Iron Carbene Complexes. Part 3.[1] Aminolysis of Di-iron Alkoxycarbene Complexes with Ammonia and Dimethylamine. *X*-Ray Crystal Structure of $[Fe_2(\mu\text{-}SPh)_2(CO)_5\{C(NMe_2)Ph\}]$†

Jan L. M. Dillen, Marthie M. van Dyk, and Simon Lotz*
Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

Reaction of the mercapto-bridged di-iron carbene complexes $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2\{C(OEt)Ph\}]$ and $[(OC)_3Fe\{\mu\text{-}S(CH_2)_3S\}Fe(CO)_2\{C(OEt)Bu\}]$ with ammonia and dimethylamine afforded the aminocarbene complexes, $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2\{C(NR^4R^5)Ph\}]$ (R^4,R^5 = H or Me) and $[(OC)_3Fe\{\mu\text{-}S(CH_2)_3S\}Fe(CO)_2\{C(NR^4R^5)Bu\}]$ (R^4,R^5 = H or Me). Competitive to the aminolysis reaction is substitution of the carbene ligand by an amine. The structure of $[(OC)_3Fe(\mu\text{-}SPh)_2\text{-}Fe(CO)_2\{C(NMe_2)Ph\}]$ was confirmed by *X*-ray crystallography. The crystals are monoclinic, space group $P2_1/n$ with $a = 9.987(3)$, $b = 18.955(5)$, $c = 14.557(3)$ Å, $\beta = 107.74(2)°$, and $Z = 4$. The carbene ligand is in the *trans* position to the iron–iron bond and the phenyl groups of the bridging sulphur atoms are in an *anti* orientation.

The aminolysis of alkoxycarbene complexes is a well known procedure and is often employed to stabilize metal carbene complexes.[2,3] Many monoiron carbene complexes with amino and diamino substituents on the carbene carbon have been synthesized using a number of different methods.[4–7] Few examples are found, however, where iron alkoxycarbene complexes are aminolysed with primary and secondary amines. Whereas the complex $[Fe(CO)_4\{C(NMe_2)Ph\}]$ could be obtained in an almost quantitative yield from the ethoxycarbene and dimethylamine, the corresponding reactions with butyl and methyl substituents on the carbene carbon were less successful. These low yields were ascribed to a possible base-induced rearrangement of the α-protons.[8]

Bridged heteroatom di-iron carbene complexes are very scarce and the few examples we know of are $[Fe_2\{SC(S)SCH_2CH_2S\}(CSCH_2CH_2S)(CO)_5]$,[9] $[Fe_2(CO)_6(dppe)\{CN(Me)CH_2CH_2NMe\}]$ (dppe = $Ph_2PCH_2CH_2PPh_2$),[6] $Fe_2(PPh_2)_2(CO)_5\{CO(CH_2)_2CH_2\}]$.[10] Recently we reported the synthesis and characterization of bridged alkylthio di-iron alkoxycarbene complexes.[11] In this paper we report on the reactivity of some of these complexes towards ammonia and dimethylamine. We are also interested in the structural features of iron carbene complexes and a single-crystal *X*-ray diffraction determination of *anti*-$[Fe_2(\mu\text{-}SPh)_2(CO)_5\{C(NMe_2)Ph\}]$ was carried out.

Results and Discussion

Reaction of the Alkoxycarbene Di-iron Complexes with Amines.—Aminocarbene complexes of the type $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2\{C(NR^4R^5)Ph\}]$ or $[(OC)_3Fe\{\mu\text{-}S(CH_2)_3S\}Fe(CO)_2\{C(NR^4R^5)Bu\}]$ were prepared by bubbling the appropriate amine through a diethyl ether solution of the corresponding alkoxycarbene complex (Scheme 1). Red-brown crystals, stable under a nitrogen atmosphere, were isolated after column chromatography and characterized by elemental analysis and i.r. and ^1H n.m.r. spectra (Tables 1 and 2). The formation of $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2\{C(NHMe)Ph\}]$ or $[(OC)_3Fe\{\mu\text{-}S(CH_2)_3S\}Fe(CO)_2\{C(NHMe)Bu\}]$ in relatively low yields from the reaction with dimethylamine is ascribed to the presence of methylamine impurities in the dimethylamine. Earlier we reported a similar observation on aminolysing metallacyclic alkoxycarbene complexes of chromium with dimethylamine.[12] Aminolysis with ammonia is complete after only 20 min whereas the reaction time with the bulkier dimethylamine is twice as long. An interesting feature of the reaction is the substitution of the carbene ligand by an amine ligand as shown in Scheme 2. Substitution of carbene ligands by ligands such as phosphines, thioethers, *etc.* is known and has been reported for chromium carbene complexes.[13,14] As far as we are aware no examples have been reported where carbene substitution competes with carbene aminolysis. A second carbonyl is also substituted by an amine due to the presence of the excess of amine and affords $[Fe_2(CO)_4(\mu\text{-}SPh)_2(NHR^4R^5)_2]$ or $[(OC)_2(R^4R^5HN)Fe\{\mu\text{-}S(CH_2)_3S\}Fe(NHR^4R^5)(CO)_2]$ which are of variable stabilities. The formation of the very stable complex $[Fe_2(CO)_6(\mu\text{-}SPh)_2]$ or $[(OC)_3Fe\{\mu\text{-}S(CH_2)_3S\}\text{-}Fe(CO)_3]$ is assisted by the available carbon monoxide and unstable iron carbonyl species. We are presently studying carbene substitution reactions of iron and will report separately on this aspect.

$$[(OC)_3Fe(SR^1)(SR^2)Fe(CO)_2\{C(OEt)R^3\}] \xrightarrow{NHR^4R^5} [(OC)_3Fe(SR^1)(SR^2)Fe(CO)_2\{C(NR^4R^5)R^3\}]$$

	R^1	R^2	R^3	R^4	R^5
(1)	Ph	Ph	Ph	H	H
(2)	Ph	Ph	Ph	H	Me
(3)	Ph	Ph	Ph	Me	Me
(4)	$(CH_2)_3$		Bu	H	H
(5)	$(CH_2)_3$		Bu	H	Me
(6)	$(CH_2)_3$		Bu	Me	Me

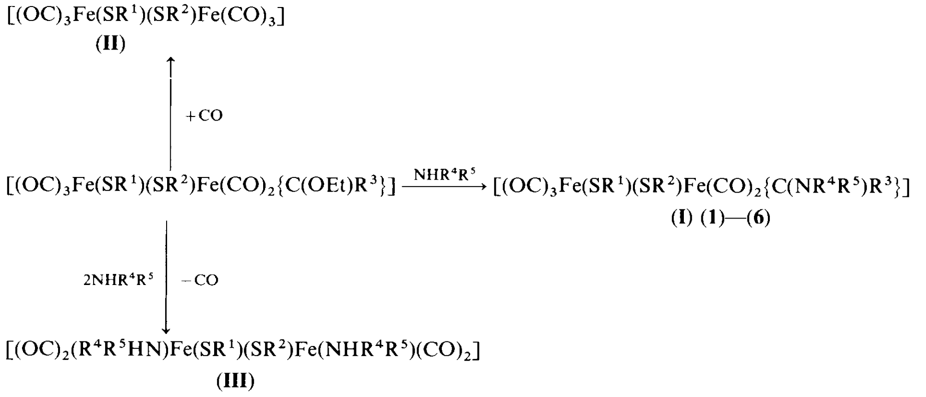
Scheme 1.

Spectroscopic Data for the Aminocarbene Complexes.—The complexes $[(OC)_3Fe(SR^1)(SR^2)Fe(CO)_2\{C(NR^4R^5)R^3\}]$ **(1)**—**(6)** can exist in solution in many different conformational forms.

---

† 1,1,1,2,2-Pentacarbonyl-2-dimethylamino(phenyl)methylene-di-μ-phenylthio-di-iron (*Fe–Fe*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



Scheme 2.

Table 1. Analytical[a] and physical data for the di-iron aminocarbene complexes

Complex	M.p.[b] (θ/°C)	Yield[c] (%)	Analysis (%) C	H	N	I.r. (cm^{-1}) ν(CO)[d]	ν(NH)
(**1**) $[Fe_2(\mu\text{-}SPh)_2\{C(NH_2)Ph\}(CO)_5]$	146—147	85	50.5	3.2	2.3	2 045, 1 995, 1 976, 1 968, 1 939	
			(50.1)	(3.0)	(2.4)	2 044, 1 994, 1 971, 1 940	3 398, 3 304
(**2**) $[Fe_2(\mu\text{-}SPh)_2\{C(NHMe)Ph\}(CO)_5]$	141—143	9	51.2	3.5	2.2	2 040, 1 994, 1 974, 1 967, 1 934	
			(51.0)	(3.3)	(2.4)	2 038, 1 992, 1 971, 1 936	3 396, 3 303
(**3**) $[Fe_2(\mu\text{-}SPh)_2\{C(NMe_2)Ph\}(CO)_5]$	130—132	38	51.9	3.6	2.2	2 032, 1 984, 1 973, 1 964, 1 932	
			(51.8)	(3.5)	(2.3)	2 030, 1 984, 1 974, 1 933	—
(**4**) $[Fe_2(\mu\text{-}SCH_2CH_2CH_2S)\{C(NH_2)Bu\}(CO)_5]$	124—126	87	35.5	4.0	3.4	2 045, 1 990, 1 977, 1 968, 1 936	
			(35.2)	(3.8)	(3.2)	2 041, 1 985, 1 964, 1 947	3 389, 3 301
(**5**) $[Fe_2(\mu\text{-}SCH_2CH_2CH_2S)\{C(NHMe)Bu\}(CO)_5]$	121—122	12	36.3	4.4	2.8	2 040, 1 990, 1 975, 1 962, 1 932	
			(36.8)	(4.2)	(2.7)	2 034, 1 989, 1 970, 1 935	3 387, 3 298
(**6**) $[Fe_2(\mu\text{-}SCH_2CH_2CH_2S)\{C(NMe_2)Bu\}(CO)_5]$	118—121	32	38.4	4.5	2.9	2 033, 1 981, 1 961, 1 958, 1 926	
			(38.2)	(4.5)	(3.0)	2 033, 1 980, 1 960, 1 929	—

[a] Required values are given in parentheses. [b] With decomposition. [c] Based on alkoxycarbene. [d] In hexane. Values in second row in CCl_4.

Table 2. Proton n.m.r. spectra for the aminocarbene complexes *

Complex	δ(NH)	δ(NMe)	δ(alkyl proton) SCH_2	SCH_2CH_2	CCH_2	CH_2	CH_3	δ(aryl proton) SPh/CPh
(**1**)	9.02 (s, br, 1 H)	—	—					7.40—7.05
	8.06 (s, br, 1 H)	—	—	—	—	—	—	(m, 15 H)
(**2**)	9.05 (s, br, 1 H)	3.13 (d, 3 H)	—	—	—	—	—	7.47—7.06
	8.08 (s, br, 1 H)	2.98 (d, 3 H)						(m, 30 H)
(**3**)	—	4.24 (s, 3 H)	—	—	—	—	—	7.50—7.08
		3.20 (s, 3 H)						(m, 15 H)
(**4**)	8.84 (s, br, 1 H)	—	2.29—2.07 (m, 4 H)	1.98—1.80 (m, 2 H)	3.02 (t, 2 H)	1.30—1.02 (m, 4 H)	0.82 (t, 3 H)	—
	8.03 (s, br, 1 H)							
(**5**)	8.87 (s, br, 1 H)	3.08 (d, 3 H)	2.17 (m, 8 H)	1.53 (m, 4 H)	3.25 (t, 4 H)	1.25 (m, 8 H)	0.91 (t, 6 H)	—
	8.08 (s, br, 1 H)	2.83 (d, 3 H)						
(**6**)	—	3.28 (d, 3 H)	2.20—1.92 (m, 4 H)	1.68—1.40 (m, 2 H)	3.12 (t, 2 H)	1.32—1.22 (m, 4 H)	0.98 (t, 3 H)	—
		2.82 (d, 3 H)						

* Spectra recorded in $CDCl_3$. Chemical shifts δ (p.p.m.) are relative to $SiMe_4$.

Factors to be considered are the position of the carbene ligand, restricted rotation around the carbene carbon–nitrogen bond (*E* and *Z* isomers for $R^4 \neq R^5$), and different orientations of the phenyl groups attached to the bridging sulphur atoms (*syn* and *anti* isomers). The favoured co-ordination site for the unique ligand, in this case the carbene ligand, is the position opposite the iron–iron bond.[15]

I.r. spectral data for complexes (**1**)—(**6**) in the ν(CO) and ν(NH) regions are given in Table 1. The spectra consist characteristically of four ν(CO) bands when measured in CCl_4 and five bands if measured in hexane. The carbonyl frequencies of the dimethylaminocarbene complexes are at lower values than those found for the aminocarbenes. This is in accordance with a greater inductive effect of the methyl substituents resulting in an increased nitrogen–carbon bond order and a corresponding lesser π-acceptor interaction of the carbene ligand with the metal. Two signals which differ by *ca.* 90 cm^{-1} were recorded in the ν(NH) region for complexes (**1**) and (**4**) resulting from the symmetric and asymmetric vibrations of the NH_2 group. In the case of complexes (**2**) and (**5**), where two isomers are possible, the lower wavenumbers were assigned to complexes which have an *E* conformation and the higher numbers to those with a *Z* conformation with regard to the carbene carbon–nitrogen double bond. These assignments were

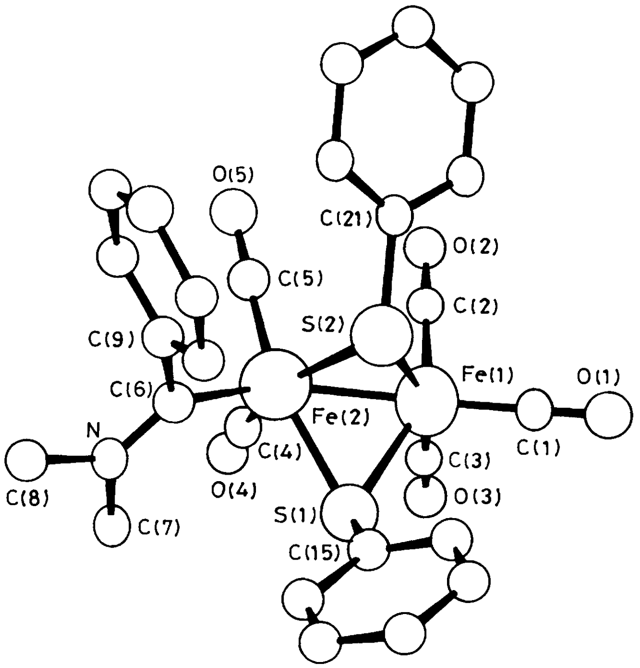


Figure. The molecular structure and atom numbering scheme for *anti*-$[Fe_2(\mu\text{-}SPh)_2(CO)_5\{C(NMe_2)Ph\}]$

Table 3. Selected bond lengths (Å) and angles for complex (**3**)

Fe(1)–Fe(2)	2.529(2)	Fe(1)–S(1)	2.288(3)
Fe(1)–S(2)	2.289(3)	Fe(1)–C(1)	1.75(1)
Fe(1)–C(2)	1.78(1)	Fe(1)–C(3)	1.77(1)
Fe(2)–S(1)	2.279(3)	Fe(2)–S(2)	2.297(3)
Fe(2)–C(4)	1.76(1)	Fe(2)–C(5)	1.76(1)
Fe(2)–C(6)	1.97(1)	S(1)–C(15)	1.76(1)
S(2)–C(21)	1.789(9)	N–C(6)	1.32(1)
N–C(7)	1.47(1)	N–C(8)	1.48(1)
O(1)–C(1)	1.17(1)	O(2)–C(2)	1.13(1)
O(3)–C(3)	1.14(1)	O(4)–C(4)	1.15(1)
O(5)–C(5)	1.15(1)	C(6)–C(9)	1.47(1)
Fe(2)–Fe(1)–S(1)	56.2(1)	Fe(2)–Fe(1)–S(2)	56.7(1)
S(1)–Fe(1)–S(2)	79.5(1)	Fe(2)–Fe(1)–C(1)	154.9(3)
S(1)–Fe(1)–C(1)	113.4(3)	S(2)–Fe(1)–C(1)	100.6(4)
Fe(2)–Fe(1)–C(2)	92.8(4)	S(1)–Fe(1)–C(2)	146.0(4)
S(2)–Fe(1)–C(2)	95.3(3)	C(1)–Fe(1)–C(2)	100.6(5)
Fe(2)–Fe(1)–C(3)	104.4(3)	S(1)–Fe(1)–C(3)	86.3(3)
S(2)–Fe(1)–C(3)	160.7(3)	C(1)–Fe(1)–C(3)	96.9(5)
C(2)–Fe(1)–C(3)	89.1(5)	Fe(1)–Fe(2)–S(1)	56.6(1)
Fe(1)–Fe(2)–S(2)	56.4(1)	S(1)–Fe(2)–S(2)	79.5(1)
Fe(1)–Fe(2)–C(4)	95.5(3)	S(1)–Fe(2)–C(4)	87.8(4)
S(2)–Fe(2)–C(4)	151.7(4)	Fe(1)–Fe(2)–C(5)	105.2(4)
S(1)–Fe(2)–C(5)	161.4(4)	S(2)–Fe(2)–C(5)	93.1(4)
C(4)–Fe(2)–C(5)	91.1(5)	Fe(1)–Fe(2)–C(6)	152.2(3)
S(1)–Fe(2)–C(6)	103.3(3)	S(2)–Fe(2)–C(6)	104.4(3)
C(4)–Fe(2)–C(6)	103.1(4)	C(5)–Fe(2)–C(6)	95.0(4)
Fe(1)–S(1)–Fe(2)	67.2(1)	Fe(1)–S(1)–C(15)	116.4(3)
Fe(2)–S(1)–C(15)	115.6(3)	Fe(1)–S(2)–Fe(2)	66.9(1)
Fe(1)–S(2)–C(21)	114.3(4)	Fe(2)–S(2)–C(21)	114.6(3)
C(6)–N–C(7)	123.4(9)	C(6)–N–C(8)	124.4(9)
C(7)–N–C(8)	112.2(8)	Fe(1)–C(1)–O(1)	176.3(9)
Fe(1)–C(2)–O(2)	178(1)	Fe(1)–C(3)–O(3)	175(1)
Fe(2)–C(4)–O(4)	174(1)	Fe(2)–C(5)–O(5)	178(1)
Fe(2)–C(6)–N	129.5(8)	Fe(2)–C(6)–C(9)	116.6(7)
N–C(6)–C(9)	113.9(9)	C(6)–C(9)–C(10)	123(1)
C(6)–C(9)–C(14)	117(1)		

Table 4. Crystal data

Formula	$C_{27}H_{21}Fe_2NO_5S_2$
M_r (g/mol)	615.3
Space group	$P2_1/n$
Crystal size (mm)	0.09 × 0.16 × 0.22
$F(000)$	1 256
a/Å	9.987(3)
b/Å	18.955(5)
c/Å	14.557(3)
β/°	107.74(2)
Z	4
D_c/g cm^{-3}	1.56
Reflections measured	4 978
Reflections used [$I > \sigma(I)$]	2 081
Variables refined	332
Weighting scheme	$1/\sigma_F^2$
$R = \Sigma\|F_o - F_c\|/\Sigma\|F_o\|$	0.061
$R' = (\Sigma w\|F_o - F_c\|^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.052
μ(Mo-K_α)/cm^{-1}	12.3

based on those reported for chromium and tungsten complexes with methylamino carbene ligands, where the different isomers were isolated and characterized independently.[16] No duplication of peaks occurred in the ν(CO) region and no conclusions could be drawn as to the existence of *syn* and/or *anti* isomers in solution. In the course of their investigations of *syn–anti* isomerism in $[Fe_2(CO)_6(\mu\text{-}SR)_2]$, Bor and co-workers[17] also observed no i.r. evidence for different forms of $[Fe_2(CO)_6(\mu\text{-}SPh)_2]$.

The ^1H n.m.r. spectra of compounds (**1**)—(**6**) are in accord with the given structures and were assigned as in Table 2. Two distinct different resonances were observed for the NH_2 protons of complexes (**1**) and (**4**) and the NMe protons of complexes (**3**) and (**6**), indicating different environments due to restricted rotation around the carbene carbon and nitrogen bond. Duplication of NH and NMe resonances of complexes (**2**) and (**5**) confirms the existence of two isomers in solution. The methyl resonances of greater δ values were assigned to the isomers with a *cis* conformation of the methyl groups with respect to the R^3 substituents (*E* isomer).[18]

X-*Ray Structure of* 1,1,1,2,2-*Pentacarbonyl*-2-*dimethylamino*-(*phenyl*)*methylene-di*-μ-*phenylthio-di-iron* (Fe–Fe) (**3**).—The conformation and atomic numbering scheme for the complex $[(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2\{C(NMe_2)Ph\}]$ (**3**) is shown in the Figure and selected bond lengths (Å) and angles (°) are listed in Table 3. The molecular structure is consistent with the i.r. and ^1H n.m.r. spectroscopic data given above. The Fe_2S_2 skeleton of the $Fe_2(CO)_5(\mu\text{-}SR)_2L$ unit has the well known butterfly structure, typical for bridged di-iron complexes of the type $[Fe_2(CO)_6(\mu\text{-}SR)_2]$. The dihedral angle between the normals to the planes Fe(1)–Fe(2)–S(1) and Fe(1)–Fe(2)–S(2) is 79.8°. The carbene ligand is in an apical position *trans* to the iron–iron bond. The phenyl groups of the bridging sulphur atoms are in an *anti* configuration and similar structural isomers were reported for $[Fe_2(\mu\text{-}SEt)_2(CO)_6]$ and $[Fe_2(\mu\text{-}SPh)_6]$.[19,20] In contrast, a *syn* conformation was reported for $[Fe_2(\mu\text{-}SMe)_2(CO)_4(PMe_3)_2]$.[21] Considerable distortion is found around the sp^2-hybridized carbene carbon due to the metal, other ligands, and the substituents on the carbene carbon.

A longer iron–carbon(carbene) bond length, 1.97(1) Å, compared to a shorter distance of 1.900(6) Å for the dithiocarbene $[Fe_2\{\mu\text{-}\overline{SC(S)SCH_2CH_2S}\}(\overline{CSCH_2CH_2S})(CO)_5]$ and the shortest distance of 1.850(7) Å for $[Fe_2(\mu\text{-}SCH_2CH_2CH_2S)\{C(OEt)Ph\}(CO)_5]$ all fall in line within the known electronic effects of these carbene moieties.

The carbene carbon–iron distance of 1.97(1) Å is comparable

Table 5. Fractional atomic co-ordinates (× 10^4 Å) for non-hydrogen atoms of complex (**3**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe(1)	5 308(2)	798(1)	3 139(1)	C(9)	9 111(10)	2 685(5)	4 211(8)
Fe(2)	7 347(2)	1 454(1)	4 281(1)	C(10)	8 972(11)	3 270(6)	4 725(9)
S(1)	7 617(3)	552(1)	3 318(2)	C(11)	8 904(13)	3 946(6)	4 320(11)
S(2)	6 067(3)	1 876(1)	2 794(2)	C(12)	8 968(12)	4 019(6)	3 410(12)
N	10 423(9)	1 756(4)	5 113(6)	C(13)	9 137(11)	3 441(6)	2 879(9)
O(1)	3 344(8)	404(5)	1 263(7)	C(14)	9 201(11)	2 772(6)	3 267(8)
O(2)	3 302(9)	1 343(5)	4 053(6)	C(15)	8 244(10)	794(5)	2 350(8)
O(3)	5 273(8)	73(4)	4 039(6)	C(16)	9 670(12)	891(6)	2 524(9)
O(4)	7 726(9)	409(4)	5 805(6)	C(17)	10 212(14)	1 015(8)	1 775(11)
O(5)	6 037(9)	2 430(5)	5 297(6)	C(18)	9 362(16)	1 063(7)	837(11)
C(1)	4 168(12)	561(6)	2 002(9)	C(19)	7 954(13)	968(6)	672(9)
C(2)	4 086(12)	1 140(6)	3 695(8)	C(20)	7 371(11)	847(5)	1 395(8)
C(3)	5 267(10)	21(6)	3 717(8)	C(21)	4 912(11)	2 591(5)	2 827(7)
C(4)	7 638(11)	838(6)	5 229(8)	C(22)	5 483(12)	3 249(6)	3 126(10)
C(5)	6 576(11)	2 051(6)	4 900(8)	C(23)	4 606(16)	3 811(7)	3 147(10)
C(6)	9 157(10)	1 960(5)	4 583(6)	C(24)	3 187(16)	3 733(8)	2 831(10)
C(7)	10 728(12)	1 046(5)	5 545(10)	C(25)	2 616(14)	3 093(9)	2 487(10)
C(8)	11 693(10)	2 216(6)	5 369(9)	C(26)	3 489(11)	2 522(6)	2 469(8)

to the value of 1.95(1) Å found for the monoiron aminocarbene complex $[\mathrm{Fe(CO)_3(PEt_3)\{\overline{CN(Me)CH_2CH_2N}Me\}}]$.[5]

The very short carbene carbon–nitrogen bond length of 1.32(1) Å comfirms restricted rotation around this bond and supports conclusions drawn from the spectroscopic data.

Experimental

All reactions and manipulations were carried out under a nitrogen atmosphere and solvents were dried prior to use. Reagent grade chemicals were used without further purification. The carbene complexes $[\mathrm{(OC)_3Fe\{\mu\text{-}S(CH_2)_3S\}Fe(CO)_2\{C(OEt)Bu\}}]$ and $[\mathrm{(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2\{C(OEt)Ph\}}]$ were prepared as reported previously.[11,22] Column chromatography on SiO_2 (0.063—0.200 nm) was performed on 2 cm × 35 cm columns at −10 °C. Microanalyses were performed by F. Pascher and E. Pascher, Microanalytical Laboratories, Remagen, Western Germany. Infrared spectra were recorded on a Bruker IFS 113V spectrometer and calibrated against polystyrene, ^{1}H n.m.r. spectra on a Bruker AC 300 MHz instrument, and mass spectra on a Perkin-Elmer RMU-6H instrument operating at 70 eV (1.12×10^{-17} J). Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected.

Synthesis.—The method described for the reaction of $[\mathrm{(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2\{C(OEt)Ph\}}]$ with dimethylamine is representative of the general procedure followed for all the reactions with the amines.

Through a stirred solution of $[\mathrm{(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2\{C(OEt)Ph\}}]$ (3.02 g, 5 mmol) in diethyl ether (20 cm^3) was bubbled a slow stream of dimethylamine. The reaction course was followed by thin-layer chromatography (SiO_2). After 40 min all of the starting carbene complex was consumed. The solvent was removed under high vacuum and the residue was chromatographed at −20 °C with hexane–dichloromethane (5:2) as eluant. The first red zone was collected, stripped of solvent, and recrystallized from pentane. Three more zones were eluted with hexane–dichloromethane (1:1) as eluant, the solvent removed under vacuum, and the products recrystallized from dichloromethane–hexane mixtures. From the first fraction red needles (0.45 g, 0.9 mmol), of $[\mathrm{(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_3}]$ were obtained, from the second fraction, red-brown crystals (0.27 g, 0.45 mmol) of $[\mathrm{(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2\{C(NHMe)Ph\}}]$ were obtained, from the third fraction, $[\mathrm{(OC)_3Fe(\mu\text{-}SPh)_2Fe(CO)_2\{C(NMe_2)Ph\}}]$ (1.15 g, 1.9 mmol), and from the fourth fraction $[\mathrm{Fe_2(CO)_4(\mu\text{-}SPh)_2(NHMe_2)_2}]$ (0.21 g, 0.4 mmol).

Crystal Structure Determination.—Reflections were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,73$ Å). Cell dimensions were obtained by a least-squares fitting of the setting angles of 24 standard reflections with $\theta = 12$—13°. A variable scan speed and an ω—2θ scan were employed. The ω-scan angle changed as $(0.85 + 0.35\tan\theta)^\circ$, the horizontal aperture as $(1.12 + 1.05\tan\theta)$ mm. The vertical slit was fixed at 4 mm. Intensity checks were performed every hour (no significant decay), and a crystal orientation every 200 reflections. Data were corrected for Lorentz and polarization effects and for absorption using an empirical method involving φ scans. The structure was solved by Patterson and Fourier methods, and refined anisotropically.[23] Hydrogen atoms were placed in calculated positions and refined riding upon their corresponding non-H atoms with the common thermal parameter $U = 0.092(9)$ A^2. Crystal data are summarized in Table 4 and the fractional atomic co-ordinates for non-hydrogen atoms are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises the atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

Financial support by the Foundation of Research and Development (FRD), Pretoria is gratefully acknowledged by S. L.

References

1 Part 2, S. Lotz, J. L. M. Dillen, and M. M. van Dyk, *J. Organomet. Chem.*, 1989, **371**, 371.
2 H. Werner, E. O. Fischer, B. Heckl, and C. G. Kreiter, *J. Organomet. Chem.*, 1971, **28**, 367.
3 H. G. Raubenheimer, G. J. Kruger, W. H. Viljoen, and A. van A. Lombard, *J. Chem. Res.*, 1982, (M) 2034.
4 E. O. Fischer, H-J. Beck, C. G. Kreiter, J. Lynch, J. Muller, and E. Winkler, *Chem. Ber.*, 1972, **105**, 162.
5 P. B. Hitchcock, M. F. Lappert, S. A. Thomas, A. J. Thorne, A. J. Carty, and N. J. Taylor, *J. Organomet. Chem.*, 1986, **315**, 27.

6 M. F. Lappert, J. J. MacQuitty, and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1981, 1583.
7 K. Ofele and C. G. Kreiter, *Chem. Ber.*, 1972, **105**, 529.
8 M. F. Semmelhack and J. Park, *Organometallics*, 1986, **5**, 2550.
9 A. Lagadec, B. Bisterklewicz, A. Darchen, D. Grandjean, A. Mousser, and H. Patin, *Organometallics*, 1988, **7**, 242.
10 J. P. Collman, R. K. Rothrock, R. G. Finke, E. J. Moore, and F. Rose-Munch, *Inorg. Chem.*, 1982, **21**, 146.
11 S. Lotz, P. H. van Rooyen, and M. M. van Dyk, *Organometallics*, 1987, **6**, 499.
12 H. G. Raubenheimer, S. Lotz, H. Kruger, and G. Gafner, *J. Organomet. Chem.*, 1979, **173**, C1.
13 H. G. Raubenheimer, J. C. A. Boeyens, and S. Lotz, *J. Organomet. Chem.*, 1976, **112**, 145.
14 F. R. Kreissl, E. O. Fischer, C. G. Kreiter, and H. Fischer, *Chem. Ber.*, 1973, **106**, 1262.
15 J. A. de Beer, R. J. Haines, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 1971, 3271.
16 E. Moser and E. O. Fischer, *J. Organomet. Chem.*, 1969, **16**, 275.
17 L. Maresca, F. Greggio, G. Sbringnadello, and G. Bor, *Inorg. Chim. Acta*, 1971, **5**, 667.
18 E. O. Fischer and M. Leupold, *Chem. Ber.*, 1972, **105**, 599.
19 L. F. Dahl and C-H. Wei, *Inorg. Chem.*, 1963, **2**, 328.
20 W. Henslee and R. Davis, *Cryst. Struct. Commun.*, 1972, **1**, 404.
21 G. le Borgne, D. Grandjean, R. Mathieu, and R. Poilblanc, *J. Organomet. Chem.*, 1977, **131**, 429.
22 S. Lotz, unpublished work.
23 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determinations, University of Cambridge, 1976.

Received 29*th November* 1988; *Paper* 8/04722G