form by apparent alkyl migration to CO. Such a transformation does not readily occur for mononuclear $(CO)_5ReR$ complexes[14] but in this study the acyl derivative 15 readily forms upon either thermolysis or treatment of the ethyl complex 6 with PPh_3 (eq 6 and 7). We do not presently understand the basis for this effect, whether it is a consequence of the ligand environment of Re or whether it is facilitated by the presence of the tungsten center, but that will be the basis for a future study in this series.

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Registry No. 1, 92763-15-0; 2, 96665-99-5; 3, 96666-00-1; 4, 96666-01-2; 5, 96666-02-3; 6, 96666-03-4; 7, 96666-04-5; 8, 96666-05-6; 9, 96666-06-7; **10a**, 96666-07-8; **10b**, 96744-22-8; **11a**, 96666-08-9; **11b**, 96744-23-9; **12a**, 96688-69-6; **12b**, 96744-98-8; **13a**, 96666-09-0; **13b**, 96744-24-0; 14, 96688-70-9; 15, 96666-10-3; diphenylphosphine, 829-85-6; benzoyl bromide, 618-32-6.

Supplementary Material Available: Tables of structure factors, complete bond lengths and angles, thermal parameters, and calculated hydrogen atom positions for 5 (26 pages). Ordering information is given on any current masthead page.

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Ferrocenyl Sulfides. Preparation and Reactivity as Bidentate Chelating Ligands

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A series of ferrocenyl sulfide derivatives, $Fe(C_5H_4SR)_2$, where R = Me, *i*-Pr, I-Bu, Ph, and $PhCH_2$, have been prepared by lithiation of ferrocene followed by reaction with the appropriate disulfide. The complexes were characterized by ^1H and ^{13}C NMR, mass spectra, and infrared spectroscopy. The ferrocenyl sulfide derivatives readily chelate palladium and platinum halides to form [3]ferrocenophane complexes $Fe(C_5H_4SR)_2MX_2$ (R = Me, *i*-Pr, *i*-Bu, Ph, $PhCH_2$; M = Pd, Pt; X = Cl, Br). ^1H, ^{13}C, and ^{195}Pt NMR spectra were obtained where possible, and infrared, ultraviolet–visible and cyclic voltammetry data of the complexes are presented. The structure of $Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$ (**6**) was determined by single-crystal X-ray diffraction measurements. Compound **6** crystallizes in the orthorhombic space group *Pbca* with lattice parameters $a = 22.168\ (11)$ Å, $b = 11.855\ (7)$ Å, $c = 16.131\ (6)$ Å, $M_r = 539.69$, $\rho(\text{calcd}) = 1.691\ \text{cm}^{-3}$, and $Z = 8$. Least-squares refinement gave a final *R* value of 0.046 for 3689 observed reflections. The dihedral angle between the $Fe\text{–}S_1\text{–}S_2$ plane and the $S_1\text{–}Pd\text{–}S_2$ plane is 104.6°. The molecule **6** is fluxional in solution where the palladium atom flips from one side of the $Fe\text{–}S_1\text{–}S_2$ plane to the other.

Introduction

Symmetrically 1,1′-disubstituted ferrocene complexes $Fe(C_5H_4R)$, where R is a potential donor such as phosphine or arsine, have generated much interest as rigid chelating ligands.[1] In particular Ni and Pd complexes of $Fe(C_5H_4PPh_2)_2$ exhibit high catalytic activity for selective cross-coupling reactions[2] whereas the analogous rhodium complexes of $Fe(C_5H_4PR_2)_2$, R = aryl, are reported to be highly selective hydroformylation catalysts.[3] In addition, chiral (ferrocenylphosphine)rhodium complexes have been shown to be highly selective catalysts in asymmetric hydrogenation.[4] Recently Seyferth[5] reported that ferrocenylphosphine oligomers are effective ligands in the cobalt catalyzed-hydroformylation of 1-hexene.

In order to extend the utility of ferrocene as a chelating ligand, we investigated the preparation and reactivity of ferrocenyl sulfide complexes. (Methylthio)ferrocene has previously been prepared from either ferrocenesulfonic acid[6] or thiocyanatoferrocene,[7] and ferrocenyl methyl sulfides have been obtained from ferrocene and mercaptans.[8]

Elschenbroich[9] recently prepared 1,1′-bis((methylthio)benzene)chromium by lithiation of bis(benzene)chromium followed by subsequent reaction with methyl disulfide. A similar approach was used in the synthesis

Scheme I

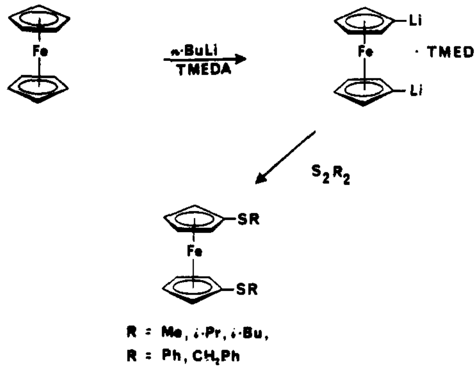

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Table I. ^{1}H NMR Data (δ) for $Fe(C_5H_4SR)_2$ Where R = Me, *i*-Pr, *i*-Bu, Ph, and CH_2Ph

compd	Ph	$H_{2,5}$	$H_{3,4}$	α-CH_2	CH	CH_3
$Fe(C_5H_4SMe)_2$ (1)		4.29 t	4.21 t			2.30 s
$Fe(C_5H_4SCHMe_2)_2$ (2)		4.31 t	4.24 t		2.86 m	1.16 d
					6.7 Hz	6.7 Hz
$Fe(C_5H_4SCH_2CHMe_2)_2$ (3)		4.28 t	4.20 t	2.50 d	1.72 m	0.97 d
				6.9 Hz	6.9 Hz	6.9 Hz
$Fe(C_5H_4SPh)_2$ (4)	7.08 m	4.49 t	4.44 t			
$Fe(C_5H_4SCH_2Ph)_2$ (5)	7.19 m	4.12 t	4.10 t	3.72 s		
	7.11 m					

Table II. ^{13}C NMR Data for $Fe(C_5H_4SR)_2$ Where R = Me, *i*-Pr, *i*-Bu, Ph, and CH_2Ph

compd	Ph	C_1	$C_{3,4}$	$C_{2,5}$	CH_2	CH	CH_3
$Fe(C_5H_4SMe)_2$ (1)		85.21 s	71.72 d	69.59 d			19.35 q
			178 Hz	177 Hz			139 Hz
$Fe(C_5H_4SCHMe_2)_2$ (2)		79.14 s	76.20 d	70.96 d		39.64 d	23.41 q
			178 Hz	176 Hz		142 Hz	126 Hz
$Fe(C_5H_4SCH_2CHMe_2)_2$ (3)		82.76 s	74.11 d	70.31 d	46.40 t	28.51 d	21.68 q
			173 Hz	177 Hz	138 Hz	129 Hz	126 Hz
$Fe(C_5H_4SPh)_2$ (4)	140.27 s	77.66 s	76.34 d	71.91 d			
	128.68 d	J = 161 Hz	181 Hz	177 Hz			
	126.38 d	J = 161 Hz					
	125.17 d	J = 161 Hz					
$Fe(C_5H_4SCH_2Ph)_2$ (5)	138.80 s	81.16 s	74.68 d	70.57 d	42.12 t		
	128.95 d	J = 161 Hz	178 Hz	177 Hz	142 Hz		
	128.30 d	J = 161 Hz					
	126.85 d	J = 161 Hz					

of 1,1′-disubstituted ferrocenyl sulfides.

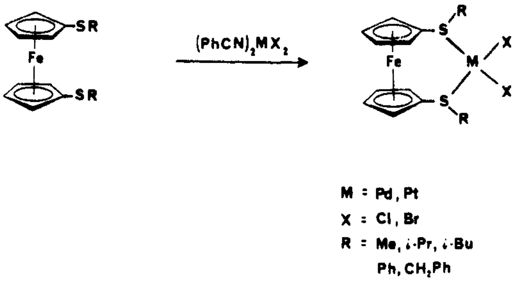
Results and Discussion

Ferrocenyl sulfide complexes of the type $Fe(C_5H_4SR)_4$, where R = Me, *i*-Pr, *i*-Bu, Ph, and CH_2Ph, **1**–**5**, have been prepared in a general, high-yield, one-step synthesis as shown in Scheme I. 1,1′-Dilithioferrocene is prepared in over 90% yield by reaction of stoichiometric quantities of *n*-butyllithium and tetramethylethylenediamine (TMEDA) with ferrocene. All five ferrocenyl sulfide derivatives are soluble in common organic solvents and are air stable in solution and the solid state.

The disulfide *tert*-butyl disulfide failed to react with 1,1′-dilithioferrocene under the reaction conditions employed and may be the result of the steric crowding of the sulfur–sulfur bond by the bulky *tert*-butyl groups which prevent nucleophilic cleavage of the sulfur–bond bond.

The ^{1}H NMR data for the ferrocenyl sulfide complexes **1**–**5**, presented in Table I, are typical of 1,1′-disubstituted ferrocene systems.[16–18] Two slightly deshielded "triplets" are observed for the cyclopentadienyl ring protons. The low-field "triplet" is assigned to the protons in the 2- and 5-positions on the ring ($H_{2,5}$) whereas the high-field "triplet" is assigned to the ring protons in the 3- and 4-positions ($H_{3,4}$).

Scheme II



The ^{13}C NMR data for the ferrocenyl sulfide complexes **1**–**5** are presented in Table II, and tentative assignments have been made. The low-field doublet in the cyclopentadienyl ring carbon region has been assigned to the nuclei at the $C_{3,4}$ positions and the high-field doublet to the nuclei at the $C_{2,5}$ positions. These assignments compare favorably with those in methoxyferrocene where the signals at 61.5 and 54.7 ppm are assigned to the $C_{3,4}$ and $C_{2,5}$ nuclei, respectively, on the basis of deuterium labeling studies.[19]

Reaction of a benzene solution of the ferrocenyl sulfide compounds **1**–**5** with bis(benzonitrile) adducts of palladium and platinum chloride and bromide salts gave rise to the monosubstituted complexes **6**–**25** (see Scheme II).

The isobutyl- and isopropylmetal complexes are soluble in methylene chloride and chloroform whereas the benzyl derivatives are only slightly soluble. The methyl and phenyl analogues are sparingly soluble in polar solvents such as acetonitrile, nitromethane, and dimethylformamide. The platinum complexes are more soluble than the palladium species, and the phenyl derivative as $Fe(C_5H_4SPh)_2PdCl_2$ is very sparingly soluble and tends to form a suspension.

With the exception of the methylmetal complexes **14**–**17**, the bimetallic derivatives were sufficiently soluble to obtain

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Table III. ^{1}H NMR and ^{13}C NMR Data for $Fe(C_5H_4S\text{-}i\text{-}Bu)_2$ and $Fe(C_5H_4S\text{-}i\text{-}Bu)_2MX_2$ Where M = Pd and Pt and X = Cl and Br

^{1}H NMR Data

complex	$H_{2,5}$	$H_{3,4}$	CH_2	CH	CH_3	T, °C
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2$ (3)	4.28 t	4.20 t	2.50 d 6.9 Hz	1.72 m 6.9 Hz	0.97 d 6.9 Hz	24
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$ (6)	5.28 br	4.42 t	2.98 d 6.8 Hz	1.80 m 6.8 Hz	1.01 d 6.8 Hz	73
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdBr_2$ (7)	5.25 br	4.40 br	3.06 br	1.81 m 6.7 Hz	1.01 d 6.7 Hz	53
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2PtCl_2$ (8)	5.14 t	4.43 t	3.08 br	1.92 m 6.5 Hz	1.01 d 6.5 Hz	101
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2PtBr_2$ (9)	5.15 br	4.46 br	2.94 br	1.89 br	1.04 br d	75

^{13}C NMR Data

complex	C_1	$C_{3,4}$	$C_{2,5}$	CH_2	CH	CH_3	T, °C
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2$ (3)	82.76 s	74.11 d 173 Hz	70.31 d 178 Hz	46.40 t 138 Hz	28.51 d 129 Hz	21.68 q 126 Hz	24
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$ (6)	79.32 s	76.23 d 184 Hz	71.72 d 178 Hz	49.50 t 146 Hz	26.42 d 134 Hz	21.38 q 127 Hz	38
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdBr_2$ (7)	79.48 s	76.36 d 176 Hz	71.85 d 177 Hz	52.85 t 146 Hz	26.89 d 129 Hz	21.39 q 126 Hz	42
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2PtCl_2$ (8)	80.22	75.93	72.08	48.21	26.55	21.85	40
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2PtBr_2$ (9)	80.09	75.32	71.35	49.21	26.42	21.54	45

^{1}H NMR. ^{1}H NMR data for the isobutylmetal complexes **6**–**9** is given in Table III.

The ^{1}H and ^{13}C NMR spectra of the bimetallic complexes exhibit a marked temperature dependence. Two independent dynamic processes, namely, sulfur inversion and bridge reversal, appear to be involved and will be discussed elsewhere in detail.[20] In the bridge reversal process the metal atom (Pd or Pt) flips from one side of the plane containing the iron and two sulfur atoms to the other. Only the high-temperature or "fast-exchange limit" spectra will be considered here.

The ferrocenyl sulfide ligand undergoes a significant change in the ^{1}H NMR spectra upon complexing to platinum or palladium halides. The low-field triplet, which has been assigned to the $H_{2,5}$ ring protons, shifts downfield by almost 1 ppm in the metal complex compared to the free ligand. The deshielding was originally thought to be due to a severe tilting of the cyclopentadienyl rings where the α-protons were farhter from the shielding iron atom.[21] The crystal structure of $Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$ (**6**, see below), however indicates that the cyclopentadienyl rings are tilted 2° from the plane. The large downfield shift of the α-protons may be due to the magnetic anisotropy or the inductive effect of the metal halide. Similarly, the alkyl protons of the ferrocene ligand also shift downfield upon coordination to the metal complex.

^{13}C NMR data were obtained only for the isobutyl complexes **6**–**9**, and the results are presented in Table III. When the isobutyl ligand complexes to the metal halide, the C_1 resonance moves upfield by roughly 3 ppm whereas the $C_{3,4}$ and $C_{2,5}$ resonances move downfield by 1–2 ppm. This shift is consistent with the inductive effect of the electron-withdrawing metal halide as electron density is "drawn" toward the C_1 atom (upfield shift) from the $C_{2,5}$ and $C_{3,4}$ nuclei (downfield shift).[22] The signal due to the methylene carbon moves downfield by 3–6 ppm while the resonance due to the methine carbon shifts upfield by at least 2 ppm.

Table IV. ^{195}Pt NMR Data for $Fe(C_5H_4SR)PtX_2$ Where R = i-Bu, i-Pr, Ph, and CH_2Ph and X = Cl and Br

compd	Cl	Br
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2PtX_2$	−3285 −3353	−3662 −3759
$Fe(C_5H_4S\text{-}i\text{-}Pr)_2PtX_2$	−3253	−3633
$Fe(C_5H_4SPh)_2PtX_2$	−3246	−3658
$Fe(C_5H_4SCH_2Ph)_2PtX_2$	−3244	−3622
$Fe(C_5H_4PPh_2)_2PtCl_2$	−4374 t	

^{195}Pt NMR data was obtained for the ferrocenyl sulfide complexes $Fe(C_5H_4SR)_2PtX_2$ (R = i-Bu, i-Pr, Ph, CH_2Ph; X = Cl, Br). As shown in Table IV, the ^{195}Pt chemical shifts of the chloride complexes are found at 3200 ppm and the bromide analogues are found 400 ppm further upfield. The shifts are consistent with general trends where bromide complexes are found upfield from chloride analogues.[23] The complex $Fe(C_5H_4PPh_2)_2PtCl_2$ has a signal, a triplet with J_{Pt-P} = 3374 Hz, about 1100 ppm upfield from the corresponding ferrocenyl sulfide complexes, consistent with previously reported data[24] where the phosphine compound $(PMe_3)_2PtCl_2$ is found about 900 ppm upfield from the sulfide complex $(SMe_2)_2PtCl_2$. This difference suggests that sulfide ligands are weaker σ donors than the phosphine analogues.

Low-temperature ^{195}Pt NMR data for $Fe(C_5H_4S\text{-}i\text{-}Bu)_2PtCl_2$ contains two separate signals of different intensity and may be due to the diastereoisomers generated by sulfur inversion. The sulfur inversion process will be discussed elsewhere.[20]

The infrared spectra of the ferrocenyl sulfide ligands are typical of ferrocene derivatives.[25] The infrared spectra of the ferrocenyl sulfide metal complexes are similar to the uncomplexed ligand except that the absorption bands at 820 and 500 cm^{-1} undergo additional splitting in the metal–sulfur complexes.

The most striking change occurs in the low-frequency region where metal–ligand vibrations are prevalent. Table V presents IR absorptions for the metal chloride and

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Table V. Infrared Data (cm^{-1}) for $Fe(C_5H_4SR)_2MX_2$ Where R = Me, *i*-Pr, *i*-Bu, Ph, and CH_2Ph, M = Pd and Pt, and X = Cl and Br in the Region 400–200 cm^{-1}

	Pd		Pt		
	Cl	Br	Cl	Br	
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2MX_2$	370 sh		372 w	372 w	(M–S)
	365 w	365 w		364 w	
	307 s		323 s		(M–X)
	290 sh	222 s	310 m		
$Fe(C_5H_4SPh)_2MX_2$	360 w	360 w	372 w	368 w	(M–S)
	328 s		330 s		(M–X)
	320 sh	210 s	318 s	220 m	
$Fe(C_5H_4SMe)_2MX_2$	355 w				(M–S)
	340 w	343 w	345 w	340 w	
	310 s		323 s		(M–X)
	290 sh	205 m	305 s	208 s	
$Fe(C_5H_4SCH_2Ph)_2MX_2$	358 m	353 m	360 m	358 m	(M–S)
	335 w	345 sh	350 m	348 m	
	315 s		332 s		(M–X)
	300 s	230 s	312 s	215 s	
$Fe(C_5H_4S\text{-}i\text{-}Pr)_2MX_2$	380 w	380 w	383 w	389 w	(M–S)
	360 w	360 w	365 w	370 w	
	320 s		328 s		(M–X)
	305 s	225 s	315 s	220 s	

Table VI. Cyclic Voltammetry Data for $Fe(C_5H_4SR)_2$ and $Fe(C_5H_4SR)_2MCl_2$ Where R = *i*-Bu, Ph, and Me and M = Pd and Pt

compd	$E_{1/2}$, ^{9}V	
$Fe(C_5H_5)_2$	0.34^a	
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2$ (3)	0.33	
	0.37^b	
$Fe(C_5H_4SMe)_2$ (1)	0.35	
	0.35^b	
$Fe(C_5H_4SPh)_2$ (4)	0.52^c	
	0.56^b	
$Fe(C_5H_4PPh_2)_2$	0.52	
	0.53^c	
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$ (6)	0.94	−0.79
	0.86^c	−0.89^c
$Fe(C_5H_4SMe)_2PdCl_2$ (14)	0.86	−0.66
$Fe(C_5H_4SPh)_2PdCl_2$ (22)	0.85	−1.45
$Fe(C_5H_4PPh_2)_2PdCl_2$	0.93	−1.20
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2PtCl_2$ (8)	0.94	
	0.94^c	−1.64 c
$Fe(C_5H_4SMe)_2PtCl_2$ (16)	0.94	
	0.93^c	−1.50^c
$Fe(C_5H_4SPh)_2PtCl_2$ (24)	1.03	
	1.06^c	−1.38^c
$Fe(C_5H_4PPh_2)_2PtCl_2$ (25)	0.92	
	0.93^c	

[a] In CH_2Cl_2 at Pt electrode vs. SCE. [b] In DMF at Pt electrode vs. SCE. [c] In CH_2Cl_2 at glassy carbon electrode vs. SCE.

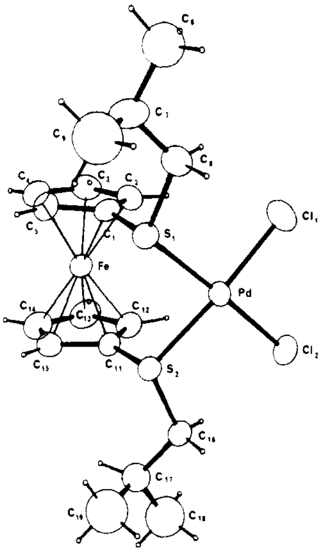

Figure 1. An ORTEP drawing of $Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$.

bromide complexes in the region 400–200 cm^{-1}. The metal–sulfur and metal–halide stretching frequencies have been tentatively assigned by comparison of the chloride and bromide analogues. The proposed assignments are in close agreement with those for the chelated thioether complex $(PhSC_3H_6SPh)MX_2$ (M = Pd, Pt; X = Cl, Br)[26] and other values in the literature.[27,28]

The ferrocenyl sulfide ligands exhibit ultraviolet and visible spectral data typical of ferrocene derivatives. In the ferrocenyl sulfide metal complexes the absorption due to the d–d transition is slightly blue shifted to 400–420 nm compared with ferrocene.[29]

The ferrocenyl sulfide palladium complexes exhibit an intense, well-defined maximum around 260 nm whereas the platinum analogues have an inflection point in the region. This band could be associated with a metal-to-ligand charge-transfer band whereas the strong absorption at 210 nm is probably a ligand-to-metal charge-transfer transition.

The electrochemistry of the complexes $Fe(C_5H_4SR)_2$ and $Fe(C_5H_4SR)_2MCl_2$, where R = *i*-Bu, Ph, and Me and M = Pd and Pt, has been examined by cyclic voltammetry. Well-defined, one-electron reversible redox waves were observed for the oxidation of ferrocene complexes in the ferrocenyl sulfide derivatives 1, 3, and 4 and the platinum complexes in DMF and CH_2Cl_2 solutions, respectively. The palladium analogues, which are sparingly soluble in these solvents (especially the phenyl derivative), gave poorly defined redox waves with large peak separations.[30]

Examination of the electrochemical data given in Table VI indicates that $E_{1/2}$ for the ferrocene ligands becomes increasingly positive in the order S–*i*-Bu < S–Me < S–Ph < P–Ph_2. This increase is consistent with ferrocene being stabilized by electron-withdrawing substituents. Upon complexation to palladium or platinum, $E_{1/2}$ for the ferrocenyl group increases by +0.40 to +0.59 V. This increase could be attributed to a through-space electrostatic interaction with the positive charge on Pd or Pt or could be viewed as Pd or Pt withdrawing electron density from the ferrocenyl group through the sulfide bridges.

In the ferrocenylplatinum and -palladium complexes an additional irreversible wave was observed at −0.6 to −1.64 V and has been attributed to $Pd^{3/2+}$ or $Pt^{3/2+}$. $E_{1/2}$ for platinum is more negative than the corresponding value for palladium and is consistent with polarographic and voltammetric data obtained for palladium and platinum bis(1,2-dithiolene) complexes.[32] The large negative $E_{1/2}$ for palladium and platinum suggest that the ferrocenyl group is a strong electron donor.

The complex $Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$ (6) was further characterized by a single-crystal X-ray diffraction study.

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Table VII. Positional Parameters and Esd's for $Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$

atom	*x*	*y*	*z*
Pd(1)	0.02486 (2)	0.05361 (3)	0.09452 (2)
Fe(1)	0.03407 (3)	−0.00389 (6)	0.32654 (4)
Cl(1)	−0.04093 (6)	0.1867 (1)	0.04318 (8)
Cl(2)	0.10334 (7)	0.1636 (1)	0.0476 (1)
S(1)	−0.05094 (6)	−0.0531 (1)	0.15645 (8)
S(2)	0.08816 (6)	−0.0853 (1)	0.14708 (8)
C(1)	−0.0432 (2)	−0.0140 (4)	0.2609 (3)
C(2)	−0.0453 (2)	−0.0915 (5)	0.3294 (3)
C(3)	−0.0390 (3)	−0.0296 (6)	0.4017 (4)
C(4)	−0.0340 (3)	0.0855 (5)	0.3816 (4)
C(5)	−0.0366 (2)	0.0962 (5)	0.2944 (3)
C(6)	−0.1249 (2)	0.0076 (5)	0.1354 (4)
C(7)	−0.1754 (3)	−0.0400 (5)	0.1873 (4)
C(8)	−0.2299 (4)	0.0337 (7)	0.1748 (6)
C(9)	−0.1887 (4)	−0.1590 (7)	0.1643 (5)
C(11)	0.1028 (2)	−0.0401 (4)	0.2496 (3)
C(12)	0.1088 (2)	0.0711 (5)	0.2793 (4)
C(13)	0.1138 (3)	0.0653 (6)	0.3662 (4)
C(14)	0.1102 (3)	−0.0486 (6)	0.3895 (4)
C(15)	0.1044 (3)	−0.1151 (5)	0.3182 (3)
C(16)	0.1625 (3)	−0.0766 (6)	0.0997 (4)
C(17)	0.2065 (3)	−0.1648 (5)	0.1278 (5)
C(18)	0.2681 (3)	−0.1361 (6)	0.0899 (5)
C(19)	0.1877 (4)	−0.2819 (7)	0.1013 (6)
H(2)	−0.048 (2)	−0.165 (4)	0.327 (3)
H(3)	−0.036 (2)	−0.059 (4)	0.452 (3)
H(4)	−0.028 (2)	0.148 (4)	0.417 (3)
H(5)	−0.030 (2)	0.163 (4)	0.259 (3)
H(6A)	−0.130 (3)	−0.019 (5)	0.077 (4)
H(6B)	−0.122 (2)	0.084 (4)	0.140 (3)
H(7)	−0.170 (2)	−0.049 (4)	0.253 (4)
H(12)	0.110 (2)	0.139 (4)	0.248 (3)
H(13)	0.115 (2)	0.123 (4)	0.400 (3)
H(14)	0.111 (2)	−0.064 (4)	0.434 (3)
H(15)	0.101 (2)	−0.196 (4)	0.314 (3)
H(16A)	0.174 (3)	−0.000 (5)	0.104 (4)
H(16B)	0.153 (3)	−0.095 (4)	0.039 (4)
H(17)	0.201 (3)	−0.155 (5)	0.196 (4)
H(8A)	−0.2416	0.0342	0.1156
H(8B)	−0.2203	0.1119	0.1939
H(8C)	−0.2642	0.0032	0.2093
H(9A)	−0.1527	−0.2060	0.1732
H(9B)	−0.2017	−0.1618	0.1051
H(9C)	−0.2229	−0.1868	0.2003
H(18A)	0.2813	−0.0606	0.1092
H(18B)	0.2647	−0.1364	0.0278
H(18C)	0.2984	−0.1945	0.1070
H(19A)	0.1844	−0.2858	0.0410
H(19B)	0.1475	−0.2995	0.1280
H(19C)	0.2182	−0.3374	0.1225

Table VIII. Selected Bond Distances (Å) with Esd's for $Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$

Cl(1)–Pd	2.303 (2)	C(15)–Fe	2.045 (6)
Cl(2)–Pd	2.302 (2)	C(1)–S(1)	1.756 (5)
S(1)–Pd	2.329 (1)	C(6)–S(1)	1.822 (6)
S(2)–Pd	2.324 (2)	C(11)–S(2)	1.768 (5)
C(1)–Fe	2.018 (5)	C(16)–S(2)	1.818 (6)
C(2)–Fe	2.045 (6)	C(2)–C(1)	1.438 (7)
C(3)–Fe	2.046 (6)	C(5)–C(1)	1.421 (7)
C(4)–Fe	2.046 (6)	C(3)–C(2)	1.385 (8)
C(5)–Fe	2.033 (6)	C(4)–C(3)	1.406 (9)
C(11)–Fe	2.011 (5)	C(5)–C(4)	1.414 (8)
C(12)–Fe	2.028 (6)	C(7)–C(6)	1.507 (8)
C(13)–Fe	2.051 (6)	C(8)–C(7)	1.505 (9)
C(14)–Fe	2.039 (6)	C(9)–C(7)	1.488 (9)
C(12)–C(11)	1.409 (7)	C(15)–C(14)	1.401 (8)
C(15)–C(11)	1.419 (7)	C(17)–C(16)	1.501 (8)
C(13)–C(12)	1.409 (8)	C(18)–C(17)	1.535 (9)
C(14)–C(13)	1.403 (9)	C(19)–C(17)	1.511 (10)

Table IX. Selected Bond Angles (deg) with Esd's for $Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$

Cl(1)–Pd–Cl(2)	88.41 (7)	S(1)–C(1)–C(5)	128.1 (3)
Cl(1)–Pd–S(1)	94.00 (7)	C(2)–C(1)–C(5)	107.4 (5)
Cl(1)–Pd–S(2)	177.82 (8)	C(1)–C(2)–C(3)	107.8 (5)
Cl(2)–Pd–S(1)	173.79 (8)	C(2)–C(3)–C(4)	109.1 (5)
Cl(2)–Pd–S(2)	95.73 (7)	C(3)–C(4)–C(5)	108.2 (5)
S(1)–Pd–S(2)	83.92 (6)	C(1)–C(5)–C(4)	107.5 (5)
C(1)–Fe–C(2)	41.5 (2)	S(1)–C(6)–C(7)	114.6 (3)
C(1)–Fe–C(3)	68.3 (2)	C(6)–C(7)–C(8)	107.7 (5)
C(1)–Fe–C(4)	68.5 (2)	C(6)–C(7)–C(9)	111.3 (6)
C(1)–Fe–C(5)	41.1 (2)	C(8)–C(7)–C(9)	110.9 (7)
C(1)–Fe–C(11)	107.8 (3)	Fe–C(11)–S(2)	120.2 (2)
C(1)–Fe–C(12)	121.5 (3)	Fe–C(11)–C(12)	70.2 (3)
C(1)–Fe–C(13)	156.9 (3)	Fe–C(11)–C(15)	70.8 (3)
C(1)–Fe–C(14)	161.5 (3)	S(2)–C(11)–C(12)	128.2 (3)
C(1)–Fe–C(15)	125.0 (3)	S(2)–C(11)–C(15)	122.9 (3)
Pd–S(1)–C(1)	101.4 (2)	C(12)–C(11)–C(15)	108.6 (5)
Pd–S(1)–C(6)	110.8 (2)	C(11)–C(12)–C(13)	107.4 (5)
C(1)–S(1)–C(6)	99.4 (3)	C(12)–C(13)–C(14)	108.0 (5)
Pd–S(2)–C(11)	103.7 (2)	C(13)–C(14)–C(15)	109.1 (5)
Pd–S(2)–C(16)	110.7 (2)	C(11)–C(15)–C(14)	106.9 (5)
C(11)–S(2)–C(16)	102.1 (3)	S(2)–C(16)–C(17)	115.0 (3)
Fe–C(1)–S(1)	127.0 (2)	C(16)–C(17)–C(18)	107.7 (5)
Fe–C(1)–C(2)	70.3 (3)	C(16)–C(17)–C(19)	112.1 (6)
Fe–C(1)–C(5)	70.0 (3)	C(18)–C(17)–C(19)	109.6 (6)
S(1)–C(1)–C(2)	124.5 (3)		

An ORTEP drawing of the structure is shown in Figure 1. The positional parameters are given in Table VII. In complex **6** the palladium atom is in a square-planar environment with two cis chlorine and two sulfur atoms.

Selected bond distances and bond angles for **6**, presented in Tables VIII and IX, respectively, are typical for ferrocene derivatives. The iron–carbon distances range from 2.011 (5) to 2.051 (6) Å with an average value of 2.036 (6) Å that compare favorably with those of ferrocene.[33] The carbon–carbon distances in the cyclopentadienyl ring vary from 1.385 (8) to 1.438 (7) Å, average 1.410 (5) Å, and the C–C–C bond angles within the two rings vary from 106.8 (5) to 109.1 (5)°, with an average angle of 108.0°.

The Pd–S bond lengths are 2.329 (1) and 2.334 (2) Å, comparable to the sum of the covalent radii (2.32 Å),[34] and suggest that there is little or no π-bonding in the Pd–S bond. The Pd–Cl bond shows no apparent trans bond lengthening indicating that the thioether ligand has a negligible trans influence.[35] The Pd–Cl bond distances have an average value of 2.303 (2) Å, almost equal to the sum of the Pauling covalent radii, 2.32 Å.[34]

Seyferth[36] recently reported a crystal structure of $Fe(C_5H_4S)_2Pd(PPh_3)_2$ and proposed the presence of a weak dative Fe→Pd bond on the basis of a Fe–Pd distance of 2.878 1 Å. In **6** the distance between the iron and palladium atom is 3.810 (2) Å and suggests that there is no direct metal–metal interaction.

In complex **6** the two cyclopentadienyl rings are eclipsed and are slightly tilted with respect to each other, the dihedral angle being 1.9°. The planes containing the cyclopentadienyl rings are almost orthogonal to the plane containing the palladium, sulfur, and chlorine atoms.

Crystal structures of similar [3]ferrocenophanes, such as 1,2,3-trithia[3]ferrocenophane, **26**,[37] 1,3-dithia-2-selena[3]ferrocenophane, **27**,[38] diiodocarbonyl(1,1′-bis(dimethylarsino)ferrocene)nickel(II), **28**,[39] (1,1′-bis(*tert*-bu-

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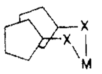
Table X. Dihedral Angle and Bridgehead Angle (deg) of Selected [3]Ferrocenophanes and [3]Ferrocenophanes

compd	X	M	dihedral angle[a]	bridgehead[b] angle
$Fe(C_5H_4S)_2Se$ (**26**)	S	Se	112.2	100.5
$Fe(C_5H_4S)_2S$ (**27**)	S	S	110.9	103.9
$Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$ (**6**)	S	Pd	104.6	83.9
$Fe(C_5H_4PPh_2)_2PdCl_2$ (**30**)	P	Pd	160.3	99.1
$Fe(C_5H_4AsMe_2)_2Ni(CO)I_2$ (**28**)	As	Ni	133.4	93.5

[a] Dihedral angle obtained from least-squares planes calculation. Dihedral angle refers to angle between FeX_2 plane and MX_2 plane.



The dihedral angle of the fourth and fifth compounds have been recalculated to give them the same sense as the first three. [b] Bridgehead angle refers to X–M–X angle.

tylphosphino)ferrocene)(norbornadiene)rhodium(I) perchlorate, **29**,[40] and (1,1′-bis(diphenylphosphino)ferrocene)palladium dichloride, **30**,[41] have been determined. In compound **28**, the ferrocenyl arsine ligand chelates to the nickel atom with a stepped conformation such that the Ni, Fe, and two As atoms are not coplanar. A similar conformation is evident in the structure of **6** where the dihedral angle between the plane containing the iron and two sulfur atoms and the plane containing the palladium, and two sulfur atoms is 104.6°. The dihedral angles of selected [3]ferrocenophanes are given in Table X. It is interesting to note that the bridgehead angle in compound **6** is significantly smaller than in Kumada's ferrocenylphosphine analogue **30**. Kumada[41] has attributed the high selectivity of $Fe(C_5H_4PPh_2)_2PdCl_2$ as a catalyst for the cross-coupling at Grignard reagents with organic halides to the large P–Pd–P angle.

Experimental Section

Air-sensitive reagents were manipulated in a prepurified argon or nitrogen atmosphere. Hexane was freshly distilled from calcium hydride. 1,1′-Bis(diphenylphosphino)ferrocene (fdpp) was prepared according to Davison's procedure,[10] and (fdpp)$PdCl_2$ was prepared following Kumada's procedure.[11] (Fdpp)$PtCl_2$ was similarly prepared. Bis(benzonitrile) complexes, $(PhCN)_2MX_2$, where M = Pd and Pt and X = Cl and Br and were prepared according to published procedures.[12]

IR spectra were obtained by use of a Perkin-Elmer 457 grating spectrophotometer or a Perkin-Elmer 239B spectrophotometer by using Nujol mulls between CsBr plates. Ultraviolet and visible spectra (UV-vis) were recorded by use of a Cary 17 spectrophotometer and acetonitrile solutions. Mass spectra (MS) were obtained by means of a Finnigan 4000 instrument with an Incos data system at 70 eV. Electrochemical measurements were made with a PAR 174 polarograph, coupled to a Hewlett-Packard Model 7045A fast X-Y recorder, by cyclic voltammetry techniques. All measurements were made in either DMF or CH_2Cl_2 solutions with 0.1 M $[n\text{-}Bu_4N][ClO_4]$ as a supporting electrolyte. A platinum "flag" electrode or a glass carbon electrode was used as the working electrode, and values were recorded relative to a standard calomel reference electrode (SCE). Sweep rates were varied from 100 mV/s to 200 mV/s over a potential range of +2.0 to −1.5 V.

All melting points were determined by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc. Knoxville, Tenn.

Proton NMR spectra were obtained by use of a Bruker WM-250 spectrometer at 250 MHz in chloroform-d_1 solutions with chemical shifts reported in parts per million downfield from a tetramethylsilane internal standard. Carbon-13 NMR (broad-o and proton decoupled and gated decoupled) were obtained by use of a Bruker WM-250 spectrometer at 62.9 MHz. Carbon-13 NMR spectra were recorded in methylene chloride with deuterium oxide as an external lock and chemical shifts, referenced to methylene chloride, are uncorrected for volume susceptibilities. Platinum-195 NMR spectra were recorded by use of a Bruker WH-180 spectrometer at 38.7 MHz in chloroform-d_1 solutions, and Na_2PtCl_6 was used as the reference.

A single crystal (approximately 0.15 × 0.30 × 0.30 mm) of (1,1′-bis(isobutylthio)ferrocene)palladium dichloride, **6**, was prepared for crystallographic studies by slow evaporation of the mixed-solvent system methylene chlorode/hexane at 25 °C. It crystallizes in the orthorhombic space group *Pbca* with eight molecules per unit cell. Crystal data are as follows: $a = 22.168$ (11) Å, $b = 11.855$ (7) Å, $c = 16.131$ (6) Å; $M_r = 539.69$; ρ(calcd) = 1.691 g cm^{-3}. Lattice dimensions were determined by using a Picker FACS-I diffractometer and Mo Kα_1 ($\lambda = 0.70926$ Å) radiation.

Intensity data were measured by using Mo Kα radiation ($2\theta_{max} = 60°$) yielding 6182 total unique data and, based on $I > 2\sigma(I)$, 3689 observed data. The data were reduced;[13] the structures were solved by direct methods;[15] and refinement was by full-matrix least-squares techniques.[14] The data were corrected for absorption.[42] The absorption coefficient was 18.46 cm^{-1}. The absorption factors ranged from 1.29 to 1.46 and averaged 1.35. The $\sigma(I)$ was based on counting statistics.[13] The final *R* value was 0.046. The final difference Fourier map showed densities ranging from +1.13 to −1.01 e/Å^3.

1,1′-Bis(methylthio)ferrocene (1). Ferrocene (3 g, 16 mmol) was added to a solution of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (5.1 mL, 33 mol) and 1.6 M *n*-butyllithium in hexane (20.67 mL, 33 mol) in oxygen-free hexane (100 mL) in a 250-mL round-bottom flask equipped with a side arm and serum cap, under nitrogen. The solution was stirred for 3 h, then methyl disulfide (2.96 mL, 33 mmol) in about 20 mL of benzene was added slowly via cannula to the bright orange solution at −10 °C, and the solution was stirred overnight. The resulting brown solution was then filtered under nitrogen, and the filtrate was evaporated to dryness. (Addition of water to destroy the excess lithio species resulted in a green and then black/blue oil which could be ferricenium.) Unreacted ferrocene was removed by sublimation (80 °C/10^{-1} mm), and **1** was obtained as a brown oil in a 70% yield. Mass spectrum: *m/e* (relative intensity) 278 (39, M$^+$), 232 (85), 217 (71), 186 (20), 152 (16), 121 (2), 56 (100, Fe).

1,1′-Bis(isopropylthio)ferrocene (2). 1,1′-Dilithioferrocene (54 mmol) was prepared as described above. Isopropyldisulfide (17.96 mL, 113 mmol) in about 150 mL of hexane was slowly added via cannula to 1,1′-dilithioferrocene (54 mmol) at −78 °C. After being stirred at room temperature for 2 days, 100 mL of water was added to the cloudy yellow solution to give a clear brown solution. The organic layer was separated, dired, and evaporated to give a brown oil. Unreacted ferrocene was removed by sublimation (80 °C/10^{-1} mm). About 13 g of **2** was obtained as a brown oil (73% yield). Traces of the disulfide can be removed by crystallization from hexane at low temperature. Mass spectrum: *m/e* (relative intensity), 334 (100, M$^+$), 292 (19), 260 (22), 250 (26), 218 (43), 195 (42), 152 (38), 121 (27), 97 (35). Anal. Calcd for $C_{16}H_{22}S_2Fe$: C, 57.48, H, 6.63. Found: C, 57.61; H, 6.60.

1,1′-Bis(isobutylthio)ferrocene (3). 1,1′-Dilithioferrocene (36 mmol) was prepared as described above. Isobutyl disulfide (13.9 mL, 72 mmol) in 40 mL of benzene was added slowly via cannula to the orange solution at −10 °C. After being stirred overnight at room temperature, the solution became clear brown and 10 mL of water was added. The organic layer was separated, dried, and evaporated to dryness. Unreacted ferrocene was removed by sublimation (80 °C/10^{-1} mm) to give 10 g of **3** (75% yield). Yellow flakes can be obtained by recrystallizing from hexane at −78 °C: mp 33–34 °C; mass spectrum, *m/e* (relative

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intensity) 362 (45, M$^+$), 274 (72), 218 (88), 152 (50), 121 (89), 56 (99), 41 (100). Anal. Calcd for $C_{18}H_{20}S_2Fe$: C, 59.66; H, 7.23. Found: C, 59.60; H, 7.21.

1,1′-Bis(phenylthio)ferrocene (4). Phenyl disulfide (18 g, 82 mmol) in about 80 mL of benzene was added slowly via cannula to 1,1′-dilithioferrocene (40 mmol) at −10 °C. The solution was stirred overnight at room temperature to give a cloudy yellow solution. About 30 mL of water was added, and 4, which precipitated from the benzene/hexane layer, was filtered and washed with petroleum ether to remove the unreacted ferrocene. About 13 g (80% yield) of 4 was obtained, and analytically pure sample was obtained by recrystallization from CH_2Cl_2 to give yellow needles: mp 172–173 °C; mass spectrum, *m/e* (relative intensity) 402 (100, M$^+$), 56 (74, Fe). Anal. Calcd for $C_{22}H_{18}S_2Fe$: C, 65.67; H, 4.48; S, 15.92. Found: C, 65.69; H, 4.36; S, 16.01.

1,1′-Bis(benzylthio)ferrocene (5). Benzyl disulfide (27.7 g, 112 mmol) in 200 mL of benzene was added slowly via cannula to 1,1′-dilithioferrocene (54 mmol) at −40 °C. After being stirred at room temperature overnight, the bright yellow suspension was filtered and washed with water. Unreacted ferrocene and benzyl disulfide were sublimed (80 °C/10^{-1} mm) from the sticky yellow powder. The yellow solid was recrystallized from CH_2Cl_2/hexane to give 10.2 g of 5 (50% yield). The filtrate was evaporated, and after sublimation an additional 9 g was isolated to give a total yield of 83%: mass spectrum, *m/e* (relative intensity) 430 (100, M$^+$), 339 (28, M$^+$ − CH_2Ph), 243 (39), 152 (6), 91 (18). Anal. Calcd for $C_{24}H_{22}S_2Fe$: C, 66.97; H, 5.15. Found: C, 67.18; H, 5.12.

Preparation of Metal Complexes. The complexes $Fe(C_5H_4SR)_2MX_2$, where R = Me, $CHMe_2$, CH_2CHMe_2, Ph, and CH_2Ph, M = Pd and Pt, and X = Cl and Br, were prepared from benzene solutions of the appropriate $(PhCN)_2MX_2$ species and a slight excess of the ferrocenyl sulfide, $Fe(C_5H_4SR)_2$, in an approximate 1:1.1 molar ratio. The resulting precipitate was filtered, washed with benzene and petroleum ether, and then recrystallized from methylene chloride/hexane by slow evaporation.

(1,1′-Bis(isobutylthio)ferrocene)palladium dichloride (6): shiny black crystals decomposed at 182–183 °C; IR (Nujol) 370 (sh), 365 (w), 307 (s), 290 (sh) cm^{-1}. Anal. Calcd for $C_{18}H_{26}Cl_2S_2FePd$: C, 40.06; H, 4.86; Cl, 13.14; S, 11.88. Found: C, 40.14; H, 5.00; Cl, 13.35; S, 12.01.

(1,1′-Bis(isobutylthio)ferrocene)palladium dibromide (7): shiny black needles decomposed at 185–187 °C; IR (Nujol) 365 (w), 222 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{26}Br_2S_2FePd$: C, 34.39; H, 4.17; Br, 25.42. Found: C, 34.50; H, 4.18; Br, 23.18.

(1,1′-Bis(isobutylthio)ferrocene)platinum dichloride (8): yellow needles decomposed at 218–220 °C; IR (Nujol) 372 (w), 323 (s), 310 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{26}Cl_2S_2FePt$: C, 34.41; H, 4.17; Cl, 11.28. Found: C, 34.43; H, 4.20; Cl, 11.39.

(1,1′-Bis(isobutylthio)ferrocene)platinum dibromide (9): yellow flakes decomposed at 225–227 °C; IR (Nujol) 372 (w), 364 (w) cm^{-1}. Anal. Calcd for $C_{18}H_{26}S_2PtFeBr_2$: C, 30.14; H, 3.65; Br, 22.28. Found: C, 30.36; H, 3.84; Br, 22.33.

(1,1′-Bis(isopropylthio)ferrocene)palladium dichloride (10): brown needles decomposed at 192–193 °C; ^{1}H NMR (50 °C) δ 5.3 (br, 4 H, $H_{2,5}$), (br s, 4 H, $H_{3,4}$), 4.04 (m, *J* = 6.8 Hz, 2 H, CH), 1.22 (d, *J* = 5.8 Hz, 12 H, CH_3); IR (Nujol) 380 (w), 360 (w), 320 (s), 305 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{22}Cl_2S_2FePd$: C, 37.56; H, 4.33; Cl, 13.86. Found: C, 37.56, H, 4.40, Cl, 14.00.

(1,1′-Bis(isopropylthio)ferrocene)palladium dibromide (11): brown needles decomposed at 188–190 °C; ^{1}H NMR δ 5.23 (br, 4 H, $H_{2,5}$), 4.45 (br, 4 H, $H_{3,4}$), 4.17 (m, *J* = 6.7 Hz, 2 H, CH), 1.24 (br, 12 H, CH_3); IR (Nujol) 380 (w), 360 (w), 225 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{22}Br_2S_2FePd$: C, 32.00; H, 3.69; Br, 26.61. Found: C, 32.19; H, 3.65; Br, 26.43.

(1,1′-Bis(isopropylthio)ferrocene)platinum dichloride (12): yellow flakes decomposed at 223–225 °C; ^{1}H NMR δ 5.51 (s, 2 H, $H_{2,5}$), 4.72 (s, 2 H, $H_{2,5}$), 4.56 (s, 2 H, $H_{3,4}$), 4.28 (s, 2 H, $H_{3,4}$), 4.27 (m, *J* = 6.4 Hz, 2 H, CH), 1.37 (d, 6 H, CH_3), 1.12 (d, 6 H, CH_3); IR (Nujol) 383 (w), 365 (w), 328 (s), 315 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{22}Cl_2S_2FePtCH_2Cl_2$: C, 29.80; H, 3.53; Cl, 20.70. Found: C, 30.19; H, 3.58; Cl, 20.76.

(1,1′-Bis(isopropylthio)ferrocene)platinum dibromide (13): yellow flakes decomposed at 214–216 °C; ^{1}H NMR δ 5.54 (br, 2 H, $H_{2,5}$), 4.75 (br, 2 H, $H_{2,5}$), 4.60 (br, 2 H, $H_{3,4}$), 4.31 (br, 2 H, $H_{3,4}$), 4.27 (m, *J* = 6.7 Hz, 2 H, CH), 1.39 (br, 6 H, CH_3), 1.16 (br, 6 H, CH_3); IR (Nujol) 389 (w), 370 (w), 220 (se cm^{-1}. Anal. Calcd for $C_{16}H_{22}Br_2S_2FePt$: C, 27.88; H, 3.22; Br, 23.19. Found: C, 28.08; H, 3.41; Br, 23.35.

(1,1′-Bis(methylthio)ferrocene)palladium dichloride (14): brown powder decomposed at 192–198 °C; IR (Nujol) 355 (w), 340 (w), 310 (s), 290 (sh) cm^{-1}. Anal. Calcd for $C_{12}H_{14}S_2PdFeCl_2$: C, 31.64; H, 3.10; Cl, 15.57. Found: C, 31.87; H, 3.18; Cl, 15.46.

(1,1′-Bis(methylthio)ferrocene)palladium dibromide (15): dark brown powder decomposed at 209–213 °C; IR (Nujol) 343 (w), 205 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{14}S_2PdFeBr_2$: C, 26.46; H, 2.59; Br, 29.35. Found: C, 25.69; H, 2.66; Br, 24.35.

(1,1′-Bis(methylthio)ferrocene)platinum dichloride (16): yellow powder decomposed at 239–244 °C; IR (Nujol) 345 (w), 323 (s), 305 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{14}S_2PtFeCl_2$: C, 26.49; H, 2.59; Cl, 13.03. Found: C, 26.51; H, 2.61; Cl, 13.07.

(1,1′-Bis(methylthio)ferrocene)platinum dibromide (17): yellow crystals decomposed at 225–230 °C; IR (Nujol) 340 (w), 208 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{14}Br_2S_2FePt$: C, 22.77; H, 2.23; Br, 25.24. Found: C, 22.90; H, 2.15; Br, 24.99.

(1,1′-Bis(benzylthio)ferrocene)palladium dichloride (18): shiny black needles decomposed at 223–225 °C; ^{1}H NMR (50 °C) δ 7.22 (m), 7.19 (m), 7.06 (m, Ph), 5.00 (br, 4 H, $H_{2,5}$), 4.34 (br s, 4 H, $H_{3,4}$), 4.32 (s, CH_2); IR (Nujol) 358 (m), 335 (w), 315 (s), 300 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{22}Cl_2S_2FePd$: C, 47.43; H, 3.65; Cl, 11.67. Found: C, 47.66; H, 3.65; Cl, 11.90.

(1,1′-Bis(benzylthio)ferrocene)palladium dibromide (19): shiny black needles decomposed at 206–207 °C; ^{1}H NMR δ 7.24 (m), 7.05 (m, Ph), 4.96 (v br, 4 H, $H_{2,5}$), 4.40 (s, 4 H, CH_2), 4.33 (br, 4 H, $H_{3,4}$); IR (Nujol) 353 (m), 345 (sh), 230 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{22}Br_2S_2FePd$: C, 41.38; H, 3.18; Br, 22.94. Found: C, 41.45; H, 3.19; Br, 22.69.

(1,1′-Bis(benzylthio)ferrocene)platinum dichloride (20): yellow flakes decomposed at 224–225 °C; ^{1}H NMR (50 °C), δ 7.34 (s), 7.20 (m), 7.04 (m, Ph), 5.45 (v br, 4 H, $H_{2,5}$), 4.60 (br, 4 H, $H_{3,4}$), 4.43 (w, 4 H, CH_2); IR (Nujol) 360 (m), 350 (m), 332 (s), 312 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{22}Cl_2S_2FePt$: C, 41.39; H, 3.18; Cl, 10.18. Found: C, 41.21; H, 3.17; Cl, 9.90.

(1,1′-Bis(benzylthio)ferrocene)platinum dibromide (21): yellow flakes decomposed at 198–200 °C; ^{1}H NMR δ 7.23 (m), 7.20 (m), 7.02 (m, Ph), 5.53 (v br, 2 H, $H_{2,5}$), 4.56 (br s, 4 H, CH_2), 4.44 (br, 2 H, $H_{2,5}$), 4.12 (br, 4 H, $H_{3,4}$); IR (Nujol) 358 (m), 348 (m), 215 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{22}Br_2S_2FePt$: C, 36.71; H, 2.82; Br, 20.35. Found: C, 36.67; H, 2.81; Br, 20.12.

(1,1′-Bis(phenylthio)ferrocene)palladium dichloride (22): brown powder decomposed at 198–201 °C; ^{1}H NMR δ 7.38 (m, 10 H, Ph), 5.27 (v br, 4 H, $H_{2,5}$), 4.65 (br, s, 4 H, $H_{3,4}$); IR (Nujol) 323 (vs), 308 (vs), 278 (s), 262 (s) cm^{21}. Anal. Calcd for $C_{22}H_{18}S_2PdFeCl_2$: C, 45.59; H, 3.13; Cl, 12.23. Found: C, 42.02; H, 2.97; Cl, 10.83.

(1,1′-Bis(phenylthio)ferrocene)palladium dibromide (23): shiny black needles decomposed at 188–189 °C; ^{1}H NMR δ 7.35 (M, 10 H, Ph), 5.41 (br, t, 4 H, $H_{2,5}$), 4.64 (t, 4 H, $H_{3,4}$); IR (Nujol) 3.16 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{18}Br_2S_2FePd$: C, 39.52; H, 2.71; Br, 23.90. Found: C, 39.45; H, 2.82; Br, 22.30.

(1,1′-Bis(phenylthio)ferrocene)platinum dichloride (24): yellow needles decomposed at 210–213 °C; ^{1}H NMR δ 7.42 (m), 7.38 (s, Ph), 5.31 (br s, 4 H, $H_{2,5}$), 4.64 (br s, 4 H, $H_{3,4}$); IR (Nujol) 350 (s), 329 (s), 317 (s), 312 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{18}Cl_2S_2FePt$: C, 39.54; H, 2.72; Cl, 10.61. Found: C, 39.74; H, 2.79; Cl, 10.66.

(1,1′-Bis(phenylthio)ferrocene)platinum dibromide (25): yellow plates decomposed at 245–247 °C; ^{1}H NMR δ 7.38 (m, 10 H, Ph), 5.30 (v br, 4 H, $H_{2,5}$), 4.61 (br, 4 H, $H_{3,4}$); IR (Nujol) 349 (sh), 324 (w), 266 (m) cm^{-1}. Anal. Calcd for $C_{22}H_{18}Br_2S_2FePt$: C, 34.89; H, 2.40; Br, 21.20. Found: C, 34.94; H, 2.51; Br, 21.23.

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Registry No. 1, 1293-94-3; 2, 96688-66-3; 3, 96665-85-9; 4, 96665-86-0; 5, 96665-87-1; 6, 94792-85-5; 7, 94792-86-6; 8, 96744-21-7; 9, 94792-62-8; 10, 94792-83-3; 11, 94792-84-4; 12, 94792-88-8; 13, 94792-89-9; 14, 96665-88-2; 15, 96665-89-3; 16, 96665-90-6; 17, 96665-91-7; 18, 96665-92-8; 19, 94792-82-2; 20, 96665-93-9; 21, 96665-94-0; 22, 96665-95-1; 23, 94792-81-1; 24, 96665-96-2; 25, 94792-87-7; $(PhCN)_2PdCl_2$, 14220-64-5; $(PhCN)_2PdBr_2$, 15003-43-7; $(PhCN)_2PtCl_2$, 14873-63-3;

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$(PhCN)_2PtBr_2$, 15130-13-9; ferrocene, 102-54-5; methyl disulfide, 624-92-0; 1,1′-dilithioferrocene, 33272-09-2; isopropyl disulfide, 4253-89-8; isobutyl disulfide, 1518-72-5; phenyl disulfide, 882-33-7; benzyl disulfide, 150-60-7.

Supplementary Material Available: A table of electronic absorption spectra of the ferrocenyl sulfides, tables of anisotropic thermal parameters, isotropic thermal parameters, and least-squares planes, a table of torsion angles, and a table of observed structure factors, standard deviations, and differences for $Fe(C_5H_4S\text{-}i\text{-}Bu)_2PdCl_2$ (29 pages). Ordering information is given on any masthead page.

Synthesis, Structure Determinations, and Reduction of $(C_5H_5)_2Zr(Cl)CH_2PMe_2$ and $(C_5Me_5)_2Zr(Cl)CH_2PPh_2$

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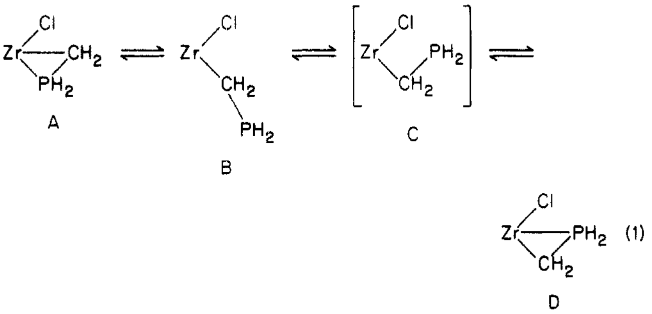
The syntheses and X-ray crystallographic analyses of $Cp_2Zr(Cl)CH_2PMe_2$ (2) and $(C_5Me_5)_2Zr(Cl)CH_2PPh_2$ (3) are reported. The former is monoclinic of space group $P2_1/n$ with a = 8.077 (3) Å, b = 14.896 (6) Å, c = 11.704 (3) Å, β = 99.27 (3)°, V = 1389.8 (8) Å^3, and Z = 4. This compound is structurally very similar to $Cp_2Zr(Cl)CH_2PPh_2$ in possessing an extended, almost anti conformation for the Cl–Zr–C–P fragment about the Zr–C bond and a nonbonded Zr···P distance of 3.72 Å. The permethylcyclopentadienyl complex is monoclinic of space group $P2_1/n$ with a = 10.285 (3) Å, b = 20.739 (5) Å, c = 14.078 (8) Å, β = 96.79 (4)°, V = 2982 (2) Å^3, and Z = 4. In spite of the much bulkier ligands, this compound contains a gauche-like Cl–Zr–C–P system with a 31° dihedral angle and a relatively short 3.56-Å Zr···P distance. One electron reduction of 2 produces a persistent P-bound Zr(III) species. In contrast, reduction of 3 gives a Zr(III) species lacking appreciable Zr–P interaction. The possible consequences of electronic and steric factors on these structures are discussed.

Introduction

Ever since the synthesis of $Cp_2Zr(Cl)CH_2PPh_2$ (1) in 1980[1] we have been intrigued by the unusual structural characteristics of this molecule. In spite of the presence of a lone pair on phosphorus and coordinative unsaturation at the metal, no bonding interaction between them exists. Indeed, a calculation on the model system $Cp_2Zr(Cl)CH_2PH_2$ gives rise to three structural minima (eq 1, structures A, B, and D). The large P···Zr nonbonding distance (3.75 Å) and the 130° Zr–C–P angle in 1 are reproduced well in structure B and are explained by a strong P–Zr repulsive electronic interaction that exists in this geometry. Two different geometries (A and D) with full Zr–P bonds are actually calculated to be more stable than the open form, although neither is observed. An electronic barrier separates B from A, while conversion to D requires rotation to C, which is not a local energy minimum, and should collapse directly to the Zr–P bonded structure. Assuming the validity of the calculations, the lack of Zr–P bonding in 1 is due both to these barriers to structural interconversion and to steric destabilization of the Zr–P bonded forms due to the substituents on phosphorus. The electronic barrier is found to vanish upon reduction of the metal and loss of chloride ion. Thus phosphine complexation to both zirconocene[1,3] and titanocene[4,5] derivatives is observed with the metal in the +3 oxidation state. Preliminary results from a study of niobocene +4 and +3 derivatives show that similar effects are operative in the group 5 metals as well.[6]



(1)

Table I. Crystal Data

	$(C_5H_5)_2ZrCl(CH_2PMe_2)$	$(C_5Me_5)_2ZrCl(CH_2PPh_2)$
mol wt, amu	331.95	596.35
d(calcd) (140 K), g cm^{-3}	1.59	1.33
max cryst dim, mm	0.075 × 0.25 × 0.50	0.08 × 0.25 × 0.30
space group	$P2_1/n$	$P2_1/n$
molecules/unit cell	4	4
cell constants[a]		
a, Å	8.077 (3)	10.285 (3)
b, Å	14.896 (6)	20.739 (5)
c, Å	11.704 (3)	14.078 (8)
β, deg	99.27 (3)	96.79 (4)
cell vol, Å^3	1389.8 (8)	2982 (2)
abs coeff μ, cm^{-1}	10.5	5.2

[a] T = 140 K; Mo Kα radiation, λ = 0.71069 Å, graphite monochromator.

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