CH=CHC$_6$H$_4$-2-SMe](depe)$_2$ (**7**). All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

(depe)$_2$ (**8**) in 52 and 21% yields, respectively (Scheme 2). The ^{31}P{^{1}H} NMR spectrum of the major isomer was observed as an AMNX pattern at δ 63.5, 81.4, 85.9 and 91.1 indicating four inequivalent phosphorus atoms. In the ^{1}H NMR spectrum of the major isomer, a doublet of triplets of doublets assignable to the hydride ligand was observed at δ −10.48 (J = 69.9, 52.2, 30.2 Hz, 1H), where two of four phosphorus atoms accidentally have a similar coupling constant. The ^{1}H–^{1}H COSY spectrum of **8** suggests that a quartet observed at δ 3.38 is assignable to the methylene protons of the 2-ethylbenzenethiolato group, although the corresponding methyl group overlapped with depe protons. Therefore, the major species was characterized as *cis*-FeH(SC$_6$H$_4$-2-Et)(depe)$_2$ (**8**). On the other hand, the minor isomer shows a singlet at δ 88.8 in the ^{31}P{^{1}H} NMR spectrum, and a quintet at δ −26.97 in the ^{1}H NMR spectrum is assignable to the hydrido ligand. This suggests that the species is a hydridoiron complex with four equivalent phosphorus atoms. The ^{1}H–^{1}H COSY spectrum suggests that the minor species also has a 2-ethylbenzenethiolato ligand. According to these spectroscopic data, the minor species was characterized as *trans*-FeH(SC$_6$H$_4$-2-Et)(depe)$_2$ (**8**). Acidolysis of the mixture by excess hydrogen chloride in Et$_2$O led to the formation of 2-ethylthiophenol in 20% yield (Scheme 2).

Table 4
Selected bond angles (°) and lengths (Å) for *trans*-FeI[(*E*)-CH=CHC$_6$H$_4$-2-SMe](depe)$_2$ (**7**)

Fe(1)–I(1)	2.774(4)	Fe(1)–P(1)	2.270(8)
Fe(1)–P(2)	2.260(9)	Fe(1)–P(3)	2.268(9)
Fe(1)–P(4)	2.255(8)	Fe(1)–C(1)	2.00(2)
S(1)–C(4)	1.76(3)	S(1)–C(9)	1.78(3)
C(1)–C(2)	1.25(3)	C(2)–C(3)	1.45(3)
C(3)–C(4)	1.42(3)	C(3)–C(8)	1.32(3)
C(4)–C(5)	1.39(4)	C(5)–C(6)	1.30(4)
C(6)–C(7)	1.37(5)	C(7)–C(8)	1.42(4)
I(1)–Fe(1)–C(1)	176.4(8)	I(1)–Fe(1)–P(1)	89.3(3)
I(1)–Fe(1)–P(2)	89.3(3)	I(1)–Fe(1)–P(3)	91.4(3)
I(1)–Fe(1)–P(4)	91.6(3)	C(1)–Fe(1)–P(1)	87.6(8)
C(1)–Fe(1)–P(2)	88.6(9)	C(1)–Fe(1)–P(3)	91.6(8)
C(1)–Fe(1)–P(4)	90.5(9)	Fe(1)–C(1)–C(2)	140(2)
C(1)–C(2)–C(3)	131(3)	C(4)–S(1)–C(9)	102(2)

In summary, a zerovalent iron complex, Fe(N$_2$)-(depe)$_2$ (**1**) can activate both C–S and C–H bonds of thiophenes, the C–H bond of furans, and the N–H bond of pyrroles without irradiation by light under ambient conditions. It is interesting to note that treatment of Fe(SC$_6$H$_4$CH=CH)(depe)$_2$ (**2a**) with MeI gave *trans*-FeI[(*E*)-CH=CHC$_6$H$_4$-2-SMe](depe)$_2$ (**7**) where the methyl nucleophile attacked the S atom in **2a**, while that with molecular hydrogen gave *cis*- and *trans*-FeH(SC$_6$H$_4$-2-Et)(depe)$_2$ (**8**) where the molecular hydrogen attacked the carbon atoms in **2a**.

3. Experimental

3.1. General

All manipulations were carried out using standard Schlenk and vacuum-line techniques. Fe(N$_2$)(depe)$_2$ (**1**) was prepared by the published procedure [7]. All substrates were purchased and purified by distillation or recrystallization. 2-Deuterio-3-methylthiophene was prepared by the treatment of 2-bromo-3-methylthiophene with magnesium followed by hydrolysis with D$_2$O and then by distillation. The content of deuterium was determined to be 98% by ^{1}H NMR data. NMR spectra were obtained from a Jeol LA-300 (300.4 MHz for ^{1}H, 75.4 MHz for ^{13}C, 121.6 MHz for ^{31}P) spectrometer using C$_6$D$_6$, CDCl$_3$, CD$_2$Cl$_2$, or toluene-d_8 as a solvent. The chemical shifts were reported in ppm from internal TMS both in ^{1}H and ^{13}C{^{1}H} NMR spectra. Chemical shifts in ^{31}P{^{1}H} NMR spectra were reported in ppm downfield from 85% H$_3$PO$_4$ in D$_2$O as an external standard. IR spectra were recorded on a Jasco FT-IR-5M or Jasco FT-IR-410 spectrometer using KBr disks. The elemental analyses were performed with a Perkin–Elmer 2400 Series II CHNS analyzer. GLC analyses were performed with Shimadzu GC-8APF, GC-14B gas liquid phase chromatographs using glass-packed Porapack-Q, capillary TC-wax and HR-1 columns. Melting points were estimated under nitrogen atmosphere with Yazawa capillary melting point apparatus and the values were uncorrected.

3.2. Reaction of **1** with benzo[b]thiophene

A THF solution (12 ml) of benzo[*b*]thiophene (109.1 mg, 0.81 mmol) was introduced to a THF solution (3 ml) of **1** (403.5 mg, 0.81 mmol), and stirred at r.t. for 7 days. The color of the solution changed from light orange solution to dark red. After removal of THF in vacuo, the residue was extracted with hexane. Fe($SC_6H_4CH{=}CH$)$(depe)_2$ (**2a**) was obtained by the crystallization from hexane at −30°C as dark red crystals in 41% isolated yield (200.2 mg, 0.33 mmol). From the mother liquor, a small amount of *trans*-FeH($C{=}CHC_6H_4S$)$(depe)_2$ (**3a**) was obtained. These chemical yields of **2a** and **3a** were calculated as 72 and 19%, respectively, by the $^{31}P\{^1H\}$ NMR spectrum with PPh_3 in a capillary tube as standard.

Fe($SC_6H_4CH{=}CH$)$(depe)_2$ (**2a**): Yield 72%; ^1H NMR (C_6D_6): δ 0.6–2.7 (m, 48H, depe), 6.89 (t, $J=7.5$ Hz, 1H, aromatic-H), 6.96 (t, $J=7.5$ Hz, 1H, aromatic-H), 7.12 (d, $J=7.5$ Hz, 1H, aromatic-H), 7.91 (dd, $J=11.7$, 6.3 Hz, 1H, olefinic-H, partially overlapped with the peak at δ 7.94), 7.94 (d, $J=7.5$ Hz, 1H, aromatic-H), 8.27 (ddt, $J=21.0$, 11.7, 3.1 Hz, olefinic-H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 55.1 (ddd, $J=26.6$, 20.6, 7.3 Hz, 1P), 66.6 (ddd, $J=207.6$, 34.5, 26.6 Hz, 1P), 69.5 (ddd, $J=207.6$, 34.5, 20.6 Hz, 1P), 76.5 (td, $J=34.5$, 7.3 Hz, 1P); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 9.0–25.7 (depe), 120.6 (s), 122.7 (s), 130.5 (s), 133.4 (s), 138.7 (s), 140.2 (s), 140.6 (s), 166.7 (m); *Anal*. Found: C, 55.36; H, 9.24; S, 5.60. Calc. for $C_{28}H_{54}FeP_4S$: C, 55.82; H, 9.03; S, 5.32%; m.p. 123–125°C (dec.).

trans-FeH($C{=}CHC_6H_4S$)$(depe)_2$ (**3a**): Yield 19%; ^1H NMR (C_6D_6): δ −18.83 (qui, $J=48.2$ Hz, 1H, Fe–*H*), 0.92 (br, 24H, PCH_2CH_3), 1.08 (sext, $J=7.1$ Hz, 4H, PCH_2CH_3), 1.35 (sext, $J=7.4$ Hz, 4H, PCH_2CH_3), 1.41 (br, 4H, PCH_2CH_2P), 1.69 (sext, $J=7.1$ Hz, 4H, PCH_2CH_3), 1.93 (br, 4H, PCH_2CH_2P), 2.16 (sext, $J=7.4$ Hz, 4H, PCH_2CH_3), 6.83 (s, 1H, olefinic-H), 6.95 (t, $J=7.7$ Hz, 1H, aromatic-H), 7.20 (t, $J=7.7$ Hz, 1H, aromatic-H), 7.64 (d, $J=7.7$ Hz, 1H, aromatic-H), 7.81 (d, $J=7.7$ Hz, 1H, aromatic-H); $^{31}P\{^1H\}$ NMR (C_6D_6):δ 92.8 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 9.4–26.3 (depe), 117.8 (s), 118.3 (s), 119.4 (s), 122.4 (s), 133.8 (s), 144.4 (s), 147.2 (s), 187.1 (qui, $J=17.9$ Hz); *Anal*. Found: C, 55.38; H, 9.78; S, 5.99. Calc. for $C_{28}H_{54}FeP_4S$: C, 55.82; H, 9.03; S, 5.32%.

3.3. Reaction of **1** with other thiophenes

Reaction of **1** with thiophene, 2-methylethiophene, 3-methylthiophene, and 2-acetylthiophene was performed by the similar method of the reaction with benzo[*b*]thiophene as described above. Yields were calculated on the basis of their NMR spectra. ^1H and $^{31}P\{^1H\}$ NMR spectral data of the products **2b**–**e** and **3b**–**e** are described as follows:

Fe(SCH=CHCH=CH)$(depe)_2$ (**2b**): Yield 44%; ^1H NMR (C_6D_6): δ 0.7–2.0 (m, 42H, depe), 2.1–2.5 (m, 2H, depe), 2.7–2.9 (m, 2H, depe), 2.9–3.1 (m, 2H, depe), 6.01 (dd, $J=9.2$, 3.3 Hz, 1H, FeSC*H*CHCHCH), 6.46 (dd, $J=9.2$, 6.5 Hz, 1H, FeSCHC*H*CHCH), 7.43 (dt, $J=11.1$, 6.3 Hz, 1H FeSCHCHC*H*CH), 7.84 (dd, $J=21.0$, 11.1 Hz, 1H, FeSCHCHCHC*H*); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 55.5 (ddd, $J=24.6$, 20.1, 7.3 Hz, 1P), 67.0 (ddd, $J=243.1$, 34.5, 24.6 Hz, 1P), 69.5 (ddd, $J=243.1$, 34.5, 20.1 Hz, 1P), 76.0 (td, $J=34.5$, 7.3 Hz); *Anal*. Found: C, 52.31; H, 9.98; S, 8.07. Calc. for $C_{24}H_{52}FeP_4S$: C, 52.18; H, 9.49; S, 5.80%.

trans-FeH($C{=}CHCH{=}CHS$)$(depe)_2$ (**3b**): Yield 51%; ^1H NMR (C_6D_6): δ −19.41 (qui, $J=48.4$ Hz, 1H, Fe–*H*), 0.97 (br, 24H, PCH_2CH_3), 1.0–1.5 (m, 12H, PCH_2CH_3, PCH_2CH_2P), 1.73 (m, 4H, PCH_2CH_3), 1.90 (br, 4H, PCH_2CH_2P), 2.13 (sext, $J=7.3$ Hz, 4H, PCH_2CH_3), 6.58 (br d, $J=1.8$ Hz, 1H, aromatic-H), 7.26 (dd, $J=5.4$, 1.8 Hz, 1H, aromatic-H), 7.54 (d, $J=5.4$ Hz, 1H, aromatic-H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 93.2 (s).

Fe[SC(COMe)=CHCH=CH]$(depe)_2$ (**2c**): Yield 53%; ^1H NMR (C_6D_6): δ 0.9–2.5 (m, 48H, depe), 2.73 (s, 3H, $COCH_3$), 7.44 (br, 1H, thiaferracyclic-H), 7.76 (br, 1H, thiaferracyclic-H), 8.98 (br, 1H, thiaferracyclic-H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 53.2 (td, $J=21.9$, 7.3 Hz, 1P), 65.0 (dt, $J=238.2$, 21.9 Hz, 1P), 68.3 (ddd, $J=238.2$, 34.6, 21.9 Hz, 1P), 74.8 (ddd, $J=34.6$, 21.9, 7.3 Hz, 1P).

trans-FeH[$C{=}CHCH{=}C(COMe)S$]$(depe)_2$ (**3c**): Yield 26%; ^1H NMR (C_6D_6): δ −18.33 (qui, $J=47.6$ Hz, 1H, Fe–*H*), 0.89 (br, PCH_2CH_3, 24H), 1.02 (sext, $J=7.5$ Hz, 4H, PCH_2CH_3, partially overlapped with the peak at δ 0.89), 1.27 (sext, $J=7.5$ Hz, 4H, PCH_2CH_3, partially overlapped with the peak at δ 1.31), 1.31 (br, 4H, PCH_2CH_2P, partially overlapped with the peak at δ 1.27), 1.63 (br sext, $J=7.5$ Hz, PCH_2CH_3, 4H), 1.79 (br, 4H, PCH_2CH_2P), 1.99 (sext, $J=7.5$ Hz, 4H, PCH_2CH_3), 2.36 (s, 3H, $COCH_3$), 6.61 (d, $J=3.6$ Hz, 1H, thienyl ring-H), 7.50 (d, $J=3.6$ Hz, 1H, thienyl ring-H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 91.9 (s).

Fe[SC(Me)=CHCH=CH]$(depe)_2$ (**2d**): Yield 24%; ^1H NMR (C_6D_6): δ 0.4–2.2 (m, 48H, depe), 2.38 (s, 3H, CH_3), 7.2 (overlapped with the peak of C_6D_5H), 7.41 (br, 1H, thiaferracyclic-H), 7.65 (dd, $J=18.2$, 11.0 Hz, 1H, thiaferracyclic-H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 55.2 (td, $J=25.0$, 6.1 Hz, 1P), 66.0 (ddd, $J=241.8$, 34.2, 25.0 Hz, 1P), 68.9 (ddd, $J=241.8$, 34.2, 25.0 Hz, 1P), 76.4 (td, $J=34.2$, 6.1 Hz, 1P).

trans-FeH[$C{=}CHCH{=}C(Me)S$]$(depe)_2$ (**3d**): Yield 62%; ^1H NMR (C_6D_6): δ −19.47 (qui, $J=47.4$ Hz, 1H, Fe–*H*), 0.98 (br, 24H, PCH_2CH_3), 1.0–1.5 (m, 12H, PCH_2CH_3, PCH_2CH_2P), 1.73 (br, 4H, PCH_2CH_3), 1.91 (br, 4H, PCH_2CH_2P), 2.18 (sext, $J=7.2$, 4H, PCH_2CH_3), 2.59 (s, 3H, CH_3), 6.36 (br, 1H, aromatic-

H), 6.89 (br, 1H, aromatic-H); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 93.6 (s).

Fe[SCH=C(Me)CH=CH](depe)$_2$ (**2e**): Yield 16%; ^{1}H NMR (C_6D_6): δ 0.8–2.5 (m, 48H, depe), 2.11 (s, 3H, CH_3), 5.68 (br, 1H, thiaferracyclic-H), 7.29 (br, 1H, thiaferracyclic-H), 8.02 (br, 1H, thiaferracyclic-H); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 55.6 (td, $J = 22.8$, 7.3 Hz, 1P), 65.8 (ddd, $J = 249.2$, 33.6, 22.8 Hz, 1P), 68.1 (ddd, $J = 249.2$, 33.6, 22.8 Hz, 1P), 76.5 (td, $J = 33.6$, 7.3 Hz, 1P).

trans-FeH[C=CHC(Me)=CHS](depe)$_2$ (**3e**): Yield 70%; ^{1}H NMR (C_6D_6): δ −19.40 (qui, $J = 47.9$ Hz, 1H, Fe–H), 1.00 (br, 24H, PCH$_2$CH_3), 1.1–1.5 (m, 12H, PCH_2CH$_3$, PCH_2CH$_2$P), 1.75 (br, 4H, PCH_2CH$_3$), 1.93 (br, 4H, PCH$_2$CH_2P), 2.18 (sext, $J = 7.3$ Hz, 4H, PCH_2CH$_3$), 2.38 (s, 3H, CH_3), 6.19 (s, 1H, thienyl ring-H), 7.07 (s, 1H, thienyl ring-H); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 93.4 (s).

Fe[SCD=C(Me)CH=CH](depe)$_2$ (**2e**-d_1): Yield 18%; ^{1}H NMR (C_6D_6): δ 0.9–2.2 (m, 24H, depe), 2.13 (s, 3H, CH_3), 7.3 (br, 1H, thienyl ring-H, partially overlapped with the peak of C_6D_5H), 8.0 (br, 1H, thienyl ring-H); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 55.6 (td, $J = 23.1$, 7.3 Hz, 1P), 65.8 (ddd, $J = 245.5$, 35.2 Hz, 1P), 68.1 (ddd, $J = 245.5$, 35.2, 23.1 Hz, 1P), 76.5 (td, $J = 35.2$, 7.3 Hz, 1P).

trans-FeH[C=CHC(Me)=CDS](depe)$_2$ (**3e**-d_1): Yield 50%; ^{1}H NMR (C_6D_6): δ −19.40 (qui, $J = 47.9$ Hz, 1H, Fe–H), 0.98 (br, 24H, PCH$_2$CH_3), 1.1–1.5 (m, 12H, PCH_2CH$_3$, PCH_2CH$_2$P), 1.72 (br, 4H, PCH_2CH$_3$), 1.92 (br, 4H, PCH$_2$CH_2P), 2.18 (br, 4H, PCH_2CH$_3$), 2.39 (s, 3H, CH_3), 6.21 (s, 1H, thienyl ring-H); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 93.5 (s).

3.4. Reaction of **1** with furans

Furan (7.8 μl, 0.16 mmol) was added into a THF solution (4 ml) of **1** (81.3 mg, 0.16 mmol) by a hypodermic syringe and the resultant reaction mixture was stirred for 12 h at r.t. After removal of all volatile matter in vacuo, the orange oil was extracted with hexane. Removal of hexane gave orange oil (84.6 mg). The NMR spectrum showed formation of *trans*-FeH(C=CHCH=CHO)(depe)$_2$ (**4a**) in 47% yield. ^{1}H NMR (C_6D_6): δ −18.15 (qui, $J = 45.2$ Hz, 1H, Fe–H), 1.00 (br, 12H, PCH$_2$CH_3), 1.1–2.1 (m, 36H, depe), 5.67 (br, 1H, aromatic-H), 6.44 (br, 1H, aromatic-H), 7.88 (br, 1H, aromatic-H); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 96.6 (s). Reactions of **1** with benzo[*b*]furan, 2,3-dihydrofuran, 2-acetylfuran, dibenzofuran, 2,5-dimethylfuran, 2,5-dihydrofuran, tetrahydrofuran, and 2,3-dihydro-benzofuran were carried out similarly in a NMR tube without isolation. Benzo[*b*]furan and 2,3-dihydrofuran gave *trans*-FeH(C=CHC$_6$H$_4$O)(depe)$_2$ (**4b**) and *trans*-FeH(C=CHOCH$_2$CH$_2$)(depe)$_2$ (**4c**), respectively. However, 2-acetylfuran, dibenzofuran, 2,5-dimethylfuran, 2,5-dihydrofuran, tetrahydrofuran, and 2,3-dihydrobenzofuran are remained unreacted. These products **4b** and **4c** were characterized by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra. Yields were calculated from $^{31}P\{^{1}H\}$ NMR spectra.

trans-FeH(C=CHC$_6$H$_4$O)(depe)$_2$ (**4b**): Yield 65%. ^{1}H NMR (C_6D_6): δ −17.41 (qui, $J = 45.7$ Hz, 1H, Fe–H), 0.89 (br, 12H, PCH$_2$CH_3), 0.98 (br, 12H, PCH$_2$CH_3), 1.00 (m, 4H, PCH_2CH$_3$, overlapped with the peak at δ 0.98), 1.18 (m, 4H, PCH_2CH$_3$), 1.42 (br, 8H, PCH_2CH$_2$P, PCH_2CH$_3$), 1.72 (br, 4H, PCH$_2$CH_2P), 1.87 (m, 4H, PCH_2CH$_3$), 6.11 (s, 1H, oleinic-H), 6.94 (t, $J = 7.5$ Hz, 1H, aromatic-H), 7.1 (1H, overlapped with the peak of C_6D_5H), 7.31 (d, $J = 7.5$ Hz, 1H, aromatic-H), 7.41 (d, $J = 7.5$ Hz, 1H, aromatic-H); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 95.9 (s).

trans-FeH(C=CHOCH$_2$CH$_2$)(depe)$_2$ (**4c**): Yield 95%. ^{1}H NMR (C_6D_6): δ −17.85 (qui, $J = 45.0$ Hz, 1H, Fe–H), 1.04 (br, 12H, PCH$_2$CH_3), 1.08 (br, 12H, PCH$_2$CH_3), 1.24 (sext, $J = 7.5$ Hz, 4H, PCH_2CH$_3$), 1.37 (br, 4H, PCH$_2$CH$_2$P), 1.50 (sext, $J = 7.2$ Hz, 4H, PCH_2CH$_3$), 1.78 (br, 8H, PCH_2CH$_3$, PCH$_2$CH_2P), 2.38 (sext, $J = 7.2$ Hz, 4H, PCH_2CH$_3$), 2.64 (t, $J = 8.3$ Hz, 2H, aliphatic-H), 4.00 (s, 1H, olefinic-H), 4.02 (t, $J = 8.3$ Hz, 2H, aliphatic-H); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 96.8 (s).

3.5. Reaction of **1** with pyrrole

Pyrrole (19.5 mg, 0.29 mmol) was added to a THF solution (4 ml) of **1** (144.1 mg, 0.29 mmol) and the reaction mixture was stirred for 12 h at r.t. After removal of all volatile matter in vacuo, the residue was extracted with hexane. Reducing the volume to approximately one-fifth, light yellow crystals of *trans*-FeH-NCH=CHCH=CH)(depe)$_2$ (**5a**) were obtained (80 mg, 0.15 mmol, 52% yield). The reaction in NMR tube in C_6D_6 gave **5a** in 95% yield. ^{1}H NMR (C_6D_6): δ −27.94 (qui, $J = 49.5$ Hz, 1H, Fe–H), 0.82 (br, 12H, PCH$_2$CH_3), 0.92 (br, 12H, PCH$_2$CH_3), 1.01 (br, 4H, PCH_2CH$_3$, partially overlapped with the peak at δ 0.92), 1.40 (br, 8H, PCH_2CH$_3$, PCH_2CH$_2$P), 1.74 (br, 4H, PCH_2CH$_3$), 1.79 (br, 4H, PCH$_2$CH_2P), 1.94 (br, 4H, PCH_2CH$_3$), 6.21 (br, 2H, ring-H), 6.58 (br, 2H, ring-H); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 91.8 (s); IR (KBr): ν(Fe–H) = 1854 cm^{-1}. *Anal.* Found: C, 53.94; H, 10.13; N, 2.79. Calc. for $C_{24}H_{53}FeNP_4$: C, 53.84; H, 9.98; N, 2.62%.

3.6. Reaction of **1** with indole

A THF solution (4 ml) of **1** (83.2 mg, 0.17 mmol) was added to indole (19.6 mg, 0.17 mmol) and then the reaction mixture was stirred at r.t. for 20 h. After removal of all volatile matter under reduced pressure, the residue was extracted with hexane. The hexane

solution was concentrated and kept at −30°C to give yellow crystals of a mixture of *cis*- and *trans*-FeH($NC_6H_4CH{=}CH$)(depe)$_2$ (*cis*- and *trans*-**5b**) in 27% isolated yield (24 mg, 0.045 mmol). Yields of *cis*- and *trans*-**5b** were calculated as 23 and 12% yields, respectively, by the NMR spectrum.

cis-FeH($NC_6H_4CH{=}CH$)(depe)$_2$ (*cis*-**5b**): ^{1}H NMR (C_6D_6): δ −9.20 (dq, J = 87.8, 43.7 Hz, 1H, Fe–*H*), 0.4–2.1 (m, 48H, depe), 6.83 (br, 1H, olefinic-H), 7.00 (br, 1H, olefinic-H), 7.15 (1H, overlapped with the peak of C_6D_5H), 7.92 (br, 2H, aromatic-H), 8.60 (br, 1H, aromatic-H); ^{31}P{^{1}H} NMR (C_6D_6): δ 63.1 (dt, J = 27.3, 12.8 Hz, 1P), 82.4 (ddd, J = 35.9, 27.3, 12.8 Hz, 1P), 88.8 (dt, J = 125.7, 27.3 Hz, 1P), 90.4 (ddd, J = 125.7, 35.9, 12.8 Hz, 1P); Yield 23%.

trans-FeH($NC_6H_4CH{=}CH$)(depe)$_2$ (*trans*-**5b**): ^{1}H NMR (C_6D_6): δ −29.12 (qui, J = 52.1 Hz, 1H, Fe–*H*), 0.4–2.1 (m, 48H, depe), 6.59 (br, 1H, olefinic-H), 6.8 (br, 1H, overlapped with a peak of *cis*-**5b**), 7.05 (br, 1H, overlapped with a peak of *cis*-**5b**), 7.38 (br, 2H, aromatic-H), 7.75 (br, 1H, aromatic-H); ^{31}P{^{1}H} NMR (C_6D_6): δ 91.6 (s); Yield 12%. The following data were obtained from the mixture of *cis*- and *trans*-**5b**: IR (KBr) ν(Fe–H) = 2082 cm^{-1}. *Anal*. Found: C, 57.67; H, 9.62; N, 2.53. Calc. for $C_{28}H_{55}FeNP_4$: C, 57.44; H, 9.47; N, 2.39%.

3.7. Reaction of **1** with 2-acetylpyrrole

2-Acetylpyrrole (17.1 mg, 0.16 mmol) was added to a THF solution (4 ml) of **1** (78.0 mg, 0.16 mmol) and the reaction mixture was stirred for 12 h at r.t. After removal of all volatile matter in vacuo, the residue was extracted with hexane. Removal of hexane gave a dark red oil of crude FeH[NC(COMe)=CHCH=CH](η^2-depe)(η^1-depe) (**6**) in 69% isolated yield (62.8 mg, 0.11 mmol). This product was characterized by spectroscopically. ^{1}H NMR (C_6D_6): δ −26.18 (ddd, J = 63.3, 52.8, 47.9 Hz, 1H, Fe–*H*), 0.70 (dt, J = 11.7, 8.1 Hz, 3H, PCH_2CH_3), 0.84 (dt, J = 12.6, 8.0 Hz, 3H, PCH_2CH_3), 0.9–2.1 (m, 42H, depe), 2.21 (s, 3H, $COCH_3$), 6.68 (br d, J = 2.7 Hz, 1H, aromatic-H), 7.23 (br, 2H, aromatic-H); ^{31}P{^{1}H} NMR (C_6D_6): δ −18.2 (d, J = 21.8 Hz, 1P), 48.9 (ddd, J = 125.2, 37.1, 21.8 Hz, 1P), 95.6 (dd, J = 125.2, 37.1 Hz, 1P), 98.7 (t, J = 37.1 Hz, 1P); IR (KBr): ν(Fe–H) = 2088, ν(C=O) = 1652 cm^{-1}.

3.8. Reaction of **2a** with HCl

A 10-fold excess amount of HCl in Et_2O was added into a hexane solution (2 ml) of **2a** (16.5 mg, 0.027 mmol). After stirring for 15 min. at r.t., organic products were analyzed by gas liquid chromatography using dibenzyl as an internal standard. 2,3-Dihydrobenzo[*b*]thiophene: 53% yield; benzo[*b*]thiophene, 10% yield.

3.9. Reaction of **2a** with MeI

MeI (360 μl, 1.1 mmol) was added to a THF solution (5 ml) of **2a** (66.3 mg, 0.11 mmol). The color of the solution immediately changed from orange to light yellow. After removal of solvent in vacuo, the residue was extracted with benzene. Evaporation of all volatile matter under reduced pressure, followed by crystallization from a mixture of benzene–hexane gave red crystals of *trans*-FeI[(*E*)-CH=CHC_6H_4-2-SMe](depe)$_2$ (**7**) (42.0 mg, 52%). ^{1}H NMR (C_6D_6): δ 0.85 (sext, J = 7.5 Hz, 4H, PCH_2CH_3), 1.05 (br t, J = 7 Hz, 24H, PCH_2CH_3), 1.18 (m, 4H, PCH_2CH_2P), 1.41 (sext, J = 7.5 Hz, 4H, PCH_2CH_3), 1.85 (sext, J = 7.5 Hz, 4H, PCH_2CH_3), 2.01 (sext, J = 7.5 Hz, 4H, PCH_2CH_2P), 2.05 (s, 3H, SCH_3), 2.84 (sext, J = 7.5 Hz, 4H, PCH_2CH_3), 6.43 (d, J = 16.5 Hz, 1H, olefinic-H), 6.84 (t, J = 7.5 Hz, aromatic-H), 6.99 (d, J = 7.5 Hz, 1H, aromatic-H), 7.07 (t, J = 7.5 Hz, 1H, aromatic-H), 7.20 (d, J = 7.5 Hz, 1H, aromatic-H), 8.06 (dqui, J = 16.5, 6.7 Hz, 1H, olefinic-H); ^{31}P{^{1}H} NMR (C_6D_6): δ 70.2 (s); ^{13}C{^{1}H} NMR (C_6D_6): δ 5.9–25.7 (depe), 122.4 (s), 123.3 (s), 125.1 (s), 126.3 (s), 129.0 (s), 130.7 (s), 137.5 (br, s), 137.9 (s), 179.7 (qui, J = 21.5 Hz); *Anal*. Found: C, 46.21; H, 8.20; S, 4.90. Calc. for $C_{29}H_{57}FeIP_4S$: C, 46.79; H, 7.72; S, 4.31%.

3.10. Reaction of **2a** with H_2

A THF solution (10 ml) of **2a** (74.7 mg, 0.12 mmol) was transferred into an autoclave by a hypodermic syringe and 50 atm. of H_2 was charged. After stirring for 7 days at r.t., the reaction mixture was transferred to a Schlenk tube under nitrogen atmosphere. After removal of solvent, an orange powder was obtained. Recrystallization of the powder from cold hexane gave red crystals of the mixture of *cis*-FeH(SC_6H_4-2-Et)(depe)$_2$ (*cis*-**8**) and *trans*-FeH(SC_6H_4-2-Et)(depe)$_2$ (*trans*-**8**) in 73% isolated yield (54.6 mg, 0.088 mmol). The molar ratio of *cis*- and *trans*-**8** was determined to be 2.5:1 by the NMR spectrum.

cis-**8**: ^{1}H NMR (C_6D_6): δ −10.48 (dtd, J = 69.9, 52.2, 30.2 Hz, 1H, Fe–*H*), 0.7–2.6 (m, 51H, depe, $C_6H_4CH_2CH_3$), 3.38 (q, J = 7.6 Hz, $C_6H_4CH_2CH_3$), 6.8–7.2 (m, 2H, aromatic-H, overlapped with the peaks of *trans*-**8** and C_6D_5H), 7.29 (t, J = 7.7 Hz, 1H, aromatic-H), 8.58 (d, J = 7.7 Hz, 1H, aromatic-H); ^{31}P{^{1}H} NMR (C_6D_6): δ 63.5 (dt, J = 26.2, 18.4 Hz, 1P), 81.4 (ddd, J = 133.7, 35.5, 18.4 Hz, 1P), 85.9 (ddd, J = 133.7, 35.5, 26.2 Hz, 1P), 91.1 (td, J = 35.5, 18.4 Hz, 1P).

trans-**8**: ^{1}H NMR (C_6D_6): δ −26.97 (qui, J = 50.3 Hz, 1H, Fe–*H*), 0.7–2.6 (m, 51H, depe, $C_6H_4CH_2CH_3$), 3.27 (q, J = 7.5 Hz, 2H, $C_6H_4CH_2CH_3$), 6.8–7.2 (m, overlapped with the peaks of *cis*-**8** and C_6D_5H); ^{31}P{^{1}H} NMR (C_6D_6): δ 88.8 (s).

3.11. Thermolysis of **2a**

Compound **2a** (13.0 mg, 0.022 mmol) was heated at 170°C for 1 h under argon in a glass tube without solvent. After the pyrolysis, dibenzyl (3.0 mg, 0.0165 mmol) as an internal standard and hexane (0.6 ml) was introduced in the tube. The GLC analysis of the hexane solution showed re-formation of benzo[*b*]thiophene (0.013 mmol, 58%).

3.12. Reaction of **2a** with CO

Compound **2a** (14.2 mg, 0.023 mmol) was placed in a NMR tube with a PTFE valve (Aldrich®) and benzene-d_6 (600 μl) was introduced into the NMR tube by a trap-to-trap distillation. Carbon monoxide (1 atm.) was charged to the NMR tube and warmed at 50°C for 48 h. 1,4-Dioxane was added to the NMR tube as an internal standard and the NMR spectrum indicated the formation of benzo[*b*]thiophene in 94% yield.

4. Crystallography

Deep red needles of **2a** suitable for X-ray analysis were obtained from a hexane solution at −30°C. After removing the solution layer, the needles were carefully washed with cold hexane and dried under vacuum. A selected single crystal was sealed in a thin glass capillary (GLAS, 0.7 mm o.d.) under nitrogen. The diffraction experiment was performed by a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) at −70°C. A total of 3001 reflections was collected with a maximum 2θ value of 55.5° and the reflection data/parameter ratio is 12.1 ($I > 3.0\sigma(I)$). The R_{merge} value is 0.053. Because the product of the linear absorption coefficient ($\mu = 0.790$ mm^{-1}) and the maximum size of the crystal ($x = 0.25$ mm) is 0.2, the data were corrected for empirical Lorentz and polarization effects and for secondary extinction. The structure was solved by direct methods (SHELXS-86 [18]), expanded by Fourier techniques (DIRDIF-94 [19]), and refined by full-matrix least-squares techniques based on the texsan program [20]. The crystal system is monoclinic and the space group is determined as $C2/c$ (no. 15) suggesting the unit cell has a 1:1 disorder of the thiaferracycle fragment. It is worth noting that, although the refinement with the alternative possible space group Cc failed, the trial suggested that the atoms of two depe ligands have the C_2 symmetry and the thiaferracycle fragments disordered with a 1:1 population have a C_2 symmetry on the same C_2 axis as the depe ligands. Disorder with a 1:1 population may be caused when the reflection data were measured with half of the real lattice constants. However, that possibility was excluded because no spot was observed in the reciprocal lattice on the imaging plate. The congeners due to the thiaferracycle fragment were treated as half-occupied and those due to the depe ligands were related by a rotational displacement. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on the ideal positions and were not refined. The final R (R_w) value was 0.063 (0.085). The bond lengths and angles for **2a** cannot be discussed in detail because of the disorder of the thiaferracycle fragment. The crystallographic data of **2a** are outlined in Table 5.

Single crystals of *trans*-**5a** suitable for X-ray crystallography were obtained from cold hexane at −30°C. A selected crystal was mounted in a glass capillary tube. The reflections were collected with a Rigaku AFC-5S at r.t. with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Using criterion $|F_o| > 3.0\sigma(|F_o|)$, 4312 out of 7242 ($3 < 2\theta < 55.0°$) reflections were used for calculation and the reflection data/parameter ratio is 15.68. The product of the linear absorption coefficient ($\mu = 0.753$ mm^{-1}) and the maximum crystal size ($x =$ 0.70 mm) is 0.53 and the absorption correction was therefore performed with ψ-scan methods. The R_{int} value is 0.104. The structure was solved with direct methods (SAPI-91) and expanded by Fourier techniques (DIRDIF-94), and refined by full-matrix least-squares techniques based on the texsan program. The crystal system is monoclinic and the space group $P2_1/n$ (no. 14). All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located on ideal positions and were not refined. The final R (R_w) value is 0.044 (0.041). The crystallographic data are outlined in Table 5.

Single crystals of **7** suitable for X-ray crystallography were obtained from a mixture of benzene and hexane. A deep red crystal with suitable size was selected and mounted in a glass capillary tube. The reflections were collected with a Rigaku AFC-5R at r.t. with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Using criterion $|F_o| > 3.0\sigma(|F_o|)$, 1612 out of 4509 ($6 < 2\theta < 54.9°$) reflections were used for calculation and the reflection data/parameter ratio is 5.99. The product of the linear absorption coefficient ($\mu = 1.546$ mm^{-1}) and the maximum crystal size ($x = 0.20$ mm) is 0.31 and the absorption correction was therefore applied with ψ-scan methods. The R_{int} value is 0.104. The structure was solved with Paterson methods (PATTY) and expanded by Fourier techniques (DIRDIF-92), and refined by full-matrix least-squares techniques based on the texsan program. The crystal system is orthorhombic and the space group $P2_12_12_1$ (no. 19). All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located on ideal positions and were not refined. The final R (R_w) value is 0.062 (0.071). The crystallographic data are outlined in Table 5. These crystallographic data are available by application to the Cambridge Crystallographic Data Centre (CCDC 116677-116679).

Table 5
Crystallographic data for Fe(SC$_6$H$_4$CH=CH)(depe)$_2$ (**2a**), *trans*-FeH(NCH=CHCH=CH)(depe)$_2$ (**5a**), and *trans*-FeI[(*E*)-CH=CHC$_6$H$_4$-2-SMe](depe)$_2$ (**7**)

	2a	**5a**	**7**
Chemical formula	$C_{28}H_{54}FeP_4S$	$C_{24}H_{53}NFeP_4$	$C_{29}H_{57}FeIP_4S$
Formula weight	602.54	535.43	744.48
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)
a (Å)	13.569(4)	9.986(5)	13.486(3)
b (Å)	16.898(4)	18.153(5)	24.653(8)
c (Å)	14.542(3)	16.005(7)	10.605(3)
β (°)	114.08(2)	93.44(4)	
V (Å^3)	3044	2896(1)	3525(1)
Z	4	4	4
D_{calc} (g cm^{-1})	1.315	1.228	1.402
μ (cm^{-1})	7.90	7.53	15.46
2θ (°)	55.5 (max.)	3.0–55.0	3.0–54.9
Scan type		2θ–ω	2θ–ω
Diffractometer	Rigaku RAXIS-IV	Rigaku AFC5S	Rigaku AFC5R
Radiation	Mo Kα	Mo Kα	Mo Kα
Monochromator	graphite	graphite	graphite
No. data collected	3001	7242	4509
No. of observed	1843 ($\|F_o\| > 3\sigma\|F_o\|$)	4313 ($\|F_o\| > 3\sigma\|F_o\|$)	1612 ($\|F_o\| > 3\sigma\|F_o\|$)
Method of phase determination	direct methods (SHELXS-86)	direct methods (SAPI-91)	Paterson methods (PATTY)
R [a]	0.063	0.044	0.062
R_w [b]	0.085	0.041	0.071
Goodness-of-fit indicator	1.53	2.32	1.87

[a] $R = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma|F_o|$.
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{0.5}$.

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