The Synthesis and Structure of P−C−P Bridged Ferrocene

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Keywords: Sandwich complexes / Phosphane ligands / Asymmetry / Bridging ligands

The reaction of dilithioferrocene **12** with methylene-bis(dialkylaminochlorophosphanes) **13a,b** (**a** = CH_3, **b** = C_2H_5) leads to the formation of compounds **14a,b** in which the two cyclopentadiene rings are bridged by a P–C–P chain. Because of the cyclic structure, *cis*- and *trans*-isomerism is expected. The *cis*- and *trans*-isomers of the sulfur derivative **16b** have been separated by column chromatography.

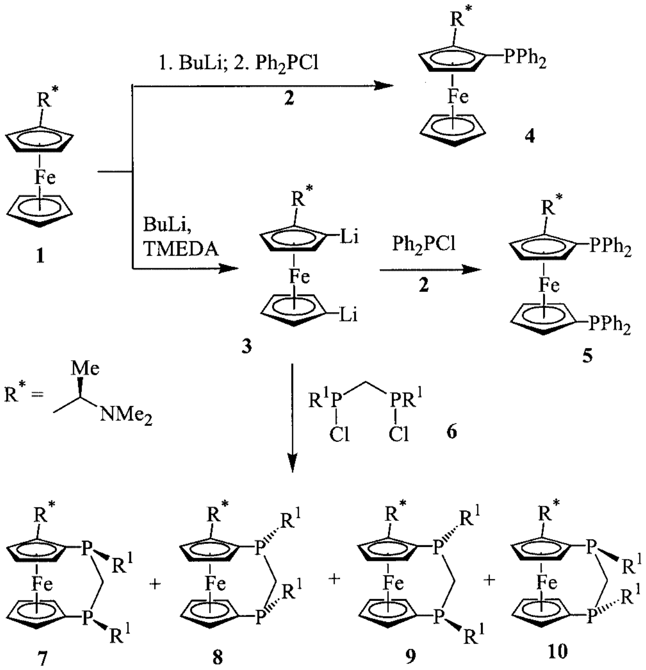
Introduction

Phosphane-substituted ferrocene derivatives have been intensively investigated in the last two decades. Particular attention was paid to the study of non-racemic ferrocene derivatives, as they have found wide application as ligands for catalysts of numerous asymmetric reactions. The chemistry of chiral ferrocene derivatives has been extensively reviewed up to 1997.[1−3]

The main method of synthesis of non-racemic ferrocene derivatives is based on the lithiation of *N*,*N*-dimethyl-1-ferrocenylethylamine (**1**; Scheme 1) followed by the addition of chlorophosphane **2**. This reaction can result in the formation of either the monophosphane **4** or the diphosphane derivative **5**.

The presence of the asymmetric substituent R* (*N*,*N*-dimethyl-1-ethylamine) at one of the rings brings about selective lithiation of the ring.

The bridging of dilithioferrocene **3** with methylene-bis(dichlorophosphane) **6** should give rise to isomerism caused by different positions of the substituents R at the phosphorus atom. Taking into account that one of the ferrocene rings bears the substituent R*, four isomers **7−10** are possible. These ligands may be useful in the design of asymmetric catalysts.



Scheme 1

Results and Discussion

To the best of our knowledge, there are no examples in which two cyclopentadiene rings are bridged by a diphosphane unit. P-B bridged species are known[4] and a P-bridged derivative has also been reported.[5] In addition, there have been several P−N−P-bridged ferrocenes reported where the bridge is part of a cyclic triphosphazene.[6−9] For the first step of the proposed ap-

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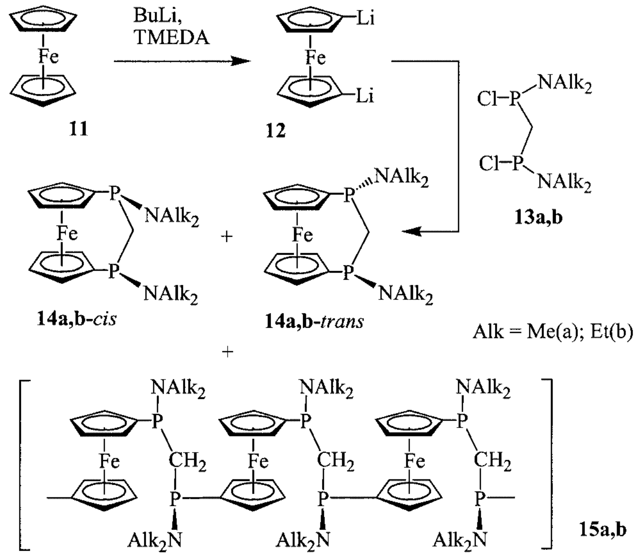
proach we have chosen a simple model, namely bridging of the unsubstituted ferrocene **11** with methylene-bis(dialkylaminochlorophosphanes) **13a,b** (**a** = CH_3, **b** = C_2H_5; Scheme 2). The dialkylamino-substituted chlorophosphanes **13a,b** are easier to synthesise than other methylene-bis(chlorophosphanes).



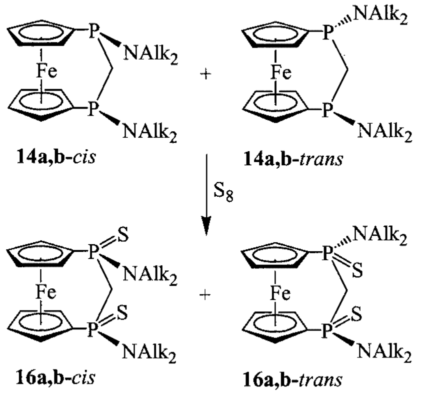
Scheme 2

The lithiation of both rings of the ferrocene **11** proceeds easily with *n*BuLi at room temperature, in the presence of TMEDA.[10] The dilithium derivative **12** crystallizes from the reaction mixture as a complex with TMEDA and can be isolated as dark-red crystals. This compound was immediately used for the reaction with **13a,b** in a solution of THF. The *cis*- and *trans*-isomers of the reaction products **14a,b** possess different spectral characteristics and show separate singlets in their ^{31}P NMR spectra. The presence of the two reaction centers in each starting compound led to the formation of oligomeric/polymeric by products. In their ^{31}P NMR spectra these compounds display broad signals with chemical shifts close to that of the respective monomers. Dilution of the reaction mixture and lowering of the temperature reduced the formation of these by products.

Both isomers were formed in approximately equal proportions (*cis*:*trans* = 45:55), and do not interconvert at room temperature. The differences in physical characteristics allowed the isomers to be separated. Unlike **14a,b-*trans***, the **14a,b-*cis*** isomers possess a more compact structure and crystallize more readily from the reaction mixture. The isolation of the pure *trans*-isomers in this manner was not possible as they crystallized together with the remaining *cis*-isomer. Unfortunately the purification of the **14a,b-*trans*** isomers by column chromatography was not possible either, as the P−N bond in trivalent phosphorus compounds is rather sensitive to moisture.

Compounds in which a plane of symmetry divides the P−P or P−C−P system into two equal parts display signals of substituents at the phosphorus atoms in the NMR spectra as an $AX_nA'X'_n$ spin system. Thus, PH- or PC-coupling may appear, not as doublets, but as pseudo-triplets. Recently, for example, we have noted this to be the case for carbodiphosphoranes.[11] ^{13}C NMR spectroscopic studies of **14a,b-*cis*** isomers revealed that the carbon atoms of the ferrocene cyclopentadienyl rings also appear as pseudo-triplets.

Compounds **14a**,**b** easily react with sulfur to give the sulfur derivatives **16a**,**b** quantitatively (Scheme 3). They are not sensitive to moisture and oxygen and can be used for the separation of *cis*- and *trans*-isomers by column chromatography. For separation purposes, the diethylamino derivative **16b** was chosen, as it is more soluble than **16a**.



Scheme 3

The detailed structure of compounds **14b-*cis*** (Figure 1), **16b-*cis*** (Figure 2) and **16b-*trans*** (Figure 3) have been determined by X-ray analysis. Selected bond lengths and angles are collected in Table 1. Both *cis* molecules have very similar Fe−Cp carbon distances with a spread of only 3 pm. The *trans* molecule shows a slightly greater spread of distances (5 pm). In all three derivatives, the Cp rings are planar with no carbon atom more than 0.5(5) pm from its mean plane. The Cp rings in each molecule are almost coplanar with "tilt" angles of 5.07(3)°, 2.9(3)°, and 3.1(5)° for **14b-*cis***, **16b-*cis*** and **16b-*trans***, respectively. In addition, one of the phosphorus atoms in each molecule lies somewhat more out of the Cp plane than does the other, with deviations from the mean Cp planes being P(1): 13(1), 3(1), 3(1) pm, and P(2): 6(1), 11(1), 17(1) pm for **14b-*cis***, **16b-*cis*** and **16b-*trans***, respectively. One important structural feature is the degree to which the Cp rings are staggered or eclipsed, since there is a variation in these molecules despite the fact that the rings are bridged by a P−C−P unit in each case. The C(11)-ring centroid-ring centroid-C(16) torsion angles are 3.0°, −7.6°, and −17.3°, for **14b-*cis***, **16b-*cis*** and **16b-*trans***, respectively. Thus, these molecules adopt more of an eclipsed, rather than a staggered, conformation; however, **16b-*trans*** is essentially halfway between the eclipsed and staggered geometries. These structures can be compared with the known Si−O−Si bridged ferrocenes $O(R_2SiCp)_2Fe$ (R = Me, Ph),[12] as well as the P−N−P phosphazene-bridged ferrocenes mentioned above.[6−9] All are similar in structure with a slight trend towards increasing torsion angles (i.e., eclipsed to staggered) in the order P−N−P, P−C−P, Si−O−Si. This tendency may simply be due to crystal packing forces.[13]

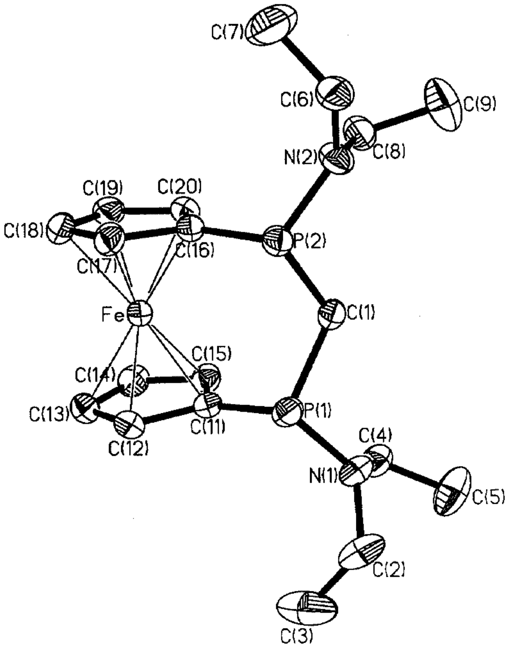


Figure 1. Perspective view and labeling scheme for the molecule **14b-*cis***

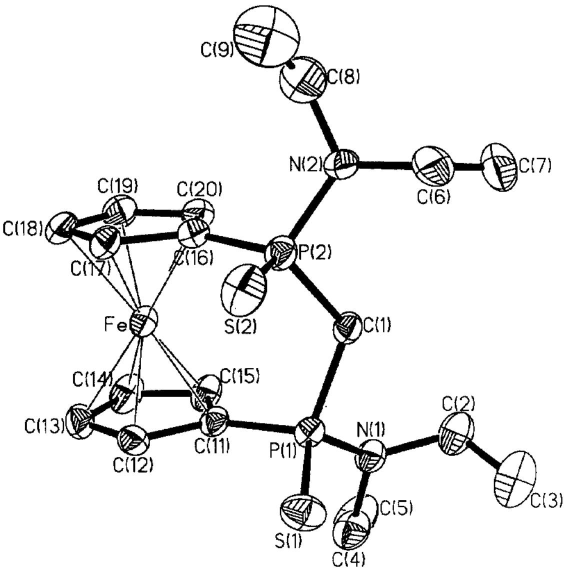


Figure 2. Perspective view and labeling scheme for the molecule **16b-*cis***

Finally, the P−C−P angle in these derivatives shows a large variation from the ideal tetrahedral angle of 107.9(1)° in **14b-*cis*** to 122.7(4)° in **16b-*trans***. Large variations in P−C−P-containing molecules have been observed before[14] and illustrate the ability of this unit to accommodate various geometrical constraints.

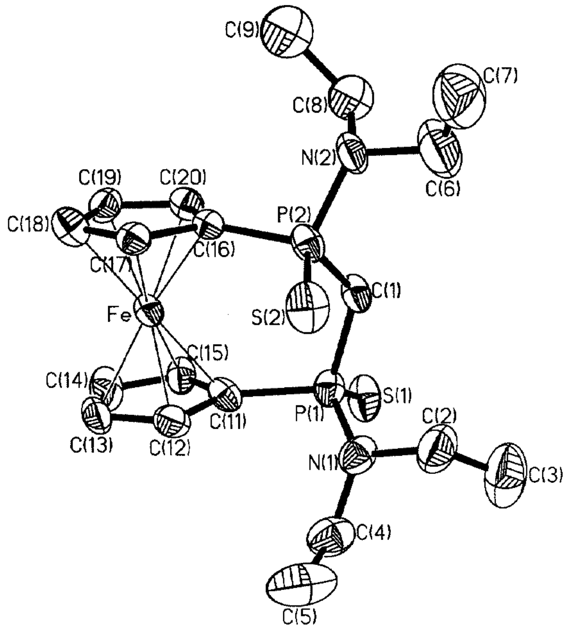


Figure 3. Perspective view and labeling scheme for the molecule **16b-*trans***

Experimental Section

General Remarks: All operations were performed under nitrogen in a dry box. The solvents were dried by the usual procedures. The NMR spectra were recorded with JEOL FX-90Q, Bruker DPX 200 and Bruker AMX 360 spectrometers. The ^{1}H and ^{13}C chemical shifts were referenced to tetramethylsilane (TMS). The ^{31}P chemical shifts were referenced to 85% aqueous orthophosphoric acid as an external standard. As usual, high frequency shifts are given positive signs. The digital resolutions were 0.25 Hz, 0.5 Hz and 1.25 Hz for the ^{1}H, ^{13}C and ^{31}P NMR spectra, respectively. Compounds **13a,b** were obtained from methylenebis(dichlorophosphane)[15] and *N*,*N*-dimethyl- or *N*,*N*-diethyltrimethylsilylamine in petroleum ether at 0 °C and isolated in 60% yield by distillation [b.p. 77−78 °C (**13a**), 108−110 °C (**13b**); 0.04 Torr].

Compound 12: Ferrocene (710 mg, 3.81 mmol) was dissolved in diethyl ether (12 mL) in a closed flask at 40 °C and, after cooling to room temperature, the solution obtained was added to a mixture of TMEDA (1.155 g; 9.96 mmol) and *n*BuLi (9.5 mmol of 1.6 M solution in hexane) in diethyl ether (6 mL). After 16 h the reaction mixture was decanted from the precipitated red crystals of **12** which were quickly dried under a stream of dry nitrogen (yield 1.180 g, 2.74 mmol, 72%) and immediately dissolved in THF (20 mL).

Compound 14a-*cis*: A freshly obtained solution of **12** (1.180 g, 2.74 mmol) in THF (20 mL) (see above) was cooled to −80 °C and a solution of **13a** (644 mg, 2.74 mmol) in THF (10 mL) was added to it in portions while stirring, keeping the temperature constant. The mixture was stirred at −80 °C for 20 min, then slowly warmed to −15 °C and left at this temperature overnight. The solvents were then evaporated in vacuo and the dry residue was extracted with petroleum ether (70−100 °C, 3 × 10 mL, boiling each portion for 1 min). The solvents were evaporated from the combined extracts in vacuo, the residue was re-extracted with boiling petroleum ether (70−100 °C, 5 mL) and the solution obtained was left at −15 °C. After 16 h, 130 mg of **14a-*cis*** contaminated with **14a-*trans*** was isol-

Table 1. Selected bond lengths (pm) and bond angles (deg)

14b-*cis*		**16b-*cis***		**16b-*trans***	
Fe−C(11)	203.7(2)	Fe−C(11)	203.2(4)	Fe−C(11)	201.2(7)
Fe−C(12)	204.7(2)	Fe−C(12)	203.8(4)	Fe−C(12)	202.0(7)
Fe−C(13)	205.7(2)	Fe−C(13)	205.2(4)	Fe−C(13)	201.8(7)
Fe−C(14)	204.1(2)	Fe−C(14)	204.2(5)	Fe−C(14)	205.6(7)
Fe−C(15)	202.7(2)	Fe−C(15)	203.3(4)	Fe−C(15)	203.1(7)
Fe−C(16)	203.9(2)	Fe−C(16)	202.1(4)	Fe−C(16)	200.9(6)
Fe−C(17)	204.6(2)	Fe−C(17)	204.1(4)	Fe−C(17)	203.3(6)
Fe−C(18)	205.5(2)	Fe−C(18)	205.9(4)	Fe−C(18)	204.5(8)
Fe−C(19)	204.4(2)	Fe−C(19)	203.8(4)	Fe−C(19)	204.6(7)
Fe−C(20)	202.7(2)	Fe−C(20)	202.5(4)	Fe−C(20)	201.0(6)
P(1)−N(1)	169.8(2)	P(1)−S(1)	194.2(2)	P(1)−S(1)	195.6(3)
P(1)−C(1)	184.8(2)	P(1)−N(1)	167.2(3)	P(1)−N(1)	165.2(6)
P(1)−C(11)	183.0(2)	P(1)−C(1)	181.9(4)	P(1)−C(1)	181.4(7)
P(2)−N(2)	169.4(2)	P(1)−C(11)	179.2(4)	P(1)−C(11)	180.9(7)
P(2)−C(1)	184.4(2)	P(2)−S(2)	194.1(2)	P(2)−S(2)	194.8(3)
P(2)−C(16)	183.4(2)	P(2)−N(2)	167.5(4)	P(2)−N(2)	165.2(6)
N(1)−C(2)	146.3(2)	P(2)−C(1)	182.6(4)	P(2)−C(1)	182.1(7)
N(1)−C(4)	146.7(3)	P(2)−C(16)	179.4(4)	P(2)−C(16)	178.9(6)
N(2)−C(8)	145.6(3)	N(1)−C(4)	146.7(6)	N(1)−C(4)	146.9(9)
N(2)−C(6)	146.6(3)	N(1)−C(2)	147.2(6)	N(1)−C(2)	147.8(10)
		N(2)−C(8)	145.4(8)	N(2)−C(8)	146.4(11)
		N(2)−C(6)	149.3(6)	N(2)−C(6)	149.7(12)
N(1)−P(1)−C(1)	102.81(10)	N(1)−P(1)−C(1)	101.2(2)	N(1)−P(1)−C(11)	103.4(3)
N(1)−P(1)−C(11)	107.26(10)	N(1)−P(1)−C(11)	101.8(2)	N(1)−P(1)−C(1)	107.8(3)
C(11)−P(1)−C(1)	99.74(11)	C(11)−P(1)−C(1)	108.2(2)	C(11)−P(1)−C(1)	107.4(3)
N(2)−P(2)−C(1)	102.11(11)	N(1)−P(1)−S(1)	118.16(14)	N(1)−P(1)−S(1)	118.5(2)
N(2)−P(2)−C(16)	107.20(11)	C(11)−P(1)−S(1)	112.0(2)	C(11)−P(1)−S(1)	110.0(2)
C(16)−P(2)−C(1)	100.17(11)	C(1)−P(1)−S(1)	114.2(2)	C(1)−P(1)−S(1)	109.1(2)
C(2)−N(1)−C(4)	116.1(2)	N(2)−P(2)−C(1)	100.5(2)	N(2)−P(2)−C(16)	105.3(3)
C(2)−N(1)−P(1)	115.2(2)	N(2)−P(2)−C(16)	103.9(2)	N(2)−P(2)−C(1)	105.8(3)
C(4)−N(1)−P(1)	121.9(2)	C(16)−P(2)−C(1)	105.7(2)	C(16)−P(2)−C(1)	103.9(3)
C(8)−N(2)−C(6)	116.0(2)	N(2)−P(2)−S(2)	117.2(2)	N(2)−P(2)−S(2)	114.3(3)
C(8)−N(2)−P(2)	123.7(2)	C(16)−P(2)−S(2)	112.8(2)	C(16)−P(2)−S(2)	112.7(2)
C(6)−N(2)−P(2)	115.8(2)	C(1)−P(2)−S(2)	115.1(2)	C(1)−P(2)−S(2)	113.9(3)
P(2)−C(1)−P(1)	107.89(12)	C(4)−N(1)−C(2)	114.6(4)	C(4)−N(1)−C(2)	114.6(6)
C(15)−C(11)−C(12)	106.2(2)	C(4)−N(1)−P(1)	115.5(3)	C(4)−N(1)−P(1)	117.6(5)
C(15)−C(11)−P(1)	132.1(2)	C(2)−N(1)−P(1)	122.6(3)	C(2)−N(1)−P(1)	121.3(5)
C(12)−C(11)−P(1)	121.5(2)	C(8)−N(2)−C(6)	117.0(4)	C(8)−N(2)−C(6)	104.6(10)
C(20)−C(16)−C(17)	106.2(2)	C(8)−N(2)−P(2)	122.2(3)	C(8)−N(2)−P(2)	124.2(9)
C(20)−C(16)−P(2)	132.1(2)	C(6)−N(2)−P(2)	116.2(3)	C(6)−N(2)−P(2)	116.7(6)
C(17)−C(16)−P(2)	121.6(2)	P(1)−C(1)−P(2)	119.7(2)	P(1)−C(1)−P(2)	122.7(4)
		C(12)−C(11)−C(15)	107.1(4)	C(12)−C(11)−C(15)	107.1(6)
		C(12)−C(11)−P(1)	126.6(3)	C(12)−C(11)−P(1)	128.7(6)
		C(15)−C(11)−P(1)	126.3(3)	C(15)−C(11)−P(1)	124.1(5)
		C(20)−C(16)−C(17)	107.7(4)	C(20)−C(16)−C(17)	106.2(6)
		C(20)−C(16)−P(2)	128.4(3)	C(20)−C(16)−P(2)	130.5(5)
		C(17)−C(16)−P(2)	123.8(3)	C(17)−C(16)−P(2)	122.9(5)

ated. The pure *cis*-isomer was obtained after recrystallization from dichloromethane/hexane at −15 °C. Yield 80 mg, (8.4%). M.p. 217−218 °C. ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 3.27$ (dt, $^{2}J_{\mathrm{H,H}} = 11.4$, $^{2}J_{\mathrm{P,H}} = 2.6$ Hz, 1 H, P-CH$_2$-P), 4.18 (pseudo t, $^{3}J_{\mathrm{P,H}} = 5.6$ Hz, 12 H, NC*H*$_3$), 5.22 (dt, $^{2}J_{\mathrm{H,H}} = 11.4$, $^{2}J_{\mathrm{P,H}} = 4.4$ Hz, 1 H, P-CH$_2$-P), 5.67−5.81 [m, 2 H, Fe(Cpd$_2$)], 5.87−6.04 [m, 4 H, Fe(Cpd$_2$)], 6.09−6.24 [m, 2 H, Fe(Cpd$_2$)] ppm. ^{13}C NMR (22.5 MHz, CDCl$_3$): $\delta = 32.4$ (t, $^{1}J_{\mathrm{P,C}} = 17.56$ Hz, 1 C, P-*C*-P), 41.6 (pseudo t, $^{2}J_{\mathrm{P,C}} = 6.7$ Hz, 4 C, N*C*H$_3$), 69.9 [pseudo t, $^{2}J_{\mathrm{P,C}} = 5.8$ Hz, 2 C, Fe(Cpd$_2$)], 70.1 [pseudo t, $^{2}J_{\mathrm{P,C}} = 2.9$ Hz, 2 C, Fe(Cpd$_2$)], 71.9 [s, 4 C, Fe(Cpd$_2$)], 77.1 [pseudo t, $^{1}J_{\mathrm{P,C}} = 24.4$ Hz, 2 C, Fe(Cpd$_2$)] ppm. ^{31}P NMR (36.2 MHz, CDCl$_3$): $\delta = 42.3$ (s, 2 P, *P*-C-*P*) ppm. $C_{15}H_{22}FeN_2P_2$ (348.15): calcd. C 51.75, H 6.37; found C 50.78, H 6.27.

Compound 14b-*cis*: A freshly obtained solution of **12** (1.180 g, 2.74 mmol) in THF (20 mL) (see above) was cooled to −80 °C and a solution of **13b** (798 mg, 2.74 mmol) in THF (10 mL) was added to it in portions while stirring, keeping the temperature constant. The mixture was stirred at −80 °C for 20 min, then slowly warmed to −15 °C and left at this temperature overnight. The solvents were then evaporated in vacuo and the dry residue was extracted with hexane (5 × 15 mL, boiling each portion for 1 min). The combined extracts were evaporated in vacuo and the residue was dissolved in hexane (3 mL) at boiling and left at −15 °C for 48 h. Recrystallization was not needed as the *cis*:*trans* ratio was 98:2. Yield 234 mg, (21%). M.p. 113−116 °C. ^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 0.98$ (t, $^{3}J_{\mathrm{H,H}} = 7.0$ Hz, 12 H, NCH$_2$C*H*$_3$), 1.62 (dt, $^{2}J_{\mathrm{H,H}} = 11.4$, $^{2}J_{\mathrm{P,H}} = 2.6$ Hz, 1 H, P-CH$_2$-P), 2.8−3.3 (m, 8 H, NC*H*$_2$CH$_3$), 3.83

(dt, $^{2}J_{\mathrm{H,H}} = 11.4$, $^{2}J_{\mathrm{P,H}} = 4.1$ Hz, 1 H, P-$\mathrm{CH_2}$-P), 4.1−4.2 [m, 2 H, Fe($\mathrm{Cpd_2}$)], 4.3−4.4 [m, 4 H, Fe($\mathrm{Cpd_2}$)], 4.5−4.7 [m, 2 H, Fe($\mathrm{Cpd_2}$)] ppm. ^{13}C NMR (22.5 MHz, $\mathrm{CDCl_3}$): δ = 14.5 (pseudo t, $^{3}J_{\mathrm{P,C}} = 2.0$ Hz, 4 C, $\mathrm{NCH_2}CH_3$), 35.5 (t, $^{1}J_{\mathrm{P,C}} = 17.6$ Hz, 1 C, P-*C*-P), 43.9 (pseudo t, $^{2}J_{\mathrm{P,C}} = 6.8$ Hz, 4 C, $\mathrm{N}CH_2\mathrm{CH_3}$), 69.3 [pseudo t, $^{2}J_{\mathrm{P,C}} = 5.9$ Hz, 2 C, Fe($\mathrm{Cpd_2}$)], 69.5 [pseudo t, $^{2}J_{\mathrm{P,C}} = 3.0$ Hz, 2 C, Fe($\mathrm{Cpd_2}$)], 71.4 [s, 2 C, Fe($\mathrm{Cpd_2}$)], 76.2 [pseudo t, $^{1}J_{\mathrm{P,C}} = 25.4$ Hz, 2 C, Fe($\mathrm{Cpd_2}$)], 81.0 [pseudo t, $^{3}J_{\mathrm{P,C}} = 12.6$ Hz, 2 C, Fe($\mathrm{Cpd_2}$)] ppm. ^{31}P NMR (36.2 MHz, $\mathrm{CDCl_3}$): δ = 37.0 (s, 2 P, *P*-C-*P*) ppm. $\mathrm{C_{19}H_{30}FeN_2P_2}$ (404.26): calcd. C 56.45, H 7.48, N 6.93; found C 55.86, H 7.48, N 6.74.

Compounds 16a,b-*cis*: Sulfur (20 mg, 0.63 mmol) was added to a solution of **14a-*cis*** or **14b-*cis*** (0.12 mmol) in dichloromethane (0.5 mL) and the reaction mixture was stirred at room temperature for 2 h. According to NMR spectroscopic data the reaction proceeds quantitatively. The reaction solution was diluted with hexane until it became turbid and left at −15 °C overnight. The crystalline product that formed was separated and dried in vacuo. Yield after crystallization 46−50%.

16a-*cis*: M.p. 230 °C (dec.). ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): δ = 2.47 (d, $^{3}J_{\mathrm{PH}} = 15.5$ Hz, 12 H, $\mathrm{NC}H_3$), 3.36 (t, $^{2}J_{\mathrm{P,H}} = 15.5$ Hz, 1 H, P-$\mathrm{CH_2}$-P), 3.38 (t, $^{2}J_{\mathrm{P,H}} = 17.0$ Hz, 1 H, P-$\mathrm{CH_2}$-P), 4.38−4.54 [m, 4 H, Fe($\mathrm{Cpd_2}$)], 4.50−4.64 [m, 2 H, Fe($\mathrm{Cpd_2}$)], 5.01−5.17 [m, 2 H, Fe($\mathrm{Cpd_2}$)] ppm. ^{13}C NMR (22.5 MHz, $\mathrm{CDCl_3}$): δ = 37.2 (s, 4 C, $\mathrm{N}CH_3$), 44.2 (t, $^{1}J_{\mathrm{P,C}} = 73.1$ Hz, 1 C, P-*C*-P), 69.9−70.6 [m, 4 C, Fe($\mathrm{Cpd_2}$)], 71.8−72.7 [m, 2 C, Fe($\mathrm{Cpd_2}$)], 73.2−74.0 [m, 2 C, Fe($\mathrm{Cpd_2}$)], 77.3−78.3 [m, $^{2}J_{\mathrm{P,C}} = 17.6$ Hz, 2 C, Fe($\mathrm{Cpd_2}$)] ppm. ^{31}P NMR (36.2 MHz, $\mathrm{CDCl_3}$): δ = 66.6 (s, 2 P, *P*-C-*P*) ppm. $\mathrm{C_{15}H_{22}FeN_2P_2S_2}$ (412.27): calcd. C 43.70, H 5.38, N 6.80; found C 43.61, H 5.23, N 7.24.

16b-*cis*: M.p. 175−180 °C (dec.). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ = 1.06 (t, $^{3}J_{\mathrm{H,H}} = 7.0$ Hz, 12 H, $\mathrm{NCH_2C}H_3$), 2.87−3.10 (m, 8 H, $\mathrm{NC}H_2\mathrm{CH_3}$), 3.20 (dt, $^{2}J_{\mathrm{H,H}} = 13.8$, $^{2}J_{\mathrm{P,H}} = 17.1$ Hz, 1 H, P-$\mathrm{CH_2}$-P), 3.40 (q, $^{2}J_{\mathrm{H,H}} = 13.8$, $^{2}J_{\mathrm{P,H}} = 13.8$ Hz, 1 H, P-$\mathrm{CH_2}$-P), 4.37−4.46 [m, 4 H, Fe($\mathrm{Cpd_2}$)], 4.47−4.55 [m, 2 H, Fe($\mathrm{Cpd_2}$)], 5.04−5.12 [m, 2 H, Fe($\mathrm{Cpd_2}$)] ppm. ^{13}C NMR (22.5 MHz, $\mathrm{CDCl_3}$): δ = 14.5 (m, 4 C, $\mathrm{NCH_2}CH_3$), 40.90 (m, 4 C, $\mathrm{N}CH_2\mathrm{CH_3}$), 44.32 (t, $^{1}J_{\mathrm{P,C}} = 71.2$ Hz, 1 C, P-*C*-P), 69.45−70.15 [m, 4 C, Fe($\mathrm{Cpd_2}$)], 71.65−72.38 [m, 2 C, Fe($\mathrm{Cpd_2}$)], 72.80−73.45 [m, 2 C, Fe($\mathrm{Cpd_2}$)], 77.65−78.55 [m, $^{2}J_{\mathrm{P,C}} = 17.6$ Hz, 2 C, Fe($\mathrm{Cpd_2}$)] ppm. ^{31}P NMR (36.2 MHz, $\mathrm{CDCl_3}$): δ = 60.0 [s, 2 P, *P*-C-*P*) ppm. $\mathrm{C_{19}H_{30}FeN_2P_2S_2}$ (468.38): calcd. C 48.72, H 6.46; found C 47.86, H 6.48.

Compound 16b-*trans*: An excess of sulfur (300 mg) was added to the mother liquor left after crystallization of **14b-*cis***, which contained about 970 mg of dissolved compounds (*cis*:*trans* = 15:85) (see above) and the mixture was stirred vigorously at room temperature for 12 h. The reaction mixture was dried in vacuo, dissolved in a minimum amount of dichloromethane and passed through a column with silica gel (45 g) using dichloromethane (about 1200 mL) as solvent. Fractions with $R_\mathrm{f} = 0.65$ yielded 200 mg of **16b-*trans***. (R_f **16b-*cis*** = 0.45). M.p. 128−129 °C (dec.). ^{1}H NMR (90 MHz, $\mathrm{CDCl_3}$): δ = 1.06 (t, $^{3}J_{\mathrm{H,H}} = 7.1$ Hz, 12 H, $\mathrm{NCH_2C}H_3$), 2.91−3.40 (m, 8 H, $\mathrm{NC}H_2\mathrm{CH_3}$), 3.61 (t, $^{2}J_{\mathrm{P,H}} = 14.6$ Hz, 2 H, P-$\mathrm{CH_2}$-P), 4.27−4.44 [m, 2 H, Fe($\mathrm{Cpd_2}$)], 4.44−4.60 [m, 2 H, Fe($\mathrm{Cpd_2}$)], 4.78−4.92 [m, 2 H, Fe($\mathrm{Cpd_2}$)], 4.92−5.07 [m, 2 H, Fe($\mathrm{Cpd_2}$)] ppm. ^{13}C NMR (22.5 MHz, $\mathrm{CDCl_3}$): δ = 13.8 (pseudo t, $^{3}J_{\mathrm{P,C}} = 2.4$ Hz, 4 C, $\mathrm{NCH_2}CH_3$), 40.3 (pseudo t, $^{2}J_{\mathrm{P,C}} = 1.5$ Hz, 4 C, $\mathrm{N}CH_2\mathrm{CH_3}$), 47.3 (t, $^{1}J_{\mathrm{P,C}} = 61.4$ Hz, 1 C, P-*C*-P), 71.9 [t, $^{3}J_{\mathrm{P,C}} = 6.0$ Hz, 4 C, Fe($\mathrm{Cpd_2}$)], 73.9 [t, $^{2}J_{\mathrm{P,C}} = 4.8$ Hz, 2 C, Fe($\mathrm{Cpd_2}$)], 74.8 [t, $^{2}J_{\mathrm{P,C}} = 4.8$ Hz, 2 C, Fe($\mathrm{Cpd_2}$)], 78.2 [m, $^{2}J_{\mathrm{P,C}} = 8.3$ Hz, 2 C, Fe($\mathrm{Cpd_2}$)] ppm. ^{31}P NMR (36.2 MHz, $\mathrm{CDCl_3}$): δ = 62.2 (s, 2 P, *P*-C-*P*) ppm. $\mathrm{C_{19}H_{30}FeN_2P_2S_2}$ (468.38): calcd. C 48.72, H 6.46; found C 48.16, H 6.41.

X-ray Crystallographic Study: Crystals of complexes **14b-*cis***, **16b-*cis***, and **16b-*trans*** are all orange in color. The diffraction data of the three structures were collected on a Bruker P4 diffractometer. Diffraction data for **14b-*cis*** were collected at room temperature, while data for **16b-*cis*** and **16b-*trans*** were collected at −45 °C. The pertinent crystallographic data and conditions for data collection are summarized in Table 2. The data were corrected for Lorentz and polarization effects. ψ-Scan absorption studies were carried out

Table 2. Crystal data for compounds **14b-*cis***, **16b-*cis***, and **16b-*trans***

	14b-*cis*	**16b-*cis***	**16b-*trans***
Formula	$\mathrm{C_{19}H_{30}N_2P_2Fe}$	$\mathrm{C_{19}H_{30}N_2P_2S_2Fe}$	$\mathrm{C_{19}H_{30}N_2P_2S_2Fe}$
Mol. wt.	404.2	468.4	468.4
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	6.291(1)	14.036(1)	10.590(1)
b, Å	20.152(1)	12.883(1)	7.837(1)
c, Å	15.802(1)	12.544(1)	27.029(2)
β, °	92.242(5)	98.093(6)	98.615(7)
V, Å^3	2003.1(4)	2245.7(3)	2217.9(4)
Z	4	4	4
$D_{\mathrm{calcd,}}$ g cm^{-3}	1.34	1.38	1.40
Abs coeff, mm^{-1}	0.916	1.01	1.02
Crystal dmns, mm	0.30 × 0.25 × 0.15	0.35 × 0.35 × 0.20	0.35 × 0.35 × 0.15
Scan type	w/2θ	w/2θ	w/2θ
2θ range, °	3.5−50.0	3.5−44.0	3.5−44.0
Scan speed, min, max, °	3.5, 35.0	3.5, 35.0	3.5, 35.0
Decay of data,%	3.85	2.70	6.20
Data collected	3867	2898	2878
Obsd reflctns, $F > 4\sigma(F)$	2897	2424	2220
Parameters refined	218	241	236
Goodness-of-fit	1.03	1.05	1.08
R_1	0.033	0.042	0.058
wR_2	0.085	0.116	0.150

on the three structures with T_{min} and T_{max} 0.713 and 0.784 for **14b-*cis***, 0.806 and 0.987 for **16b-*cis***, 0.764 and 1.000 for **16b-*trans***. The crystal structures were solved by direct methods and subsequent difference Fourier syntheses using the *SHELXTL-Plus* package.[16] Full-matrix least-squares refinement was performed. Scattering factors, as well as anomalous-dispersion correction for heavy atoms, were taken from ref.[17] All structures were refined on F^2 (SHELXL-93).[18] One methyl [C(9)] of **16b-*cis*** is disordered, with site occupancy factors of C(9) 0.840, C(9′) 0.160. As for **16b-*trans***, one ethyl group [C(8) and C(9)] is disordered, C(8) and C(9) 0.479, C(8′) and C(9′) 0.521. The above-mentioned disordered moieties were all elastically constrained during the final stages of refinement. H atoms of the three structures were located on a riding model. The final values of R_1 and weighted wR_2 are listed in Table 2. A full list of atomic coordinates, all bond lengths and angles, anisotropic thermal parameters, the positions of H atoms, and tables of structural factors were supplied in the supplementary materials.[19]

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft and Robert A. Welch Foundation for financial support.

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[19] CCDC-178178 (**14b-*cis***), -178179 (**16b-*cis*)** and -178180 (**16b-*trans*)** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Received May 29, 2002
[I02282]