Nitrogen Derivatives of Iron Carbonyls. Part 8. Synthesis and Structure of (μ-benzylcarboxy) (μ-propylideneamido)bis(tricarbonyliron)(Fe–Fe)

O. GAMBINO, G. GERVASIO, R. ROSSETTI and P. L. STANGHELLINI*

Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Turin, Italy

Received July 28, 1983

The paper reports the synthesis, spectroscopic properties and structural characterization of a new di-iron carbonyl compound $Fe_2(CO)_6(\mu\text{-}OCCH_2C_6H_5)$-$(\mu\text{-}NC(CH_3)_2)$, obtained in the reaction between $Fe_3(CO)_{12}$ and 2-nitropropane in toluene solution.

The complex crystallizes in the monoclinic $P2_1/n$ space group with $a = 19.70(5)$, $b = 11.62(4)$, $c = 16.78(4)$ Å and $\beta = 95.19(2)°$, $Z = 8$ and shows the presence of two independent molecules in the unit cell. The molecular structure consists basically of two $Fe(CO)_3$ units, joined by a Fe–Fe bond and bridged by the benzylcarboxy and isopropylene amido ligands. The presence of the former ligand represents a proof of activation of the solvent, which probably occurs via an unstable hydrido alkyl iron intermediate.

Introduction

Some years ago [1] we described the reaction of $Fe_3(CO)_{12}$ with nitroethane and 2-nitropropane in boiling benzene, and we characterized the iron carbonyl compounds formed in the reaction by means of i.r., n.m.r., mass spectroscopy and X-ray diffraction [2]. The reaction products, mostly di-iron carbonyl complexes, coordinate bridging N– or ON–alkyl ligands, in which the alkyl groups are clearly derived from the starting nitroalkane. The reaction with 2-nitropropane carried out in toluene solution did not give any substantial difference from the previous one, only the presence of a new di-iron compound (obtained in moderate yield) whose spectroscopic data did not allow an easy interpretation of the structure on the basis of the starting reagent.

The structure was then solved by means of the X-ray diffraction analysis and, even if substantially related to the other complexes of the series, it shows unexpectedly the presence of a benzyl carboxy bridging group, which is clearly indicative of a new reaction path *i.e.* the activation of the solvent.

Experimental

Synthesis and Spectroscopic Properties

The preparation of the complex $Fe_2(CO)_6$-$(\mu OCCH_2C_6H_5)(\mu\text{-}NC(CH_3)_2)$ was carried out by reacting equimolar quantities of $Fe_3(CO)_{12}$ and 2-nitropropane dissolved in hot toluene (*ca.* 80 °C) under CO atmosphere for *ca.* 2hrs. The filtered solution was evaporated to dryness and the residue chromatographed by TLC (adsorbent Kieselgel 60 Merck, eluent petroleum ether). All the reaction products were isolated and identified as reported previously [1]: the new compound appears as a yellow band, which moves very little from the baseline. The fraction was scraped out from the plate and the compound recovered by extraction with ethyl ether. Good crystals were obtained after repeated TLC purifications and final crystallization from n-heptane solution at −20 °C. The compound appeared as well-shaped orange crystals which melt at 63 °C, are stable in air, and which are very soluble in organic solvents.

Typical i.r. bands are at 2070m, 2028s, 1999s, 1988m, 1979m, 1961m cm^{-1} (n-heptane solution) and at 3063w, 3030w, 2957m, 2923m, 2854m, 1654m, 1602m, 1505s, 1495s, 1455m, 1426m, 1358m, 1161m, 1076m, 1030s, 703s, 684s, 670m, 624m, 605m, 594m, 577s, 565m, 530m, 499m, 461m, 436w, 415w cm^{-1} (CsI disk).

The ^1H n.m.r. spectrum shows signals at 2.48 (3: singlet), at 2.72 (3:singlet), at 3.73 (2:quadruplet), at 6.8–7.4 (5:multiplet) (CDCl₃ solution, δ/ppm values downfield positive with respect to Si(CH₃)₄). Main mass peaks (m/e, referred to ^{56}Fe) are: 455s, 427s, 399m, 371s, 364m, 343s, 336m, 315s, 308w, 306m, 287s, 280m, 278s, 259vs, 250m, 222s, 218vs, 194vs.

Crystal Structure Determination

The crystals, sealed in thin-walled glass capillaries under nitrogen, showed monoclinic symmetry with $a = 19.70(5)$, $b = 11.62(4)$, $c = 16.78(4)$ Å and $\beta = 95.19(2)°$, $U = 3825.4$ Å^3, M.W. = 455.00. The lattice parameters were determined from θ values of 25

*Author to whom correspondence should be addressed.

reflections centered on a Philips PW 1100 automatic diffractometer. A total of 3789 reflection intensities were collected on the same diffractometer up to $2\theta = 40°$ (graphite monochromatized MoK$_\alpha$ radiation, scan width $1.50°$, scanning speed $0.05°$ sec^{-1}, background 5 sec, ω scanning). Standard reflections were checked at regular intervals but no significant change was detected.

The observed systematic absences h00 with $h = 2n + 1$, 0k0 with $k = 2n + 1$, 001 with $l = 2n + 1$, h0l with $h + l = 2n + 1$, indicate the P2$_1$/n space group.

With molecular weight M.W. = 455.00, $Z = 8$ the density of 1.58 g cm^{-3} is plausible, so the hypothesis of 2 independent molecules in the asymmetric unit was assumed, and fully confirmed by the resolution and refinement of the structure.

The iron atoms were located with the aid of the Patterson map together with the automatic centrosymmetric direct methods of the SHELX-76 programs [3].

A sequence of difference maps followed by least-squares refinements allowed us to locate all the other C, O and N atoms. At this stage the anisotropic(Fe)-isotropic(C, O, N) refinement, using 2107 observed reflections with $F_o > 4\sigma(F_o)$, led to $R = \Sigma|F_o - F_c|/\Sigma|F_o| = 0.074$. A difference map showed residual peaks 0.5–0.8 e Å^{-3} high, corresponding to the majority of hydrogen atoms of the -CH$_2$, -CH$_3$ and -C$_6$H$_5$ groups.

In the final least-squares cycles the methyl, methylene and phenyl groups were treated as rigid groups and all the other atoms were refined anisotropically.

The final R was 0.056 and R_w was 0.048. The weighting scheme was w = $1/(\sigma(F)^2 + aF^2)$ where a was varied in order to maintain $\Sigma w\Delta^2$ constant for the amplitudes batched in various ranges of $|F_o|$. Correction for absorption was made according to the method of North, Phillips and Mathews [4]: the maximum and minimum transmission factors were 1.0 and 0.84. No extinction correction was applied. Atomic coordinates for the two independent molecules A and B are listed in Table I [5].

Discussion

The final structural parameters of the two crystallographically independent molecules (A and B) are collected in Table II, and a relevant view is given

TABLE I. Fractional Atomic Coordinates for the Non-Hydrogen Atoms of the Two Independent Molecules of Fe$_2$(CO)$_6$-(OCCH$_2$C$_6$H$_5$)(N=C(CH$_3$)$_2$). The Atoms Belonging to Rigid Groups are Marked by Asterisk.

	Molecule A			Molecule B		
Atom	x/a	y/b	z/c	x/a	y/b	z/c
Fe(1)	0.6112(1)	0.3290(1)	0.9020(1)	0.1052(1)	0.5606(1)	0.8907(1)
Fe(2)	0.6854(1)	0.1858(1)	0.8406(1)	0.1770(1)	0.4096(1)	0.8352(1)
C(1)	0.6753(6)	0.4306(11)	0.9337(7)	0.1711(6)	0.6547(12)	0.9252(8)
C(2)	0.5399(7)	0.4296(12)	0.8996(8)	0.0394(7)	0.6702(12)	0.8838(9)
C(3)	0.6123(6)	0.2730(12)	1.0017(8)	0.0980(7)	0.5088(11)	0.9903(8)
C(4)	0.7694(7)	0.2557(12)	0.8571(7)	0.2617(7)	0.4737(10)	0.8542(7)
C(5)	0.7073(7)	0.0973(12)	0.7625(7)	0.2013(6)	0.3137(11)	0.7593(7)
C(6)	0.7040(6)	0.0917(11)	0.9246(8)	0.1915(6)	0.3193(12)	0.9207(8)
C(7)	0.6378(6)	0.3808(12)	0.7319(8)	0.1430(5)	0.6070(11)	0.7239(7)
C(8)*	0.5972(6)	0.4899(11)	0.7253(8)	0.1119(6)	0.7257(10)	0.7159(8)
C(9)*	0.6718(6)	0.3432(11)	0.6615(7)	0.1778(6)	0.5640(12)	0.6545(7)
C(10)	0.5918(6)	0.1311(12)	0.8314(7)	0.0820(6)	0.3663(11)	0.8232(7)
C(11)*	0.5607(6)	0.0190(12)	0.7960(7)	0.0489(6)	0.2533(12)	0.7879(7)
C(12)*	0.5774(3)	−0.0800(6)	0.8515(5)	0.0689(3)	0.1537(6)	0.8420(5)
C(13)*	0.6091(3)	−0.2583(6)	0.9599(5)	0.1128(3)	0.0676(6)	0.8198(5)
C(14)*	0.6447(3)	−0.2473(6)	0.8921(5)	0.1341(3)	−0.0190(6)	0.8739(5)
C(15)*	0.6091(3)	−0.2583(6)	0.9599(5)	0.1115(3)	−0.0195(6)	0.9504(5)
C(16)*	0.5576(3)	−0.1801(6)	0.9735(5)	0.0676(3)	0.0666(6)	0.9726(5)
C(17)*	0.5418(3)	−0.0910(6)	0.9193(5)	0.0463(3)	0.1532(6)	0.9184(5)
O(1)	0.7180(5)	0.4953(7)	0.9516(5)	0.2138(4)	0.7179(7)	0.9458(5)
O(2)	0.4945(5)	0.4900(10)	0.9026(7)	−0.0025(5)	0.7382(9)	0.8821(7)
O(3)	0.6121(5)	0.2392(9)	1.0657(5)	0.0966(5)	0.4710(9)	1.0539(6)
O(4)	0.8219(5)	0.2913(9)	0.8695(6)	0.3161(4)	0.5084(8)	0.8672(5)
O(5)	0.7251(5)	0.0365(9)	0.7131(6)	0.2201(5)	0.2520(8)	0.7132(6)
O(6)	0.7138(5)	0.0350(8)	0.9800(5)	0.2021(5)	0.2637(8)	0.9763(6)
O(7)	0.5507(4)	0.1998(7)	0.8592(4)	0.0415(4)	0.4388(7)	0.8467(5)
N	0.6420(4)	0.3255(8)	0.7974(6)	0.1394(4)	0.5511(7)	0.7879(5)

TABLE II. Interatomic Bond (Å) and Angles (°) of $Fe_2(CO)_6(OCCH_2C_6H_5)(N=C(CH_3)_2)$.

	Molecule A	Molecule B		Molecule A	Molecule B
Fe(1)–Fe(2)	2.499(2)	2.487(3)	C(4)–Fe(2)–C(6)	92.0(5)	91.3(5)
Fe(1)–C(1)	1.775(14)	1.755(14)	C(4)–Fe(2)–C(10)	171.6(6)	170.0(6)
Fe(1)–C(2)	1.824(15)	1.815(15)	C(4)–Fe(2)–N	92.7(5)	91.9(4)
Fe(1)–C(3)	1.794(15)	1.793(13)	C(5)–Fe(2)–C(6)	100.6(6)	99.9(6)
Fe(1)–N	1.908(10)	1.911(10)	C(5)–Fe(2)–C(10)	92.6(6)	94.7(6)
Fe(1)–O(7)	2.009(8)	1.989(7)	C(5)–Fe(2)–N	110.0(5)	110.7(5)
Fe(2)–C(4)	1.842(14)	1.829(13)	C(6)–Fe(2)–C(10)	89.3(5)	90.8(5)
Fe(2)–C(5)	1.751(15)	1.789(14)	C(6)–Fe(2)–N	148.4(5)	148.8(5)
Fe(2)–C(6)	1.795(14)	1.779(15)	C(10)–Fe(2)–N	82.0(5)	81.3(4)
Fe(2)–C(10)	1.943(12)	1.930(12)	C(8)–C(7)–C(9)	118.0(1.2)	116.7(1.1)
Fe(2)–N	1.945(9)	1.943(9)	C(8)–C(7)–N	119.0(1.3)	119.4(1.2)
			C(9)–C(7)–N	123.1(1.2)	123.9(1.1)
Fe(2)–Fe(1)–C(1)	98.0(4)	97.8(4)	Fe(2)–C(10)–C(11)	130.6(1.0)	128.9(1.0)
Fe(2)–Fe(1)–C(2)	153.6(4)	154.0(5)	Fe(2)–C(10)–O(7)	113.7(1.0)	115.6(9)
Fe(2)–Fe(1)–C(3)	100.6(4)	102.0(5)	C(11)–C(10)–O(7)	115.7(1.0)	115.4(1.0)
Fe(2)–Fe(1)–N	50.2(3)	50.4(3)	C(12)–C(11)–C(10)	110.7(8)	109.9(8)
Fe(2)–Fe(1)–O(7)	72.8(3)	73.7(3)	Fe(1)–N–Fe(2)	80.9(4)	80.4(4)
C(1)–Fe(1)–C(2)	96.1(5)	95.0(6)	Fe(1)–N–C(7)	141.7(9)	142.2(9)
C(1)–Fe(1)–C(3)	90.7(5)	91.2(6)	Fe(2)–N–C(7)	137.4(9)	137.2(9)
C(1)–Fe(1)–N	90.8(4)	91.3(5)	Fe(1)–O(7)–C(10)	103.1(8)	101.4(7)
C(1)–Fe(1)–O(7)	170.8(5)	171.5(5)			
C(2)–Fe(1)–C(3)	101.4(6)	100.3(6)			
C(2)–Fe(1)–N	107.5(5)	106.9(5)	C(1)–O(1)	1.148(12)	1.146(12)
C(2)–Fe(1)–O(7)	92.4(5)	93.0(5)	C(2)–O(2)	1.141(13)	1.140(13)
C(3)–Fe(1)–N	150.7(5)	152.4(5)	C(3)–O(3)	1.144(10)	1.157(13)
C(3)–Fe(1)–O(7)	91.1(5)	90.4(5)	C(4)–O(4)	1.115(12)	1.146(12)
			C(5)–O(5)	1.166(14)	1.142(12)
N–Fe(1)–O(7)	83.3(3)	83.4(4)	C(6)–O(6)	1.141(12)	1.138(13)
Fe(1)–Fe(2)–C(4)	101.3(4)	100.8(4)	C(7)–C(8)	1.499(15)	1.511(15)
Fe(1)–Fe(2)–C(5)	153.3(4)	154.7(4)	C(7)–C(9)	1.475(15)	1.489(15)
Fe(1)–Fe(2)–C(6)	99.6(4)	99.7(4)	C(7)–N	1.269(13)	1.264(12)
Fe(1)–Fe(2)–C(10)	70.4(4)	69.2(4)	C(10)–C(11)	1.536(17)	1.559(16)
Fe(1)–Fe(2)–N	48.9(3)	49.3(3)	C(10)–O(7)	1.256(13)	1.249(12)
C(4)–Fe(2)–C(5)	95.3(6)	94.5(5)	C(11)–C(12)	1.498(15)	1.501(14)

in Fig. 1. Slight differences between A and B (vide infra) are probably due to crystal packing effects.

The complex has the $Fe_2(CO)_6(\mu\text{-}OCCH_2C_6H_5)$-$(\mu\text{-}NC(CH_3)_2)$ formula and basically consists of two Fe(CO)₃ groups, joined by an Fe–Fe bond and bridged by benzylcarboxy and propylideneamido ligands. The ligands form four- and three-atom rings respectively, which share the Fe–Fe edge.

The more strained Fe–Fe–N ring causes greater shortening effect on the Fe–Fe distance than the Fe–Fe–O–C ring: not surprisingly this value (2.493 Å) is exactly the average of the values reported for the complexes $Fe_2(CO)_6(OCC_6H_5)_2$ (2.568 Å) [6] and $Fe_2(CO)_6(N:C(CH_3)_2)_2$ (2.412 Å) [2], in which the Fe–Fe bond is the common edge of the same rings (two Fe–Fe–O–C and two Fe–Fe–N rings, respectively).

In general the length of an Fe–Fe bond belonging to two rings is in the order: (i) (3-atoms ring)₂ < (ii)
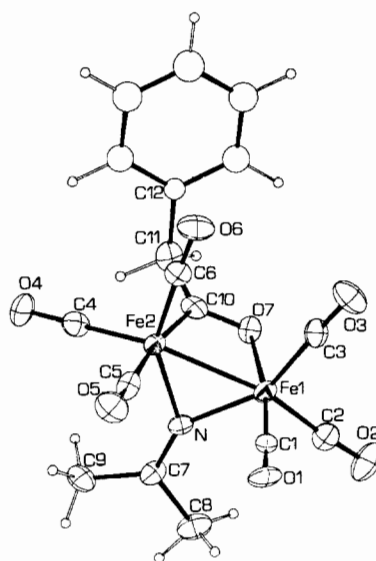

Fig. 1. ORTEP drawing of $Fe_2(CO)_6(OCCH_2C_6H_5)(N=C(CH_3)_2)$ with 25% probability ellipsoids.

TABLE III. Planes and Dihedral Angles.

Planes	Atoms[a]						Equation[b]				
α	Fe(1)	Fe(2)	N	C(7)	C(8)	C(9)	A	B	C	D	χ^{2} [c]
molecule A	−2(3)	1(3)	3(16)	−3(23)	12(22)	−11(21)	15.4	6.1	4.3	15.3	1.2
molecule B	−8(3)	14(3)	−49(14)	−15(20)	101(22)	−58(22)	15.7	5.4	5.1	9.3	73.5
β	N	C(7)	C(8)	C(9)							
molecule A	1(16)	−3(23)	1(22)	1(21)			15.5	6.1	4.2	15.3	0.0
molecule B	2(14)	−6(20)	2(21)	2(22)			16.3	4.7	5.1	8.9	0.1
γ	Fe(2)	C(10)	C(11)	O(7)							
molecule A	0(3)	0(22)	0(22)	0(14)			1.5	−5.1	14.8	12.6	0.0
molecule B	0(3)	0(21)	0(22)	0(14)			0.36	−4.8	15.2	10.8	0.0

Dihedral angles	molecule A	molecule B
α−γ	83°	81°
α-phenyl ring	76°	85°

[a] Distance (e.s.d.) in Å 10^{3} from the plane below the respective atoms. [b] Equation of the least-squares plane in the form AX + BY + CZ = D in fractional coordinates, referred to the cell axes. [c] $\chi^{2} = \Sigma (d/\sigma)^{2}$ gives the statistical significance of the planarity. [d] Distance of Fe(1): 69×10^{-3} Å (molecule A) and 100×10^{-3} Å (molecule B).

(3-atoms ring) (4-atoms ring) < (iii) (4-atoms ring)$_2$, when the heteroatom of the 3 atoms rings is nitrogen without N–N bond. Examples are: (i): Fe$_2$(CO)$_6$-(N=CHCH$_3$)$_2$ (2.415(2) Å) [2] and Fe$_2$(CO)$_6$(N=CPh$_2$)$_2$ [7] (2.403(6) Å); (ii): Fe$_2$(CO)$_6$(ON=C(CH$_3$)$_2$)(N=C(CH$_3$)$_2$) (2.484(5) Å) [8], the present Fe$_2$(CO)$_6$(OCCH$_2$C$_6$H$_5$)(N=C(CH$_3$)$_2$) (2.493(2) Å) and Fe$_2$(CO)$_6$(ON=C(CH$_3$)$_2$)(NHCH(CH$_3$)$_2$) (2.470-(1) Å) [2]; (iii): Fe$_2$(CO)$_6$(OCC$_6$H$_5$)$_2$ (2.568 Å) [6]. The reverse order occurs when the heteroatom of the 3-membered ring is a large atom, like As [9].

The NC(7)–C(8)–C(9) skeleton of the propylideneimido ligand is planar, the N–C(7) double bond distance (1.26 Å) indicating a formal sp^2 hybridization of the C(7) valence orbitals. Moreover, in the molecule A the two iron atoms belong to the same plane, whereas the form B shows a slight distortion (Table III).

The benzylcarboxy ligand shows a good planarity of the C(10), C(11), O(7) and Fe(2) framework, whereas the Fe(1) atom is *ca.* 0.1 Å out of plane. Both the Fe(2)–C(10) and the C(10)–O(7) bonds have partial double bond character, when their lengths are compared with those of the formal single bonds [12]. A large π-electron delocalization on the Fe(2)–C(10)–O(7) system is thus suggested, indicating a carbenic character of the C(10) atom [13].

The phenyl ring is folded with respect to the FeC$_2$O plane, by a different extent in the two A and B molecules (Table III).

Spectroscopic data agree with the reported structure. Infrared spectra shows six bands in the CO stretching region, indicating that the local C$_{2v}$ symmetry is completely removed by the two structurally and electronically different bridging groups [14]. The absence of a strong CO chetonic absorption around 1700 cm^{-1} is due to the reduced C–O bond order, which probably shifts this mode in the 1500 cm^{-1} zone, together with the phenyl ring stretching modes.

Signals in the proton n.m.r. spectrum are easily assigned on the basis of chemical shift, multiplicity and intensity values; in particular, the methylene protons give rise to an AB system, centered at 3.73 δ, with coupling constant value J$_{AB}$ = 14.2 Hz.

Mass spectra show, as expected, the main peaks corresponding to the molecular ion M$^+$ and to the (M – nCO)$^+$ ions (n = 1–7). Medium–strong intensity peaks correspond to the ions formed from M$^+$ by elimination of the benzyl fragment and by subsequent loss of CO and/or H$_2$.

The reaction mechanism of the reduction of nitroalkane by iron carbonyls has been inferred on the basis of the structure of the organic and organometallic products [1, 15]. The commonly accepted main path is the formation of a nitrene species, which, together with partial dehydrogenation of the isopropyl group, leads to the formation of the bridging propylideneamido ligand. On the other hand, the presence of the benzylcarboxy group evidences another reaction path, *i.e.* the activation of the solvent, and gives the direct proof of that the solvent was previously indicated as a probable source of hydrogen atom to obtain amines formamides and ureas [15]. A plausible way could be an oxidative addition of an electron-deficient iron centre to the methylic C–H bond of the toluene, to give an hydrido alkyl intermediate:

$$Fe + CH_3-C_6H_5 \longrightarrow Fe(H)(CH_2C_6H_5)$$
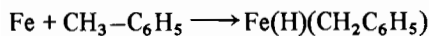
<div align="center">I</div>

Subsequent steps could be benzyl migration on a CO group bonded to Fe and oxygen coordination to an adjacent iron atom. Hydrogen can be easily abstracted from the intermediate with the probable help of the isopropylic H, which has been reported to be particularly reactive [1b].

The activation of very unreactive materials such as saturated hydrocarbons is an interesting topic in organometallic chemistry, and recently it has been possible to isolate stable hydrido alkyl metal complexes formed by insertion of a transition metal centre on a saturated C–H bond [16]. In the present reaction the non-isolation of a hydrido intermediate can be related to the oxidative effect of the nitro and/or nitroso groups; unstable hydrido derivatives like (I) should play an important role in the reduction of the nitro compounds. Finally, it is noteworthy that no complexes containing toluenic or phenyl groups were recovered when the reaction was carried in benzene solution, indicating that the metal-centre insertion seems to favour the primary C–H bonds.

Acknowledgement

References

1 a) S. Aime, L. Milone, R. Rossetti and P. L. Stanghellini, *Gazz. Chim. Ital.*, *105*, 617 (1975). b) S. Aime, G. Gervasio, L. Milone, R. Rossetti and P. L. Stanghellini, *J. Chem. Soc. Dalton*, 534 (1978).
2 a) S. Aime, G. Gervasio, L. Milone, R. Rossetti and P. L. Stanghellini, *J. Chem. Soc. Chem. Comm.*, 370 (1976). b) G. Gervasio, R. Rossetti and P. L. Stanghellini, *J. Chem. Res.*, *(M)* 3943, *(S)* 334 (1979). c) G. Gervasio, P. L. Stanghellini and R. Rossetti, *Acta Crystallogr. Sect. B, B 37*, 1198 (1981).
3 G. M. Sheldrick, 'SHELX 76, a system of computer programs', Cambridge University, Cambridge, England 1976.
4 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A, A24*, 351 (1968).
5 Listing of the structure factor amplitudes and of the thermal parameters is available from the Editor upon request.
6 P. F. Lindley and O. S. Mills, *J. Chem. Soc. (A)*, 1279 (1969).
7 D. Bright and O. S. Mills, *J. Chem. Soc. Chem. Comm.*, 245 (1967).
8 G. B. Khare and R. J. Doedens, *Inorg. Chem.*, *15*, 86 (1976).
9 *E. g.*: Fe₂(CO)₆(As(CH₃)₂)₂ (two Fe–Fe–As rings: 2.74-(3) A) [10], Fe₂(CO)₆(As(CH₃)₂)(OCN(CH₃)₂) (one Fe–Fe–O–C and one Fe–Fe–As rings: 2.639(3) Å) [11].
10 E. Keller and H. Vahrenkamp, *Chem. Ber.*, *110*, 430 (1977).
11 E. Keller, A. Trenkle and H. Vahrenkamp, *Chem. Ber.*, *110*, 441 (1977).
12 M. R. Churchill and S. W. Y. Ni Chong, *J. Am. Chem. Soc.*, *95*, 5931 (1973).
13 F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, *16*, 487 (1972).
14 G. Bor, *J. Organomet. Chem.*, *94*, 181 (1975). G. Bor, S. F. A. Kettle and P. L. Stanghellini, *Inorg. Chim. Acta*, *18*, L18 (1976).
15 A. J. Carty, *Organomet. Chem. Rev.*, *A7*, 191 (1972).
16 M. Berry, K. Elmitt and M. L. H. Green, *J. Chem. Soc. Dalton*, 1950 (1979). A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, *104*, 352 (1982).