

Iron Carbene Complexes

Part 4*. Substitution Reactions of Diiron Carbene Complexes with P(OMe)₃, PPh₃ and ^tBuNC Ligands

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Abstract

Reaction of LiPPh₂ with [Fe₂{μ-SPh}₂(CO)₆] did not result in the formation of the carbene salt, but in the substitution of the sulphido bridged ligand(s) to yield [Fe₂{μ-SPh}_n{μ-PPh₂}_{2-n}(CO)_{6-m}(L)_m] (*n* = 1, *m* = 1, L = PPh₃; *n* = 1, *m* = 2, L = PPh₃; *n* = 0, *m* = 2, L = PPh₃). Reaction of [Fe₂(μ-SPh)₂(CO)₅{C(OEt)-Ph}] with P(OMe)₃ and ^tBuNC resulted in substitutions of the carbene group, as well as a carbonyl ligand on the other iron atom, affording [Fe₂{μ-SPh}₂(CO)₄(L)₂] (L = P(OMe)₃, ^tBuNC). These complexes were studied spectroscopically and an X-ray analysis on the mixed bridged complex, [Fe₂{μ-SPh}{μ-PPh₂}(CO)₅(PPh₃)] was performed. The crystals are triclinic, space group *P* $\bar{1}$ with *a* = 10.325(4), *b* = 10.890(5), *c* = 19.626(8) Å, α = 69.54(4), β = 71.05(4), γ = 67.85(4)° and *Z* = 2.

Introduction

Recently we reported the synthesis of the diiron carbene complexes [Fe₂{μ-(S(CH₂)₃S)}(CO)₅{C(OEt)R}] (R = Bu, Ph, Me) and [Fe₂{μ-SPh}₂(CO)₅{C(OEt)R}] (R = Ph, Bu) and we now wish to report on the extension of this work [1, 2]. The reactivity of sulphido bridged diiron complexes, [Fe₂{μ-SR}₂(CO)₆], and LiPPh₂ was investigated, the purpose of this study being the synthesis of diiron carbene complexes with a diphenylphosphine substituent on the carbene ligand. Heteroatom substituents on carbene ligands notably enhance the stability of such compounds – a fact clearly demonstrated in [Fe(CO)₄{C(OEt)NⁱPr₂}] [3]. Reagents such as LiPMe₂ were used before to synthesize carbene complexes with heteroatom substituents and Fischer and coworkers reported the formation of the very unstable bis-carbene complex [Cr(CO)₄{C(OEt)PMe₂}₂] [4].

*Part 3 is ref. 1.

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Secondly, the reaction of π-acidic ligands with [Fe₂{μ-SR}₂(CO)₅{C(OEt)R'}] was studied to gather information on substitution patterns of complexes with carbene and carbonyl ligands. The group of Haines showed that carbonyl substitution in [Fe₂{μ-SMe}₂(CO)₆] by various ligands, led to mono, bis and tris-substituted derivatives [5]. The structural features of these complexes were studied spectroscopically and conclusions were made on the position and degree of substitution. Competitive to carbonyl substitution, however, was the replacement of a carbene ligand by PMe₃ in [Cr(CO)₅{C(OMe)Me}] [6]. This was found to be dependent on the reaction temperature and the phosphine concentration.

Experimental

All reactions and manipulations were carried out under nitrogen atmosphere and with solvents dried prior to use. Reagent grade chemicals were used without further purification and iron pentacarbonyl was filtered before use. Column chromatography on SiO₂ (0.063–0.200 mm) was performed on 2 cm × 30 cm columns at –10 °C. Microanalyses were performed by F. Pascher and E. Pascher, Microanalytical Laboratories, Remagen, F.R.G. Infrared spectra were recorded on a Bruker IFS 113 V spectrometer and calibrated against polystyrene. ¹H and ³¹P NMR spectra were recorded on a Bruker AC 300 MHz instrument and mass spectra on a Perkin Elmer RMU-6H instrument operating at 70 eV. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Analytical and physical data of the new compounds are given in Table 1.

Bis{(μ-phenylsulphido)tricarbonyliron}

A previously described method for the preparation of [Fe₂{μ-SPh}₂(CO)₆] was not used but instead the procedure described below was employed [7].

A solution of 20 cm³ (150 mmol) [Fe(CO)₅] and 2.32 g (10 mmol) PhSCH₂SPh was irradiated for 2 h. The mixture was refluxed for 1 h at 150 °C and

TABLE 1. Physical, analytical and infrared data

Complex	Melting point (°C)	Yield (%)	Analysis (%) ^a			Infrared (ν_{CO}) (cm ⁻¹) ^b	
			C	H	X(N, P)		
1 [Fe ₂ { μ -SPh}{ μ -PPh ₂ }(CO) ₅ (PPh ₃)	136–139	30	66.51 (66.84)	4.57 (4.35)	8.51(P) (8.86)	2032(s)	1973(vs) 1941(s)
2 [Fe ₂ { μ -SPh}{ μ -PPh ₂ }(CO) ₄ (PPh ₃) ₂]	152–154	20	60.63 (60.92)	3.42 (3.74)	6.41(P) (7.67)	2034(s)	1971(vs) 1941(m)
3 [Fe ₂ { μ -PPh ₂ }(CO) ₄ (PPh ₃) ₂]	160–162	25	68.93 (68.72)	4.70 (4.50)	10.88(P) (11.07)	2065(s)	2027(vs) 2000(s)
4 [Fe ₂ { μ -SPh}(CO) ₄ (CNBu ^t) ₂]	147–149	31	51.75 (51.33)	4.82 (4.63)	4.32(N) (4.60)	2043(s)	1978(vs) 1945(s)

^aCalculated values are given in parentheses. ^bMeasured in hexane.

thereafter refluxed and irradiated simultaneously for another hour. The reaction mixture was cooled and the excess [Fe(CO)₅] was removed *in vacuo*. The residue was dissolved in tetrahydrofuran and filtered through Al₂O₃ (neutral, activity 1) and anhydrous Na₂SO₄. After removal of the solvent the residue was chromatographed on SiO₂ (–10 °C) with hexane as eluent. The red zone was collected, stripped of solvent and after crystallization from hexane yielded 3.24 g (70%) of [Fe₂{ μ -SPh}(CO)₆].

Reaction of Bis(μ -phenylsulphidotricarbonyliron) with Diphenylphosphidolithium

The organolithium reagent LiPPh₂ was prepared according to a published procedure [8].

To 4.98 g (10 mmol) of [Fe₂{ μ -SPh}(CO)₆] an equimolar THF solution of LiPPh₂ was stirred at –70 °C for 1 h and at room temperature for another hour. The solution was cooled to –20 °C, and 1.9 g (10 mmol) of [Et₃O][BF₄] added while vigorous stirring was maintained. After the addition of 250 cm³ of water the reaction products were extracted with three 50 cm³ portions of hexane. The combined hexane portions were filtered through SiO₂ and Na₂SO₄ (anhydrous). After removal of the solvent the residue was chromatographed on SiO₂ with a hexane–dichloromethane mixture (5:2) as eluent. The first eluted orange band gave, upon crystallization from hexane, 1.25 g (1.11 mmol) of [Fe₂{ μ -PPh₂}(CO)₅(PPh₃)₂ (3), whereas the second red zone afforded 1.49 g (1.85 mmol) of [Fe₂{ μ -SPh}{ μ -PPh₂}(CO)₅(PPh₃) (1) after crystallization from a hexane–dichloromethane mixture. A small, third, amber coloured band was of very low yield and was not collected. The fourth red band gave 1.0 g (0.96

mmol) of [Fe₂{ μ -SPh}{ μ -PPh₂}(PPh₃)₂(CO)₄] (2) after crystallization from a hexane–dichloromethane mixture.

Reaction of [*Phenyl(ethoxy)carbene*]-bis(μ -phenylsulphido)pentacarbonyldiiron] with (a) Trimethylphosphite and (b) *t*-Butylisocyanide

The starting diiron carbene complex [Fe₂{ μ -SPh}(CO)₅{C(OEt)Ph}] was prepared from [Fe₂{ μ -SPh}(CO)₆] as reported previously [1, 2].

(a) To a solution of 3.02 g (5 mmol) of [Fe₂{ μ -SPh}(CO)₅{C(OEt)Ph}] in 50 cm³ benzene, 0.40 cm³ (7 mmol) of P(OMe)₃ was added. The reaction was complete after 1 h as was indicated by thin layer chromatography and the solvent removed *in vacuo*. The residue was chromatographed with a hexane–dichloromethane mixture (5:2) as eluent. The first red band gave, on crystallization from hexane, 0.55 g (1.1 mmol, 22%) of [Fe₂{ μ -SPh}(CO)₆]. The second red zone yielded 1.12 g (1.6 mmol, 37%) of [Fe₂{ μ -SPh}(CO)₄{P(OMe)₃}]₂ after crystallization from hexane [5].

(b) The same procedure as above was carried out on a 5 mmol scale for [Fe₂{ μ -SPh}(CO)₅{C(OEt)Ph}] and with 0.78 cm³ (7 mmol) of ^tBuNC. Again the first red band afforded [Fe₂{ μ -SPh}(CO)₆]. The main product 0.91 g (1.5 mmol) of [Fe₂{ μ -SPh}(CO)₄(CNBu^t)₂] was crystallized from the second red zone.

Data Collection and Structure Determination

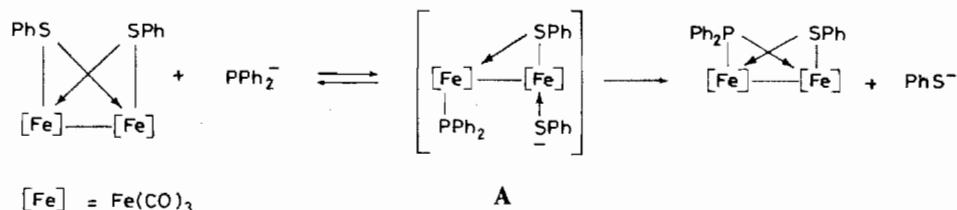
All diffraction measurements were performed at room temperature on an Enraf-Nonius CAD-4F diffractometer using graphite monochromated Mo K α radiation. The unit cell was determined from 25

TABLE 2. Crystal data of 1

Formula	Fe ₂ C ₄₁ H ₃₀ O ₅ SP ₂
M _r (g/mol)	928.5
Space group	P $\bar{1}$
a (Å)	10.325(4)
b (Å)	10.890(5)
c (Å)	19.626(8)
α (°)	69.54(4)
β (°)	71.05(4)
γ (°)	67.85(4)
Z	2
D _{calc} (g/cm ³)	1.65
μ (Mo K α) (cm ⁻¹)	9.0
Scan method ($\omega:2\theta$)	1:1
Scan range (°)	3 \leq θ \leq 25
Reflections used	5537
Variables refined	465
R = $\Sigma F_o - F_c / \Sigma F_o $	0.096
R _w = $\Sigma w(F_o - F_c)^2 / \Sigma w(F_o ^2)$ ^{1/2}	0.075

randomly selected reflections, using the automatic search index and least-square routines. The refined cell constant and other relevant crystal data are listed in Table 2. Data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied by measuring the intensities of nine reflections with χ near 90° and for different ψ values (0 \leq ψ \leq 360°, every 10°) using the EAC program from the Enraf-Nonius packages. The maximum and minimum transmission factors were 1.00 and 0.69 respectively, with an average value of 0.87. Three standard reflections were measured periodically to check orientation and crystal stability and the decay during data collections was less than 1%.

The structure was solved by conventional Patterson and Fourier methods and refined by blocked-matrix least-squares techniques using SHELX [9]. All the hydrogen atoms were placed in calculated positions with a common temperature factor that refined to $a = 0.13(1)$ Å². All the non-hydrogen atoms were refined anisotropically by using all the data and $\sigma^{-2}(F)$ weights. The maximum residual electron density in the final difference map was 1.11 e Å⁻³ at a distance of 1 Å from Fe₁. Scattering factors for iron were taken from the literature [10].



Scheme 1.

Results and Discussion

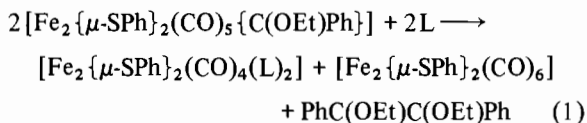
The lithium reagent LiPPh₂ reacted with [Fe₂{ μ -SPh}₂(CO)₆] to give after purification, [Fe₂{ μ -SPh}{ μ -PPh₂}(CO)₅(PPh₃)] (1), [Fe₂{ μ -SPh}{ μ -PPh₂}(CO)₄(PPh₃)₂] (2) and [Fe₂{ μ -PPh₂}(CO)₄(PPh₃)₂] (3). Two aspects are important for the formation of the products 1–3. The first concerns the replacement of a sulphido bridge with a phosphido bridged ligand and the second with unreacted triphenylphosphine present in the lithiated mixture, which substitutes a carbonyl or carbonyls. A possible pathway for the exchange of the bridged ligand is outlined in Scheme 1. The Ph₂P⁻ attacks an iron atom, whereby the iron-sulphur bond is broken and an anionic intermediate (A), with only one bridged sulphido ligand, forms. Either a PhS⁻ or a Ph₂P⁻ may be released from A to afford a mixed bridged sulphido and phosphido complex or the starting compound. This process may be repeated, leading to the formation of the bis-phosphido bridged complex. Carbonyl substitution as a result of the excess triphenylphosphine affords the final products 1–3. Analytical, physical and infrared data (Table 1) and nuclear magnetic resonance measurements (Table 3) are in accordance with the given formulations. The ³¹P NMR spectrum of 1 was recorded in C₆D₆ and two distinct resonances were observed, namely doublets at 110.3 and 51.1 ppm. The higher field resonance appeared after the normal short accumulation time, whereas the lower field resonance could only be detected after approximately thirty minutes. This, and the increased shift of electron density away from the bridged phosphorous ligand, as opposed to the terminal one, made it possible to assign the low field doublet to the bridged phosphorous atom. The higher δ value of 110.3 ppm compares with the reported value of 142.5 ppm for the complex [Fe₂{ μ -PPh₂}(CO)₆], which has bridged phosphido ligands and the lower value of 51.1 with the value of 44.2 ppm of the terminal phosphine ligand in [Fe{C(OEt)Bu}{PPh₃}(CO)₃] [11, 12]. Four peaks of varying intensity were observed at 137.1, 135.3, 33.1 and 32.1 ppm for the complex 3 which has two bridged and two terminal phosphine ligands, indicating a slight non-equivalence of the two bridged and two terminal phosphorous atoms respectively.

TABLE 3. ^1H and ^{31}P NMR and mass spectral data

Complex	Chemical shifts, δ		Mass peaks (m/z) (I (%))
	^1H NMR ^a	^{31}P NMR ^b	
	t^{Bu}		
1	7.30–7.20(m, 6H)	110.3(d)/(PP) 24.8 51.1(d)	no M^+
	7.15–7.47(m, 9H)		
	6.9–6.6(m, 15H)		
2	7.46–6.59(m)		no M^+
3	7.59–7.17(m)	137.1, 135.3 33.1 and 32.1	
4	7.58–7.33(m, 4H)	1.49(s, 9H) 1.27(s, 9H)	690(4), 634(8), 606(3), 578(42), 547(1) 485(3), 454(100), 423(1), 361(6), 330(62) 253(23), 176(26), 144(13), 112(12)
	7.30–7.15(m, 6H)		608(3), 580(2), 552(5), 524(13), 496(56) 439(84), 413(100), 356(10), 330(30) 253(21), 176(16), 144(9), 112(28)
5^c			

^aMeasured in CDCl_3 relative to TMS.^bMeasured in C_6D_6 relative to H_3PO_4 , coupling constants in Hz.^c $[\text{Fe}_2\{\mu\text{-SPH}\}_2(\text{CO})_4\{\text{P}(\text{OMe})_3\}_2]$ see ref. 6.

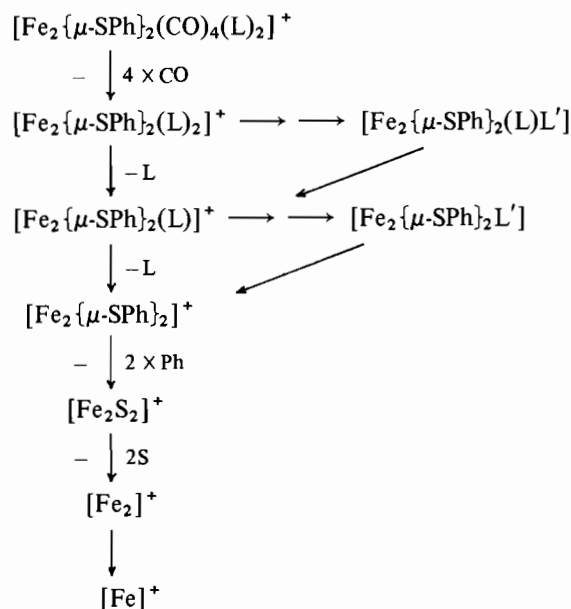
The diiron carbene complex $[\text{Fe}_2\{\mu\text{-SPh}\}_2(\text{CO})_5\{\text{C}(\text{OEt})\text{Ph}\}]$ reacts with a slight excess of $\text{P}(\text{OMe})_3$ or ${}^t\text{BuNC}$ resulting in the substitution of the carbene ligand as well as a carbonyl on the other iron atom to yield $[\text{Fe}_2\{\mu\text{-SPh}\}_2(\text{CO})_4(\text{L})_2]$ ($\text{L} = \text{P}(\text{OMe})_3$ (**5**) or ${}^t\text{BuNC}$ (**4**)). An interesting feature of these reactions is the simultaneous formation of $[\text{Fe}_2\{\mu\text{-SPh}\}_2(\text{CO})_6]$ which represents the substitution of the carbene ligand by the available carbonyl ligand.



($\text{L} = \text{P}(\text{OMe})_3, {}^t\text{BuNC}$)

Spectroscopic and analytical data of **4** are given in Tables 2 and 3. The existence of two isomers, i.e. of *syn* and *anti* structural assignment, in solution may be the reason for two ${}^t\text{Bu}$ resonances in the ${}^1\text{H}$ NMR spectrum of **4**. A general fragmentation pattern emerges from the spectra of $[\text{Fe}_2\{\mu\text{-SPh}\}_2(\text{CO})_4(\text{L})_2]$ ($\text{L} = \text{P}(\text{OMe})_3, {}^t\text{BuNC}$) and is represented in Scheme 2. After initial loss of the carbonyl ligands, two possible routes exist for the fragmentation of the L ligands. The ligands are lost as a whole or in fragments of m/z values of 31, 62, 31 or 57 and 26 for $\text{L} = \text{P}(\text{OMe})_3$ and ${}^t\text{BuNC}$ respectively. The principle ion peaks correspond with the fragments $\{\text{Fe}_2(\mu\text{-SPh})_2(\text{L})\}^+$. Although the fragment corresponding to $\{\text{FeS}\}^+$ has been reported before it was not observed in these two cases [13–15].

The molecular geometry of $[\text{Fe}_2\{\mu\text{-SPh}\}\{\mu\text{-PPh}_2\}(\text{CO})_5(\text{PPh}_3)]$ is shown in the perspective drawing in



Scheme 2.

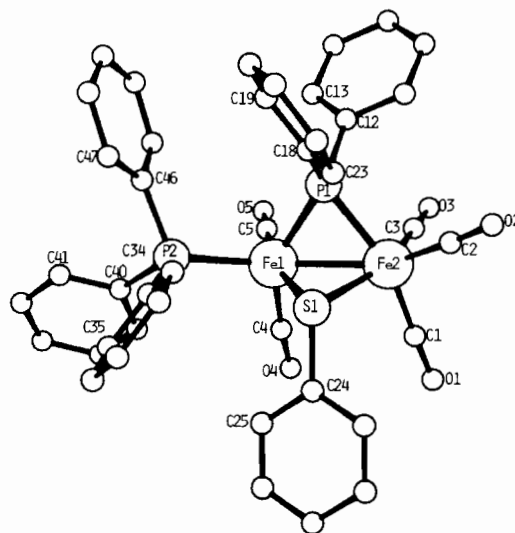


Fig. 1. Perspective drawing of $[\text{Fe}_2\{\mu\text{-SPh}\}\{\mu\text{-PPh}_2\}(\text{CO})_5(\text{PPh}_3)]$.

Fig. 1, which also defines the atomic numbering scheme. Selected bond distances and angles are given in Table 4. The Fe_2SP skeleton of the two iron atoms and the bridging heteroatoms exhibits the well known butterfly structure, typical of bridging diiron complexes of the type $[\text{Fe}_2(\mu\text{-SR})_2(\text{CO})_6]$. Due to the steric effects of the phenyl groups of the bridging ligands, the phenyl group on the sulfur is in an equatorial position. The triphenylphosphine ligand occupies one of the apical coordination sites. The $\text{Fe}_1\text{-Fe}_2$ bond distance of 2.574(1) Å is shorter than the Fe-Fe distance of 2.614(3) Å found in $[\text{Fe}_2\{\mu\text{-SPh}\}\{\mu\text{-PPh}_2\}(\text{CO})_6]$, but longer than the 2.516(2) Å found in $[\text{Fe}_2\{\mu\text{-SPh}\}_2(\text{CO})_6]$ [16, 17]. The average $\text{Fe-C}(\text{carbonyl})$ bond length of 1.735(10) Å for the two carbonyls on the same iron as the phosphine ligand is significantly shorter than the average value of 1.790(9) Å of the three carbonyls on the other iron atom.

Supplementary Material

Tables of anisotropic temperature factors, bond lengths, bond angles and observed and calculated structure factors are available on request from the authors.

Acknowledgement

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TABLE 4. Selected bond lengths (Å) and valence angles (°) of 1

Bond lengths			
Fe(1)–Fe(2)	2.574(1)	Fe(1)–S(1)	2.285(2)
Fe(1)–P(2)	2.279(2)	Fe(1)–P(1)	2.231(3)
Fe(1)–C(4)	1.744(12)	Fe(1)–C(5)	1.727(9)
Fe(2)–S(1)	2.282(2)	Fe(2)–P(1)	2.245(3)
Fe(2)–C(1)	1.774(10)	Fe(2)–C(2)	1.801(12)
Fe(2)–C(3)	1.797(9)	S(1)–C(24)	1.777(10)
P(1)–C(12)	1.805(8)	P(1)–C(18)	1.834(12)
P(2)–C(34)	1.829(8)	P(2)–C(40)	1.827(11)
P(2)–C(46)	1.804(10)		
Valence angles			
Fe(2)–Fe(1)–S(1)	55.6(1)	Fe(2)–Fe(1)–P(2)	150.1(1)
S(1)–Fe(1)–P(2)	99.1(1)	Fe(2)–Fe(1)–P(1)	55.1(1)
S(1)–Fe(1)–P(1)	78.6(1)	P(2)–Fe(1)–P(1)	108.4(1)
Fe(2)–Fe(1)–C(4)	91.4(3)	S(1)–Fe(1)–C(4)	91.6(3)
P(2)–Fe(1)–C(4)	106.4(3)	P(1)–Fe(1)–C(4)	144.9(3)
Fe(2)–Fe(1)–C(5)	108.4(3)	S(1)–Fe(1)–C(5)	164.0(3)
P(2)–Fe(1)–C(5)	96.5(3)	P(1)–Fe(1)–C(5)	93.3(4)
C(4)–Fe(1)–C(5)	87.2(5)	Fe(1)–Fe(2)–S(1)	55.7(1)
Fe(1)–Fe(2)–P(1)	54.7(1)	S(1)–Fe(2)–P(1)	78.3(1)
Fe(1)–Fe(2)–C(2)	147.8(4)	S(1)–Fe(2)–C(2)	105.0(3)
P(1)–Fe(2)–C(2)	99.1(4)	Fe(1)–Fe(2)–C(3)	104.4(3)
S(1)–Fe(2)–C(1)	93.4(3)	P(1)–Fe(2)–C(1)	158.7(3)
C(2)–Fe(2)–C(1)	102.1(5)	Fe(1)–Fe(2)–C(3)	97.7(3)
S(1)–Fe(2)–C(3)	153.3(3)	P(1)–Fe(2)–C(3)	88.3(3)
C(2)–Fe(2)–C(3)	99.9(4)	C(8)–Fe(2)–C(3)	90.9(5)

References

- J. L. M. Dillen, M. M. van Dyk and S. Lotz, *J. Chem. Soc., Dalton Trans.*, (Nov.) (1988) accepted for publication.
- S. Lotz, P. H. van Rooyen and M. M. van Dyk, *Organometallics*, **6** (1987) 499.
- E. O. Fischer, J. Schneider and K. Ackermann, *Z. Naturforsch., Teil B*, **39** (1984) 468.
- E. O. Fischer, *Pure Appl. Chem.*, **30** (1972) 353.
- J. A. de Beer, R. J. Haines, R. Greatrex and N. N. Greenwood, *J. Chem. Soc. A*, (1971) 3271.
- F. R. Kreissl, E. O. Fischer, C. G. Kreiter and H. Fischer, *Chem. Ber.*, **106** (1973) 1262.
- J. A. de Beer and R. J. Haines, *J. Organomet. Chem.*, **36** (1972) 297.
- G. W. Luther and G. Beyerl, *Inorg. Synth.*, **17** (1977) 186.
- G. M. Sheldrick, *SHELX-76 Program System*, University of Cambridge, U.K., 1976.
- (a) J. A. Ibers and W. C. Hamilton, *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, U.K., 1974; (b) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53** (1970) 1891.
- Y.-F. Yu, A. Wojcicki, M. Calligaris and G. Nardin, *Organometallics*, **5** (1986) 47.
- S. Lotz, unpublished results.
- D. Seyferth and G. B. Womack, *Organometallics*, **5** (1986) 2360.
- D. Seyferth, G. B. Womack, M. Cowie and B. W. Hames, *Organometallics*, **3** (1984) 891.
- D. Seyferth and A. M. Kiwan, *J. Organomet. Chem.*, **286** (1985) 219.
- G. Le Borgne and R. Mathieu, *J. Organomet. Chem.*, **208** (1981) 201.
- W. Henslee and R. E. Davis, *Cryst. Struct. Commun.*, **1** (1972) 403.