Preparation and Structural Characterization of η^2- and η^3-Heteroallyl Complexes of Cyclopentadienyliron(II), $(\eta^5\text{-}C_5H_5)Fe(L)S_2CR$ (L = $Ph_2PCH_2PPh_2$; R = Me, Ph)

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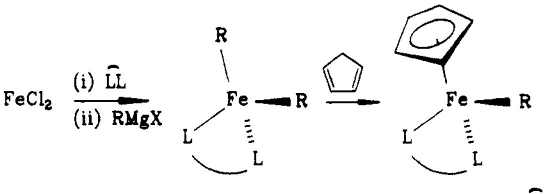
The one-pot reaction of iron(II) chloride with consecutively bis(diphenylphosphino)methane, Grignard reagent, and cyclopentadiene affords the new four-membered chelates $C_5H_5Fe(dppm)R$ (**1**, R = Me; **2**, R = Ph). Crystals of **2** are monoclinic, space group $P2_1/c$, with a = 13.795 (2) Å, b = 13.163 (2) Å, c = 16.441 (3) Å, β = 98.12 (1)°, and Z = 4. Carbon disulfide insertion into the Fe–R bonds of **1** and **2** readily produces terminal η^2- and η^3-coordinated linkage isomers, $C_5H_5Fe(dppm)S_2CR$ (**3a**, S_2CR = η^2-S_2CMe-*S,S′*; **3b**, S_2CR = η^3-S_2CMe-*S,C,S′*; **4a**, S_2CR = η^2-S_2CPh-*S,S′*; **4b**, S_2CR = η^3-S_2CPh-*S,C,S′*). Crystallization of **3** and **4** under specific conditions of temperature and solvent is highly selective and yields only one isomer. Complex **3a** also crystallizes in space group $P2_1/c$, with a = 13.518 (2) Å, b = 9.635 (2) Å, c = 22.617 (2) Å, β = 91.71 (1)°, and Z = 4, whereas its dimorphic linkage isomer has a = 21.046 (2) Å, b = 10.176 (4) Å, c = 13.269 (6) Å, β = 91.86 (2)°, and Z = 4. Detailed variable-temperature ^1H, ^{13}C, and ^{31}P NMR studies have shown that whereas **3b** is the dominant isomer of the dithioacetate product (**3**) in solution (**3a**/**3b** = 5/95), the major isomer of **4** adopts the η^2 form of dithiobenzoate (**4a**/**4b** = 70/30).

Complexes of the type $Fe(LL)R_2$ (LL = bidentate phosphine ligand; R = alkyl) have been isolated, characterized,[1,2] and used in insertion reactions with CO.[3] We recently used $Fe(LL)R_2$ (R = alkyl, aryl) to prepare, by protonolysis of one Fe–R bond with cyclopentadiene, η^5-cyclopentadienyl complexes of iron containing five-membered bidentate phosphine ligands (compare Scheme I). Other methods to prepare these products were mentioned in our recent communication.[4] An attempt by Lehmkuhl to use the smaller bis(diphenylphosphino)methane (dppm) as the stabilizing ligand and then treat $C_5H_5Fe(dppm)Cl$ with a Grignard reagent failed.[5] $C_5H_5Fe(dppm)Me$ was formed in the reduction of CO in $[C_5H_5Fe(CO)(dppm)]^+$ to Me with $LiAlH_4$, but no data were reported.[6]

A complex of the type $C_5H_5Fe(LL)R$ (LL = dppe = 1,2-bis(diphenylphosphino)ethane; R = Me) was shown to undergo SO_2 insertion into the Fe–C bond. CS_2 insertion, however, occurred only with the corresponding hydride compound.[7]

We now report the preparation of complexes of the type $C_5H_5Fe(dppm)R$ (R = Me, Ph) according to our new method mentioned above (see Scheme I).[4] Unlike the known compounds, with five-membered chelate rings, the new complexes insert CS_2 into the remaining Fe–R bond to afford unprecedented isomeric mixtures of η^2-S,S′- and η^3-S,C,S′-coordinated dithioacetate and dithiobenzoate complexes of iron. The distribution of the two bond types in solution and in the dimorphic material was studied by variable-temperature (VT) and two-dimensional NMR spectroscopy as well as by X-ray single-crystal and powder diffraction methods.

Scheme I



A

1 : R = Me; $\widehat{LL}$ = dppm

2 : R = Ph; $\widehat{LL}$ = dppm

For iron only the η^2 bonding system is known.[8] A few dihetera π-allylic ligand systems have been reported for molybdenum[9-13] and ruthenium.[14] Schenk recently reported compounds in which dithioesters act as η^3 ligands in trisubstituted group 6 carbonyl complexes.[15,16]

Results and Discussion

Preparation of the Compounds $C_5H_5Fe(dppm)R$. Compounds **1** and **2** were synthesized in high yields according to Scheme I. Dppm and then the Grignard reagent were added to a tetrahydrofuran (THF) suspension of

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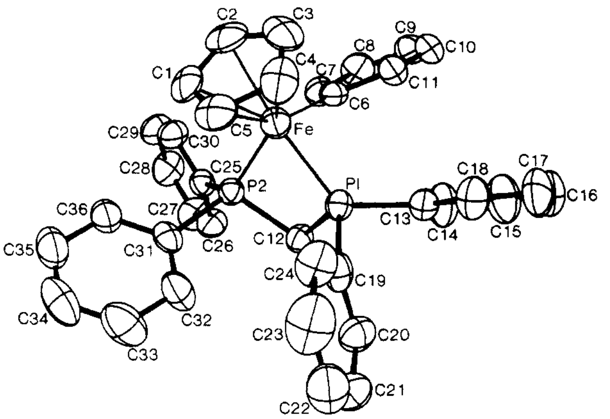


Figure 1. X-ray crystal structure of $[(\eta^5\text{-}C_5H_5)Fe(dppm)Ph]$ (**2**).

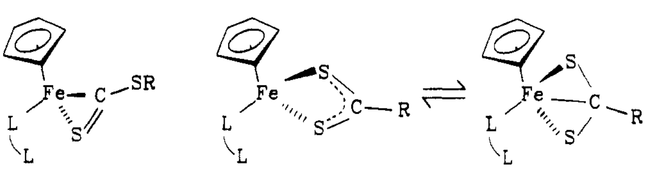
Table I. Selected Bond Distances (Å) and Bond Angles (deg) in 2, 3a, and 3b

	2	3a	3b
Fe–C(1)	2.089 (4)	2.064 (7)	2.106 (3)
Fe–C(2)	2.098 (5)	2.051 (6)	2.104 (3)
Fe–C(3)	2.097 (5)	2.047 (6)	2.083 (3)
Fe–C(4)	2.087 (5)	2.057 (6)	2.074 (3)
Fe–C(5)	2.091 (4)	2.055 (6)	2.082 (3)
Fe–P(1)	2.199 (1)	2.196 (2)	2.245 (1)
Fe–P(2)	2.174 (1)		
P(1)–C(8)		1.837 (5)	1.838 (2)
P(2)–C(8)		1.864 (5)	1.855 (3)
P(1)–C(12)	1.833 (4)		
P(2)–C(12)	1.830 (4)		
Fe–S(1)		2.265 (2)	2.291 (1)
Fe–S(2)		2.260 (2)	2.300 (1)
S(1)–C(6)		1.683 (6)	1.735 (3)
S(2)–C(6)		1.676 (7)	1.711 (3)
Fe–C(6)	2.009 (4)		2.039 (3)
C(6)–C(7)		1.484 (7)	1.499 (4)
P(1)–Fe–P(2)	73.8 (0)		
P(1)–Fe–S(1)		94.0 (1)	84.5 (1)
P(1)–Fe–S(2)		90.9 (1)	90.8 (1)
P(1)–Fe–C(6)	85.0 (1)		112.4 (1)
P(2)–Fe–C(6)	96.8 (1)		
S(1)–Fe–S(2)		74.3 (1)	80.3 (1)
S(1)–C(6)–S(2)		109.0 (4)	118.4 (2)
S(1)–Fe–C(6)			46.8 (1)
P(1)–C(12)–P(2)	91.6 (2)		
Fe–P(1)–C(12)	94.4 (1)		
Fe–P(2)–C(12)	95.3 (1)		

$FeCl_2$ at −78 °C. The acidic nature of cyclopentadiene (pK_a 17) allows protonolysis of a Fe–C σ-bond in the 14e complex A, and the 18e complexes (**1** and **2**), each containing a η^5-C_5H_5 ligand and one metal–carbon bond, were obtained. The products were purified by column chromatography and recrystallization. The red **1** (90% yield) and dark red **2** (71% yield) are air-sensitive in solution but stable in the crystalline form. In the ^1H NMR spectrum of **1** (C_6D_6; see Experimental Section) the methyl triplet is observed at δ 0.24 whereas the corresponding resonance for $C_5H_5Fe(dppe)Me$ is at δ −1.3 in CS_2[17] and at δ −0.78 in C_6D_6.[5] The PCH_2P protons are diastereotopic and resonate as two doublets of triplets at δ 3.50 and 4.20 for **1** and at δ 3.27 and 3.87 for **2**. The stereochemical influence of the cyclopentadienyl and R groups on these protons is not large enough to enable assignment of the signals to particular protons by using NOE difference ^1H NMR spectrometry.

X-ray Crystal Structure of 2. In order to gain insight into the structural characteristics of organoiron compounds containing a four-membered diphosphine chelate ring, a single-crystal X-ray diffraction study of the phenyl complex **2** was undertaken. A molecular drawing is shown in Figure 1, and some important bond lengths and angles are given in Table I. The central iron atom has a distorted-octahedral piano-stool geometry, which has been observed in other half-sandwich iron complexes.[18,19] The P(1)–Fe–P(2) angle (73.8 (0)°) is smaller than the corresponding angles reported for piano-stool complexes with larger chelate rings (for example 83.33 (7)° in $Fe(dippe)(CH_2C_6H_4Me)_2$; dippe = 1,2-bis(diisopropylphosphino)ethane)[2] but the same as the P–Fe–P angle (73.5 (1)°) observed in $Fe(CO)_3dppm$.[20] The smaller angle is an inescapable consequence of the steric constraint inherent in the dppm ligand itself. The P(1)–C(12)–P(2) angle of 91.6 (2)° compares with a 90.8 (2)° angle in the carbonyl complex, and both are significantly smaller than the corresponding angle in dppm ligands bound in a monodentate manner (vide infra).

Scheme II



B.: $\widehat{LL}$ = dppm

3a : R = Me

4a : R = Ph

3b : R = Me

4b : R = Ph

The Fe–P(1) and Fe–P(2) bond lengths in **2** differ somewhat (2.199 (1) and 2.174 (1) Å), which is in accordance with the results for $Fe(CO)_3dppm$ (2.209 (3) and 2.225 (3) Å).[20] The Fe–C(6) σ-bond in **2** (2.009 (4) Å) is similar to that in $C_5H_5Fe(CO)(PPh_3)Ph$ (2.11 (2) Å).[18]

Preparation of the Compounds $C_5H_5Fe(dppm)S_2CR$. An excess of CS_2 was added to compounds **1** and **2**, and over a period of 18 h one molecule of CS_2 inserted into each of the Fe–R bonds to afford the microcrystalline products **3** and **4** in yields of ca. 80% after purification by column chromatography. Due to the air sensitivity of solutions of **3** and **4** the microcrystalline products were often contaminated with dppm.

Two well-separated signals for the phosphorus atoms in the room-temperature ^{31}P NMR spectra of both products indicated that one phosphorus atom was not coordinated, thus ruling out the possibility of simple monodentate bonding by the sulfur-containing ligand.

The stereochemical structures of products **3** and **4** could not be deduced from their 200-MHz room-temperature ^1H, ^{13}C, and ^{31}P NMR spectra. From the essentially identical infrared spectra (Nujol, $CHCl_3$) of **3** and **4** in the 800–1200-cm^{-1} region (ν(C=S) = 1100 cm^{-1}), we initially inferred that the bonding of the $MeCS_2^-$ and $PhCS_2^-$ ligands was similar. At least two well-known modes of coordination leading to 18e species were available to the RCS_2^- moiety (Scheme II): (i) formation of a η^2-dithioester complex (bound through C and S; B)[21] or (ii) formation of a η^2-dithiocarboxylate complex (bound through two S atoms; **3a**).[22]

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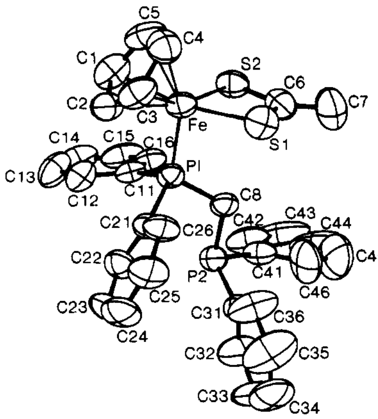

Figure 2. X-ray crystal structure of $[(\eta^5\text{-}C_5H_5)Fe(\eta^2\text{-}S_2CMe\text{-}$*S,S'*)dppm] (**3a**).

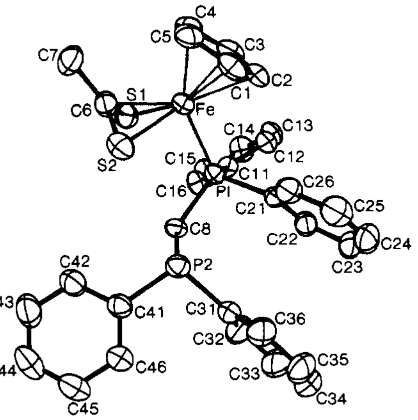

Figure 3. X-ray crystal structure of $[(\eta^5\text{-}C_5H_5)Fe(\eta^3\text{-}S_2CMe\text{-}$*S,C,S'*)dppm] (**3b**).

We eventually found no further evidence for type B, and the η^2-dithiocarboxylate complexes **3a** and **4a** as well as their unusual η^3-bonded isomers (**3b** and **4b**) were finally identified in the solid state and in solution. The infrared spectra of our new compounds did not differentiate between the bonding modes of the dithiocarboxylate ligands. For example, the Nujol mull and chloroform spectra of **3a** are identical despite the fact that the same crystals dissolved in THF-d_8 display a **3a**/**3b** isomer ratio of 5/95 (see VT NMR experimental results later). Infrared absorptions for η^3-thioxanthate ligands in the crystalline molybdenum complex $MoO(S_2CS\text{-}i\text{-}C_3H_7)_2$ were observed as two medium-intensity absorptions in the 870–890-cm^{-1} region in Nujol, while the absorptions for the η^2-thioxanthate ligands were observed at 990 and 940 cm^{-1} in CH_2Cl_2 solution. The absorptions in the 870–890-cm^{-1} region were absent in the solution spectra, and it was concluded that the η^3-thioxanthate bonding mode only existed in the solid state.[9] Carmona and co-workers, on the other hand, concluded that since the infrared spectra of $MoO[S_2C(PMe_3)S\text{-}i\text{-}Pr\text{-}S,S'](S_2CS\text{-}i\text{-}Pr\text{-}S,C,S')$ in the solid state and in solution were essentially identical, the η^3-thioxanthate coordination was maintained in solution.[13]

Recrystallization of compound **3** from THF/hexane and CH_2Cl_2/hexane mixtures yielded crystals of different colors (**3a**, brown; **3b**, blue). To unequivocally establish the bonding and structural characteristics of the products, we embarked upon a detailed X-ray crystallographic study of the crystalline material of **3** as well as a VT NMR study of solutions containing compounds **3** and **4**, respectively.

X-ray Crystal Structures of 3a and 3b. Views of the two molecules are shown in Figures 2 and 3. Selected bond distances and angles are summarized in Table I. Apart from the coordination of the sulfur-containing ligand, the molecular structures of **3a** and **3b** are very similar, each containing a η^5-cyclopentadienyl ring and a monodentate dppm ligand. In **3a** the iron atom has the expected distorted-octahedral piano-stool geometry, similar to the geometry in complex **2**; two coordination positions are taken up by the η^2-S,S'-coordinated dithioacetate group. The ligands in **3b** include an unusual and, to our knowledge, completely novel (for iron) η^3-S,C,S'-coordinated dithioacetate. The ligands occupy distorted-trigonal-bipyramidal positions with C(6) (Figure 3) largely displaced from the ideal axial position.

The Fe–C(6) bond length of 2.039 (3) Å is shorter than the central Fe–C bond length in $(\eta^3\text{-}C_3H_5)Fe(CO)_3Br$ (2.058 (11) Å) and $(\eta^3\text{-}C_3H_5)Fe(CO)_3I$ (2.09 (2) Å),[23] longer than the 2.009 (4) Å distance for the σ-bond in the aryl complex **2**, and significantly shorter than the separation of the iron and carbon atoms of the π-bonded cyclopentadienyl ring (average 2.091 (3) Å), which, in turn, is somewhat longer than the same bonds in **3a**. The metal–dithio ligand connectivities and bond distances in **3b** suggest an interaction of the iron with the ligand π-system for which a molecular orbital bonding description similar to that proposed for metal–π-alkyl interactions[24] can be envisaged. Other examples in which dithio acid ligands are attached to metal atoms in a η^3-S,C,S' mode have been reported for molybdenum[9-13,15,16] and ruthenium[14] complexes. The structures of **3a** and **3b** do not differ significantly. The extra bond to C(6) in **3b** causes the Fe–S(1)–S(2) plane to tilt by 9.5° relative to the Fe–P(1) bond, as shown by the decrease of the P(1)–Fe–S(1) angle. The P(1)–Fe–S(2) angle remains the same. The fact that the Fe–P(1), Fe–S(1), and Fe–S(2) as well as the (average) C_5H_5–Fe bonds are shorter in **3a** than in **3b** indicates that the extra Fe–C bond formed in **3b** withdraws electron density from the other bonds.

The results from the X-ray study also allow a comparison of the geometries of the two differently coordinated disulfur ligands in **3a** and **3b** and that of KS_2CCH_3.

The 109.0 (4)° S(1)–C(6)–S(2) angle in **3a** is contracted compared to those in the other two compounds (118.4 (2)° in **3b** and 123.5 (6)° in KS_2CCH_3).[25] This trend correlates with one observed for Mo complexes with η^2-S,S' and η^3-S,C,S' ligands.[9,12,13] The former angle does not differ much from known angles in various η^2-coordinated thioxanthate[26] and dithiocarbamate[27] complexes irrespective of the metal, its oxidation state, or other coordinated ligands present.[28] Despite the decrease in this angle compared to the 123.5° angle in the potassium salt of the ligand, the two C–S distances in **3a** (average 1.680 (7) Å) do not differ much from those in the free ligand (1.67 (1) Å)[25] but are shorter than the same bonds in **3b** (1.723 (3) Å). The 118.41 (2)° S(1)–C(6)–S(2) angle in **3b** also compares well with a similar angle in the η^3-coordinated xanthate ligand of $MoO[S_2C(PMe_3)O\text{-}i\text{-}Pr](S_2CO\text{-}i\text{-}Pr)$ (119.4 (3)°).[12]

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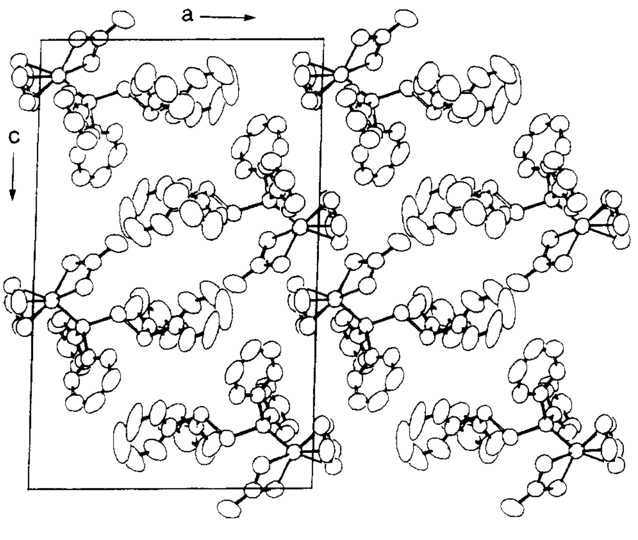

Figure 4. Crystal packing for **3a**.

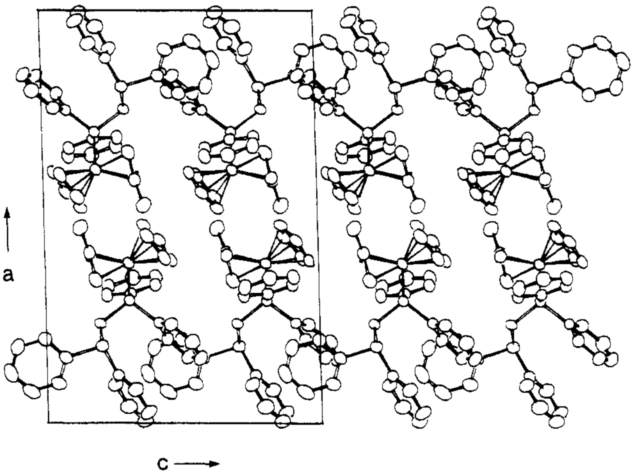

Figure 5. Crystal packing for **3b**.

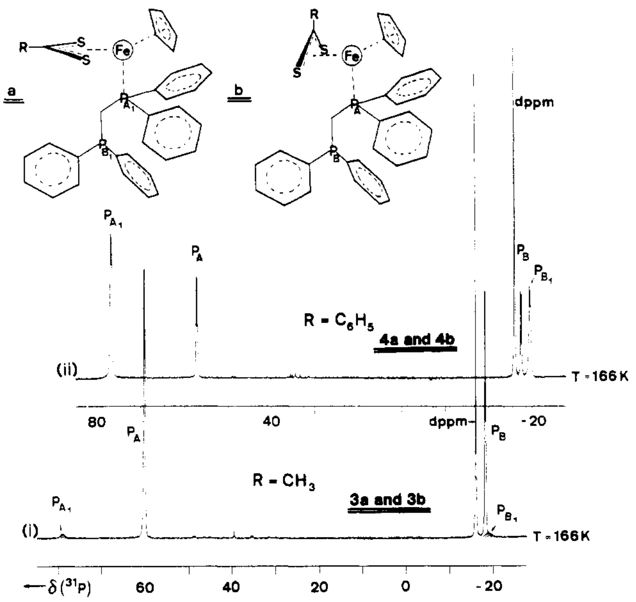

Figure 6. ^{31}P NMR spectra (162 MHz) of **3** (i) and of **4** (ii) dissolved in THF-d_8 at 166 K. In spectrum i the signals of the minor component are shaded.

The differences between the two linkage isomers are also reflected in the crystal packing. Figures 4 and 5 show packing diagrams of the two crystal forms containing in both cases the outline of the unit cell and a layer of symmetry-related molecules. The shortest distances for non-H intermolecular contacts are in both cases not less than 3.30 Å, indicating an absence of bonding influences other than van der Waals interactions. The similarity in the axial lengths (inverse in the case of *a* and *c*) seems to be purely coincidental.

To ensure that the single crystals used for the structure determinations represented the synthesized product, powder X-ray diffraction patterns of the bulk material were measured and compared with calculated patterns generated from the single-crystal structure data of **3a** and **3b**.[29] Each was shown to contain one isomer exclusively—an indication of the high selectivity in the crystallization of these dimorphic products.

Structures of 3 and 4 in Solution. The solution structures of complexes **3** and **4** were established by utilization of variable-temperature ^{1}H, ^{13}C, and ^{31}P NMR spectrometry with modern one- and two-dimensional pulse techniques.[30] The 162-MHz ^{31}P NMR spectrum of **3** dissolved in THF-d_8 at low temperature (166 K, see Figure 6) shows signals of two {AX} spin systems and a singlet stemming from a noncoordinated dppm ligand.[31] The two doublets around 60 ppm were assigned to coordinated phosphorus atoms P_A and P_{A1} of the chelating ligand, while the signals around −20 ppm lie close to those of free dppm (with δ ca. −15 ppm) and, therefore, belong to the noncoordinated phosphorus atoms P_B and P_{B1}. Since the ^{31}P NMR data for the two {AX} spin systems are similar and exchange occurred between P_A and P_B and between P_{A1} and P_{B1}, as evidenced by line-shape analysis in the temperature range from 170 to 270 K, it can be assumed that the resonances originate from the isomer pair **3a** and **3b**, which have been identified in the solid state by X-ray analysis. The ^{31}P NMR spectrum of **4** also consists of signals for two {AX} spin systems and a singlet (dppm). These resonances originate from the isomer pair **4a** and **4b** similar to those identified for **3**.

Integration of the signals indicated an isomer ratio of 5/95 for **3** and 70/30 for **4**. When the temperature was increased, the intensity of the individual chemical shifts and the position of the averaged chemical shift for **3** indicated that this ratio was not altered significantly. Thus, it can be accepted that, also at 300 K, complex **3** is present in solution as practically (95%) one isomer.

The ^{1}H NMR spectrum, therefore, should indicate the stereochemical structure of the major isomer even if fast exchange with the minor isomer is taking place. In fact, the ^{1}H NOE difference experiments,[32] shown in Figure 7, confirmed that the major isomer has the η^3-heteroallyl structure **3b**. The strongest evidence for this assignment came from the NOE of the η^5-cyclopentadienyl protons H_1 with the methyl protons H_7 (compare traces ii and iv in Figure 7). In **3a** the larger separation of the methyl and

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[29] Experimental details: Philips PW 1700 automated powder diffractometer, monochromated Cu Kα radiation, step size 0.02° in 2θ, step line 1 s. Smith, D. K.; Nichols, M. C.; Zolensky, M. E. POWD10-A FORTRAN IV Program for Calculating X-ray Powder Diffraction Patterns, Version 10; Pennsylvania State University, College of Earth and Medical Sciences: University Park, PA, 1983.

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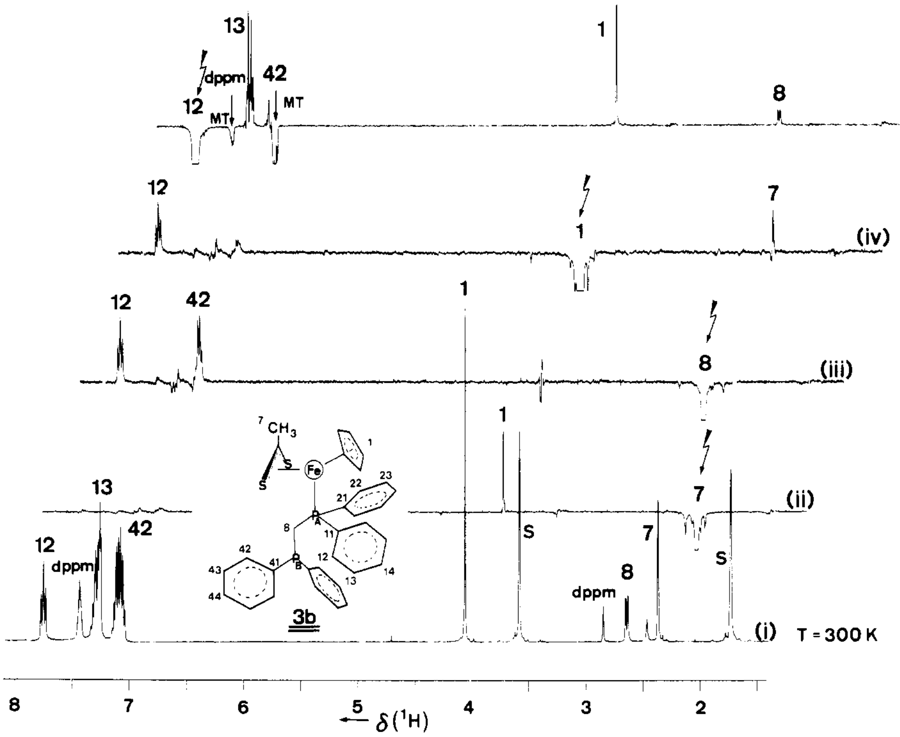

Figure 7. ¹H NMR spectra (400 MHz) of **3b** (95%) dissolved in THF-d_8 at 300 K: (i) normal spectrum; (ii–v) NOE difference spectra, where the irradiated signal is marked by an arrow and absorption lines stem from spatially neighboring protons. MT denotes effects from magnetization transfer (i.e. chemical exchange).

Table II. Crystallographic Data for 2, 3a, and 3b and Structure Determination Details

	2	3a	3b
		Crystal Data	
formula	$C_{36}H_{32}FeP_2$	$C_{32}H_{30}FeP_2S_2$	$C_{32}H_{30}FeP_2S_2$
cryst habit	red needles	brown needles	blue rhombuses
cryst size, mm	0.11 × 0.08 × 0.09	0.72 × 0.18 × 0.13	0.50 × 0.35 × 0.20
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
unit cell determn	least-squares fit to 25 rflns, θ(Cu) < 34°	least-squares fit to 25 rflns, θ(Mo) < 16°	least-squares fit to 25 rflns, θ(Mo) < 20°
unit cell dimens			
a, Å	13.795 (2)	13.518 (2)	21.046 (2)
b, Å	13.163 (2)	9.635 (2)	10.176 (4)
c, Å	16.441 (3)	22.617 (2)	13.269 (6)
β, deg	98.12 (1)	91.71 (1)	91.86 (4)
packing			
V, Å³	2955 (1)	2944 (1)	2840 (2)
Z	4	4	4
D_{calc}, g cm⁻³	1.313	1.346	1.395
M_r	582.45	596.52	596.52
$F(000)$	1208	1228	1228
		Experimental Data	
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation	Cu Kα (1.54184 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
monochromator	graphite	graphite	graphite
collecn mode	ω–2θ scans, θ range 3–65°	ω–2θ scans, θ range 3–25°	ω–2θ scans, θ range 3–27°
scan width, deg	0.6 + 0.14 tan θ	0.57 + 0.34 tan θ	0.50 + 0.34 tan θ
scan speed, deg min⁻¹	variable, 5.5 (max)	variable, 4.1 (max)	variable, 5.5 (max)
no. of reflns measd	5502	5499	6527
no. of observable reflns	4687 with $F > 0$	3830 with $I > 1\sigma$	5209 with $I > 1\sigma$
stability	3 rflns every 60 min, 11% loss in intens over 78 h	3 rflns every 60 min, 2% loss in intens	3 reflns every 60 min, no variation
cor	Lp, abs, cryst decay	Lp, abs	Lp
μ, cm⁻¹	18.6	7.2	7.4
abs cor	empirical[35]	empirical[35]	too small to be signif
		Solutions and Refinement	
computer program used	SHELX 76[36]	SHELX 76[36]	SHELX 76[36]
refinement	least squares, full matrix	least squares, full matrix	least squares, full matrix
no. of variables	353	335	335
no. of reflns used	3976 with $F > 3\sigma$	3690 with $F > 3\sigma$	5104 with $F > 3\sigma$
weighting scheme	$w = (\sigma(F))^{-2}$	$w = (\sigma(F))^{-2}$	$w = (\sigma(F))^{-2}$
final Δ peaks	0.5 e Å⁻³ near the Fe atom	0.7 e Å⁻³ near P(2)	0.4 e Å⁻³ between Fe and P(1)
final R, R_w	0.054, 0.052	0.0655, 0.0443	0.0415, 0.0325

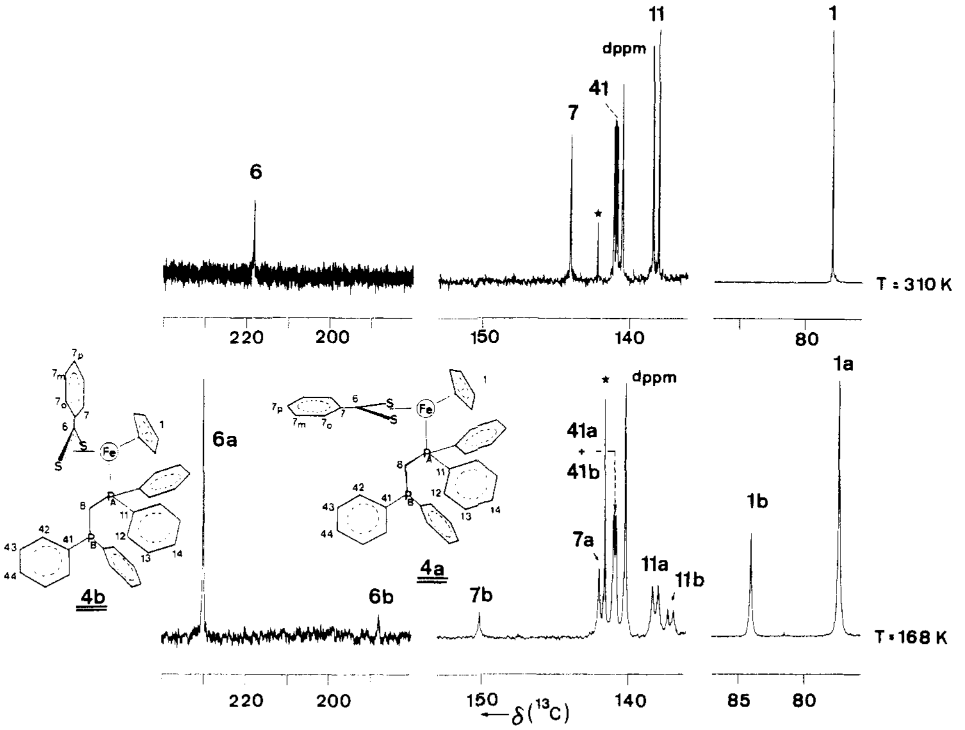

Figure 8. Expansions from the 101-MHz ^{13}C NMR spectrum of 4 dissolved in THF-d_8. The asterisks denote signals of an impurity (biphenyl).

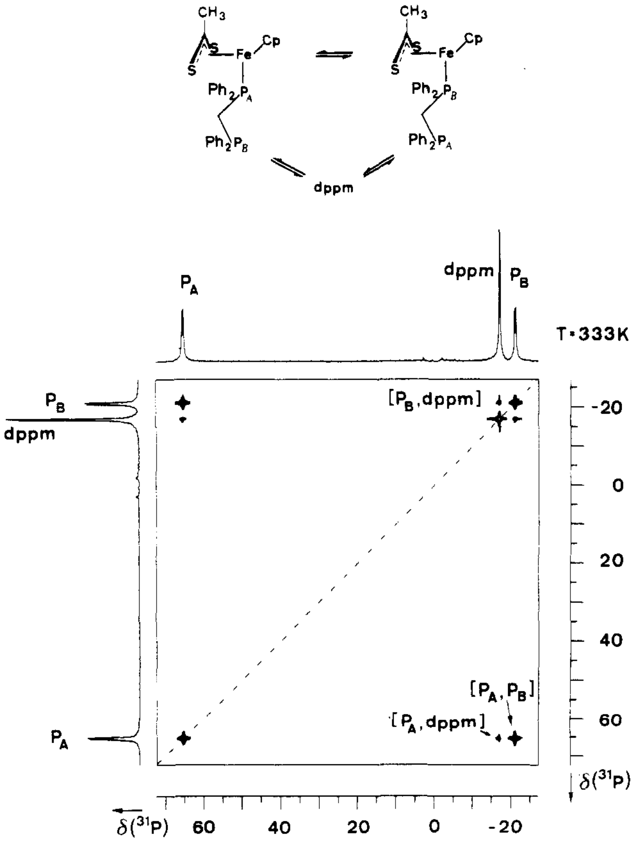

Figure 9. Two-dimensional ^{31}P NMR exchange spectrum (162 MHz) of 3 dissolved in THF-d_8 at 333 K. The chemical shifts lie on the diagonal, and the cross peaks indicate chemical exchange of the corresponding sites.

the cyclopentadienyl protons precluded the observation of a NOE.

The assignment above is also supported by variable-temperature ^{13}C NMR spectra of 4. The 70/30 isomer ratio of this product in solution is more favorable for signal assignment of the carbon atoms. At 300 K fast exchange between the two isomers **4a** and **4b** occurs. The signals, all in the expected regions, are assigned in the Experimental Section. For the identification of **4a** and **4b** chemical shifts of the cyclopentadienyl carbons (C_1) and the η^2- or η^3-bonded dithiobenzoate carbon atom (C_6) (Figure 8) were used. At 173 K the two resonances for the CS_2 fragments and the two resonances for the C_5H_5 carbon atoms of product 4 were also found in a ratio of about 70/30. In isomer **4b** the carbon atom C_6, which is bonded to iron, resonates at a lower $\delta(^{13}C)$ value (187.2 ppm) than in **4a** (230.0 ppm). The chemical shifts for the C_5H_5 carbon atoms lie at 76.9 (70%) and 84.5 (30%) ppm, respectively. Quite similar chemical shifts were found for **3a** and **3b**. The presence of two isomers in the ratio of about 5/95 is once again indicated by the signals at 75.2 (5%) and 82.9 (95%) ppm, which must be assigned to the C_5H_5 carbon atoms. In line with the results of the ^{31}P NMR study (Figure 6), this is further evidence that in product 3 the complex containing the η^3-S,C,S′-bonded species is the major isomer while it is the minor isomer in 4. Confirmation of this assignment via ^{1}H NOE experiments was not possible due to the 70/30 isomer ratio and fast isomerization even at 160 K.

As mentioned earlier, the variable-temperature ^{31}P and ^{13}C NMR spectra indicated a fast exchange between the isomeric pairs of products 3 and 4. These processes can already be detected at temperatures as low as 173 K, and at temperatures above 200 K the ^{31}P and ^{13}C spectra consisted of only one set of signals for each product even at 9.4 T. At temperatures above 300 K we observed a fluxional process involving exchange between the coordinated and dangling phosphorus atoms. In addition, the coordinated and uncoordinated (vide supra) dppm ligands also exchange. This is clearly obvious in the 2D ^{31}P NMR exchange spectrum (Figure 9). Apart from a strong cross peak belonging to P_A and P_B, there are also two cross peaks of lower intensity that stem from the exchange of P_A and P_B with dppm. Apparently this exchange process is faster in 3 than in 4 since the conventional 1D ^{31}P NMR spectra

Table III. Fractional Coordinates (×10⁴, ×10⁵ for Fe, P) and Equivalent Isotropic Temperature Factors (Å² × 10³, ×10⁴ for Fe and P) for 2

	x/a	y/b	z/c	U_{eq}[a]
Fe	78608 (5)	30416 (5)	26397 (4)	459 (2)
P(1)	69815 (8)	30716 (9)	36558 (6)	380 (2)
P(2)	84830 (8)	18921 (8)	35100 (6)	357 (2)
C(12)	7877 (3)	2352 (3)	4360 (2)	41 (1)
C(1)	8156 (4)	2231 (4)	1610 (3)	62 (1)
C(2)	8523 (4)	3202 (5)	1574 (3)	67 (2)
C(3)	7716 (5)	3862 (4)	1536 (3)	70 (2)
C(4)	6875 (4)	3288 (4)	1573 (3)	69 (2)
C(5)	7163 (4)	2261 (4)	1613 (3)	62 (1)
C(6)	8563 (3)	4237 (3)	3209 (2)	39 (1)
C(7)	9506 (3)	4233 (4)	3631 (3)	50 (1)
C(8)	9962 (4)	5122 (4)	3968 (3)	62 (1)
C(9)	9496 (4)	6026 (4)	3902 (3)	63 (1)
C(10)	8554 (4)	6055 (4)	3485 (3)	61 (1)
C(11)	8113 (4)	5201 (3)	3149 (3)	51 (1)
C(13)	6663 (3)	4201 (3)	4202 (3)	46 (1)
C(14)	7286 (4)	4618 (4)	4855 (3)	68 (1)
C(15)	7058 (5)	5524 (4)	5201 (4)	90 (2)
C(16)	6225 (5)	6012 (5)	4922 (4)	91 (2)
C(17)	5582 (5)	5623 (5)	4279 (4)	86 (2)
C(18)	5805 (4)	4728 (4)	3918 (3)	67 (1)
C(19)	5847 (3)	2346 (3)	3676 (3)	48 (1)
C(20)	5587 (3)	2038 (4)	4426 (3)	60 (1)
C(21)	4789 (4)	1409 (4)	4453 (4)	79 (2)
C(22)	4211 (4)	1123 (5)	3714 (5)	91 (2)
C(23)	4459 (4)	1449 (5)	2993 (5)	95 (2)
C(24)	5267 (3)	2066 (4)	2952 (3)	67 (1)
C(25)	9762 (3)	1658 (3)	3933 (3)	39 (1)
C(26)	10021 (4)	1408 (3)	4753 (3)	50 (1)
C(27)	11002 (4)	1291 (4)	5075 (3)	63 (1)
C(28)	11716 (4)	1401 (4)	4581 (3)	65 (1)
C(29)	11468 (4)	1623 (4)	3770 (3)	60 (1)
C(30)	10497 (3)	1756 (3)	3438 (3)	52 (1)
C(31)	8066 (3)	595 (3)	3266 (3)	42 (1)
C(32)	7188 (4)	225 (4)	3459 (3)	64 (1)
C(33)	6848 (4)	−735 (4)	3172 (4)	82 (2)
C(34)	7374 (5)	−1316 (4)	2707 (4)	81 (2)
C(35)	8263 (5)	−975 (4)	2529 (3)	75 (2)
C(36)	8608 (4)	−7 (3)	2800 (3)	57 (1)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(a_i \cdot a_j)$.

show that $^2J_{PP}$ in **3** increases steadily from 33 Hz at 166 K to 48 Hz at 348 K while the coupling constant in **4** is 40 Hz at any temperature between 166 and 333 K. (Note that in the free phosphine $^2J_{PP}$ is 125 Hz.)[31]

In summation, we conclude from the NMR studies that in solution products **3** and **4** each consist of two isomers in which the dithioacetate or dithiobenzoate ligand is either η^2 (**3a**, **4a**) or η^3 bonded (**3b**, **4b**) to the iron and thus adopt the same structures as in the crystalline state. The exchange between each pair of isomers is complicated at temperatures above 300 K by the occurrence of fluxionality and exchange between coordinated and free dppm.

Experimental Section

General Procedures. All reactions and manipulations were performed under a nitrogen atmosphere with use of standard vacuum line and Schlenk-tube techniques.

Table IV. Fractional Coordinates (×10⁴, ×10⁵ for Fe, P, S) and Equivalent Isotropic Temperatures Factors (Å² × 10³, ×10⁴ for Fe, P, S) for 3a

	x/a	y/b	z/c	U_{eq}[a]
Fe	93395 (6)	23970 (9)	41929 (4)	569 (2)
P(1)	82316 (11)	34012 (16)	36059 (7)	531 (4)
P(2)	60361 (12)	44094 (18)	33495 (7)	606 (5)
S(1)	87071 (13)	32892 (18)	50276 (8)	746 (5)
S(2)	82073 (12)	8372 (17)	44883 (8)	692 (5)
C(1)	10278 (5)	1485 (8)	3604 (4)	82 (2)
C(2)	10421 (5)	2886 (7)	3611 (3)	73 (2)
C(3)	10714 (4)	3282 (7)	4165 (4)	77 (2)
C(4)	10757 (5)	2109 (9)	4527 (3)	80 (2)
C(5)	10500 (5)	1024 (7)	4163 (4)	90 (3)
C(6)	7939 (5)	1916 (7)	5043 (3)	75 (2)
C(7)	7118 (5)	1726 (7)	5456 (3)	111 (3)
C(8)	6976 (4)	3652 (6)	3876 (2)	59 (2)
C(11)	8012 (4)	2416 (6)	2921 (3)	59 (2)
C(12)	8578 (4)	2592 (8)	2421 (3)	78 (2)
C(13)	8440 (5)	1746 (9)	1926 (3)	99 (3)
C(14)	7728 (6)	751 (9)	1929 (4)	107 (3)
C(15)	7171 (6)	539 (8)	2418 (4)	96 (3)
C(16)	7301 (5)	1342 (6)	2909 (3)	70 (2)
C(21)	8507 (4)	5203 (6)	3380 (3)	56 (2)
C(22)	8143 (5)	5773 (6)	2850 (3)	69 (2)
C(23)	8276 (5)	7180 (7)	2743 (3)	84 (2)
C(24)	8762 (5)	7996 (7)	3159 (3)	88 (2)
C(25)	9126 (5)	7431 (7)	3669 (3)	81 (2)
C(26)	9008 (4)	6036 (6)	3785 (3)	67 (2)
C(31)	5875 (4)	6187 (6)	3612 (3)	60 (2)
C(32)	5126 (6)	6929 (8)	3340 (4)	110 (3)
C(33)	4950 (8)	8306 (10)	3490 (5)	141 (4)
C(34)	5507 (7)	8936 (9)	3886 (5)	121 (4)
C(35)	6259 (6)	8267 (9)	4151 (5)	138 (4)
C(36)	6449 (5)	6876 (8)	4019 (4)	111 (3)
C(41)	4926 (5)	3600 (7)	3632 (4)	73 (2)
C(42)	4517 (5)	2525 (8)	3314 (4)	107 (3)
C(43)	3686 (7)	1831 (11)	3516 (7)	172 (6)
C(44)	3256 (9)	2263 (12)	3972 (8)	207 (8)
C(45)	3614 (9)	3313 (13)	4298 (6)	189 (5)
C(46)	4464 (6)	3984 (9)	4128 (4)	128 (3)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(a_i \cdot a_j)$.

Bis(diphenylphosphino)methane (dppm) was purchased from Strem Chemicals. Anhydrous $FeCl_2$ was prepared from $FeCl_3$,[33] and cyclopentadiene was obtained by cracking dicyclopentadiene. THF and diethyl ether were distilled from Na–benzophenone ketyl. CH_2Cl_2 and CS_2 were distilled from P_2O_5. The Grignard reagents MeMgI and PhMgBr were prepared in diethyl ether and standardized according to the method described by Griffen.[34] Column chromatography was done with use of neutral alumina (Fluka, dried in vacuo before use) as the stationary phase (dimensions of columns 14–16 cm × 3 cm). Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Mass spectra were recorded on a Finnigan Mat 8200 instrument and the infrared spectra on a Perkin-Elmer 841 spectrometer. Elemental analyses were carried out by the Council for Scientific and Industrial Research, Pretoria, South Africa. The NMR spectra of **1** and **2** and the ^1H NMR spectrum of **4** were recorded on a Varian VXR 200 FT spectrometer with ^1H and ^{13}C chemical shifts reported in ppm downfield from TMS. An 85% H_3PO_4 solution was employed as an external standard for the ^{31}P spectra. The NMR spectra of **3** and **4** were recorded on a Bruker WH 400 spectrometer. The crystal structures of **2**, **3a**, and **3b** were determined by standard crystallographic techniques summarized in Table II. Fractional coordinates are listed in Tables III–V. Additional data are available as supplementary material.

Preparation of $C_5H_5Fe(dppm)Me$ (1). A solution of 2.2 M MeMgI (4.9 mL, 10.7 mmol) was injected into a cooled (−78 °C) stirred suspension of $FeCl_2$ (0.66 g, 5.2 mmol) and dppm (2.0 g, 5.2 mmol) in 30 mL of THF. After 1 h cyclopentadiene (0.45 mL, 5.6 mmol) was injected and the dark red reaction mixture was stirred for another 30 min at −78 °C and then allowed to reach room temperature. The solvent was removed in vacuo. The residue was dissolved in the minimum amount of CH_2Cl_2 and the solution chromatographed on neutral alumina (92 g) with hexane. The red eluate was evaporated to dryness, and a pure, microcrystalline product, which was washed with three portions of cold hexane and dried in vacuo, was obtained; yield 2.4 g, 90%. MS

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Table V. Fractional Coordinates ($\times 10^4$, $\times 10^5$ for Fe, P, S) and Equivalent Isotropic Temperature Factors (Å^2 $\times$ 10^3, $\times 10^4$ for Fe, P, S) for 3b

	x/a	y/b	z/c	$U_{eq}{}^a$
Fe	38688 (2)	50113 (4)	30608 (3)	345 (1)
P(1)	29537 (3)	38779 (7)	30696 (5)	312 (2)
P(2)	18517 (4)	54496 (8)	20390 (6)	395 (2)
S(1)	40627 (4)	38023 (8)	16470 (6)	436 (2)
S(2)	34533 (4)	64070 (8)	18454 (6)	488 (2)
C(1)	4004 (2)	6165 (3)	4368 (2)	52 (1)
C(2)	3942 (1)	4840 (3)	4640 (2)	46 (1)
C(3)	4427 (2)	4123 (3)	4193 (2)	49 (1)
C(4)	4795 (1)	5015 (4)	3644 (2)	57 (1)
C(5)	4529 (2)	6266 (4)	3757 (2)	57 (1)
C(6)	4122 (2)	5502 (3)	1640 (2)	47 (1)
C(7)	4726 (2)	6145 (4)	1326 (2)	68 (1)
C(8)	2397 (1)	4021 (3)	1979 (2)	34 (1)
C(11)	3123 (1)	2118 (3)	3123 (2)	34 (1)
C(12)	3345 (1)	1556 (3)	4022 (2)	39 (1)
C(13)	3541 (1)	263 (3)	4053 (2)	47 (1)
C(14)	3509 (2)	−495 (3)	3198 (2)	51 (1)
C(15)	3280 (2)	42 (3)	2295 (2)	49 (1)
C(16)	3084 (1)	1342 (3)	2254 (2)	41 (1)
C(21)	2418 (1)	4123 (3)	4117 (2)	35 (1)
C(22)	2017 (1)	3135 (3)	4433 (2)	46 (1)
C(23)	1587 (2)	3368 (4)	5178 (2)	59 (1)
C(24)	1563 (2)	4569 (4)	5632 (3)	70 (1)
C(25)	1950 (2)	5573 (4)	5327 (3)	66 (1)
C(26)	2376 (1)	5358 (3)	4564 (2)	49 (1)
C(31)	1149 (1)	4731 (3)	2617 (2)	42 (1)
C(32)	927 (2)	3449 (4)	2488 (2)	58 (1)
C(33)	394 (2)	3016 (4)	2951 (3)	70 (1)
C(34)	53 (2)	3838 (4)	3545 (3)	70 (1)
C(35)	254 (2)	5100 (4)	3683 (3)	71 (1)
C(36)	800 (2)	5557 (3)	3229 (2)	58 (1)
C(41)	1574 (1)	5522 (3)	704 (2)	42 (1)
C(42)	2012 (2)	5632 (4)	−49 (2)	61 (1)
C(43)	1822 (2)	5778 (4)	−1048 (3)	75 (1)
C(44)	1194 (2)	5828 (4)	−1316 (3)	77 (1)
C(45)	752 (2)	5784 (5)	−585 (3)	96 (1)
C(46)	946 (2)	5628 (4)	424 (3)	78 (1)

[a] $U_{eq} = {}^1/_3 \sum_i \sum_j U_{ij} a_i{}^* a_j{}^* (a_i \cdot a_j)$.

(*m/e* (M^+)): 520 (calcd for $C_{31}H_{30}FeP_2$ 520.38). Mp: 113–116 °C. Anal. Found (calcd): C, 71.60 (71.55); H, 5.81 (5.81); P, 12.08 (11.90). ^{1}H NMR (δ, C_6D_6, 293 K, 200.06 MHz): 0.24 (3 H, t, J_{PH} = 8.8 Hz, FeMe); 3.50 and 4.20 (1 H each, dt, J_{HH} = 13.8 Hz, J_{PH} = 10.0 Hz, PCH_2P); 4.30 (5 H, s, C_5H_5); 7.08 and 7.50 (12 H and 8 H, m, C_6H_5). ^{13}C NMR (δ, C_6D_6, 293 K, 50.31 MHz): −16.2 (t, J_{PC} = 22.4 Hz, FeMe); 44.6 (t, J_{PC} = 16.5 Hz, PCH_2P); 77.0 (s, C_5H_5); 127.6–143.0 (m, C_6H_5). ^{31}P NMR (δ, C_6D_6, 293 K, 80.98 MHz): 50.0 (s).

Preparation of $C_5H_5Fe(dppm)Ph$ (2). The complex **2** was prepared in the same way as described for **1**, from $FeCl_2$ (0.39 g, 3.1 mmol), dppm (1.20 g, 3.1 mmol), 2.6 M PhMgBr (2.6 mL, 6.6 mmol), and cyclopentadiene (0.28 mL, 3.4 mmol) in THF (30 mL), as dark red crystals. Crystals suitable for a crystal structure determination were obtained from a diethyl ether/pentane (2:3) solution at −20 °C; yield 1.2 g, 71%. MS (*m/e* (M^+)): 582 (calcd for $C_{36}H_{32}FeP_2$ 582.45). Mp: 121–124 °C. Anal. Found (calcd): C, 74.31 (74.24); H, 5.69 (5.54); P, 10.78 (10.64). ^{1}H NMR (δ, C_6D_6, 293 K, 200.06 MHz): 3.27 and 3.87 (1 H each, dt, J_{HH} = 13.8 Hz, J_{PH} = 10.0 Hz); 4.43 (5 H, s, C_5H_5); 6.55–7.70 (25 H, m, C_6H_5). ^{13}C NMR (δ, C_6D_6, 293 K, 50.31 MHz): 41.3 (t, J_{PC} = 17 Hz, PCH_2P); 77.1 (s, C_5H_5); 120.0–150.0 (m, C_6H_5). ^{31}P NMR (δ, C_6D_6, 293 K, 80.98 MHz): 42.9 (s).

CS_2 Insertion Reactions $C_5H_5Fe(dppm)S_2CMe$ (3). A stirred solution of **1** (3.01 g, 5.8 mmol) in THF (40 mL) at 0 °C was treated with an excess of CS_2 (7.2 mL, 120.0 mmol). After 18 h at room temperature the reaction mixture was evaporated to dryness. The residue was dissolved in a minimum amount of CH_2Cl_2 and chromatographed on neutral alumina (81 g) with diethyl ether. Evaporation of the eluate gave **3**. Crystals suitable for the crystal structure determination of **3a** and **3b** were obtained by dissolving small portions of **3** in THF and CH_2Cl_2, respectively. Addition of the same volume of hexane and storage of the solutions at −20 °C yielded crystals of **3a** and **3b** (crystallization of **3b** from **3** was sometimes unsuccessful); yield of **3** 2.8 g, 81%. MS (*m/e* (M^+)): 596 (calcd for $C_{32}H_{30}FeP_2S_2$ 596.52). Mp: 125 °C dec (**3a**); 124 °C dec (**3b**). Anal. Found (calcd): C, 64.35 (64.43); H, 4.91 (5.07); S, 12.69 (12.73). ^{1}H NMR (δ, THF-d_8, 300 K, 400.13 MHz): 2.36 (3 H, d, J_{PH} = 2.9 Hz, Me); 2.63 (2 H, dd, J_{PH} = 8.0 Hz, J_{PH} = 2.8 Hz, PCH_2P); 4.06 (5 H, d, J_{PH} = 1.6 Hz, C_5H_5); 7.07, 7.30, and 7.75 (20 H, m, C_6H_5). ^{13}C NMR (δ, THF-d_8, 310 K, 100.61 MHz): 26.1 (t, J_{PC} = 26.5 Hz, J_{PC} = 33.5 Hz, PCH_2P); 41.1 (q, J_{PC} = 2.0 Hz, Me); 77.8 (d, C_5H_5); 128.00–142.00 (m, C_6H_5); 203.9 (s, CS_2). ^{31}P NMR (δ, THF-d_8, 310 K, 161.99 MHz): 69.9 (d, $J_{P_AP_B}$ = 47.5 Hz, Fe-P); −16.2 (d, $J_{P_AP_B}$ = 47.5 Hz, CH_2P). IR (ν(CS range), Nujol mull, cm^{-1}): 1132 (m), 837 (m). IR (ν(CS range), $CHCl_3$, cm^{-1}): 1136 (m), 838 (m).

$C_5H_5Fe(dppm)S_2CPh$ (4). The product was obtained similarly to **3**, from **2** (1.23 g, 2.1 mmol) and excess CS_2 (3.0 mL, 49.7 mmol) in THF (30 mL), as blue crystals; yield of **4** 1.2 g, 88%. MS (*m/e* (M^+)): 659 (calcd for $C_{37}H_{32}FeP_2S_2$ 658.59). Mp: 118–122 °C. Anal. Found (calcd): C, 67.51 (67.48); H, 4.96 (4.90); S, 9.79 (9.74). ^{1}H NMR (δ, $CDCl_3$, 293 K, 200.06 MHz); 2.47 (2 H, dd, J_{PH} = 6.2 Hz, J_{PH} = 1.4 Hz, PCH_2P); 4.13 (5 H, d, J_{PH} = 1.6 Hz, C_5H_5); 6.80–7.17, 7.20–8.05 (25 H, m, C_6H_5). ^{13}C NMR (δ, THF-d_8, 310 K, 100.61 MHz): 23.3 (t, J_{PC} = 21.6 Hz, J_{PC} = 33.8 Hz, PCH_2P); 77.6 (d, J_{PC} = 0.6 Hz, C_5H_5); 122.0–144.5 (m, C_6H_5), 218.3 (s, CS_2). ^{31}P NMR (δ, THF-d_8, 310 K, 100.61 MHz): 72.7 (d, $J_{P_AP_B}$ = 40.0 Hz), −17.1 (d, $J_{P_AP_B}$ = 40.0 Hz). IR (ν(CS range), Nujol mull, cm^{-1}): 1139 (w), 981 (s), 815 (w). IR (ν(CS range), $CHCl_3$, cm^{-1}): 1139 (vw), 987 (m), 814 (m).

Supplementary Material Available: Anisotropic thermal parameters, calculated hydrogen atom coordinates, and bond lengths and angles for **2**, **3a**, and **3b** (Tables A–I) and results of a powder X-ray diffraction study (Figure A) (14 pages); observed and calculated structure factors for **2**, **3a**, and **3b** (Tables J–L) (69 pages). Ordering information is given on any current masthead page.