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CUMULATED DOUBLE BOND SYSTEMS AS LIGANDS

XI *. DI- AND TRI-NUCLEAR IRON COMPLEXES RESULTING FROM THE REACTION OF [$Fe_2(CO)_9$] WITH R—N=S=N—R (R = t-C_4H_9, 4-MeC_6H_4); CRYSTAL AND MOLECULAR STRUCTURE OF [$Fe_2(CO)_6${RNC(O)S}], [$Fe_3(CO)_9$(RNS)S] AND [$Fe_3(CO)_9$(RN)S]

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Summary

Reaction of R—N=S=N—R (R = t-C_4H_9, 4-MeC_6H_4) with [$Fe_2(CO)_9$[leads to the rupture of one or two N=S double bonds as evidenced by the formation of a number of complexes containing R—NS, R—N and S fragments. In the case of R = t-C_4H_9 and 4-MeC_6H_4 the RNS fragment behaves as a four-electron donor ligand, with the NS bond still double, and as a six-electron donor ligand, with the NS bond single, bridging two iron atoms in [$Fe_2(CO)_7$(RNS)] and [$Fe_2(CO)_6$(RNS)], respectively.

Insertion of CO into the NS bond of [$Fe_2(CO)_6$(RNS)] yields [$Fe_2(CO)_6${RNC(O)S}]; a crystal structure determination has been carried out for the product with R = 4-MeC_6H_4. Heating of the solid complex affords azotoluene, which is also isolated from the reaction mixtures. In the case of R = t-C_4H_9-[$Fe_2(CO)_6S_2$], [$Fe_3(CO)_9S_2$] and [$Fe_3(CO)_9$(RNS)S] are also formed. A crystal structure determination of the last compound reveals a prismane type structure, in which both a six-electron donor RNS fragment and a four-electron donor S atom are linked to the three iron atoms.

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For R = 4-MeC_6H_4 a different trinuclear iron complex [$Fe_3(CO)_9(RN)S$] was isolated, and the structure was established by a crystal structure determination; a nitrene fragment (RN) as well as a S atom are both triply bridging to a non linear array of three iron atoms of the $Fe_3(CO)_9$ skeleton.

Introduction

Research on the coordination behaviour of *N,N'*-disubstituted sulfurdiimines, R—N=S=N—R, and *N*-sulfinylanilines, R—N=S=O, towards metal atoms has shown that, depending on the type of metal atom, the ligands may bond via the N atom, the S atom or the π-N=S bond [1—6]. Metal—π-N=S bonding is especially favoured when the metal atom is in a low oxidation state, e.g., Rh^I, Ir^I [1], Ni^0 [2] and Pt^0 [3], i.e., where extensive π-backbonding to the empty π^*-orbitals of the N=S bond is possible. The metal—π-N=S bond is particularly interesting, as it offers an opportunity of activating the N=S bond. It has been found that [$Pt(PPh_3)_2$(Ar—N=S=N—Ar)], which contains a metal—π-N=S bond, is only stable in solution at low temperature [3] and at higher temperatures is converted into a Pt^{II} complex in which the N=S bond has been ruptured [2—5] (Fig. 1A). A similar rupture of the N=S bond of 2,1,3-benzothiadiazole by Pt^0 occurs, as was demonstrated by isolation of [$Pt_2S\{N(6\text{-}\mu\text{-}N\text{-}4,5\text{-}Me_2C_6H_2)\}(\mu\text{-}PPh_2)(PPh_3)_2Ph$] from the reaction [6].

It is interesting that the rearrangement of the sulfurdiimines bonded to Pt^0 [2—5] is similar to that found in the reaction of azobenzene derivatives with iron carbonyls [7] (Fig. 1). Otsuka et al. [18] found that reaction of iron carbonyl with R—N=S=N—R afforded azobenzene for R = C_6H_5 and [$Fe_2(CO)_6(RNS)$] for R = t-C_4H_9. In the latter dinuclear iron complex the RNS group which results from a cleavage of the N=S bond is probably linked as a six electron donor to two iron atoms.

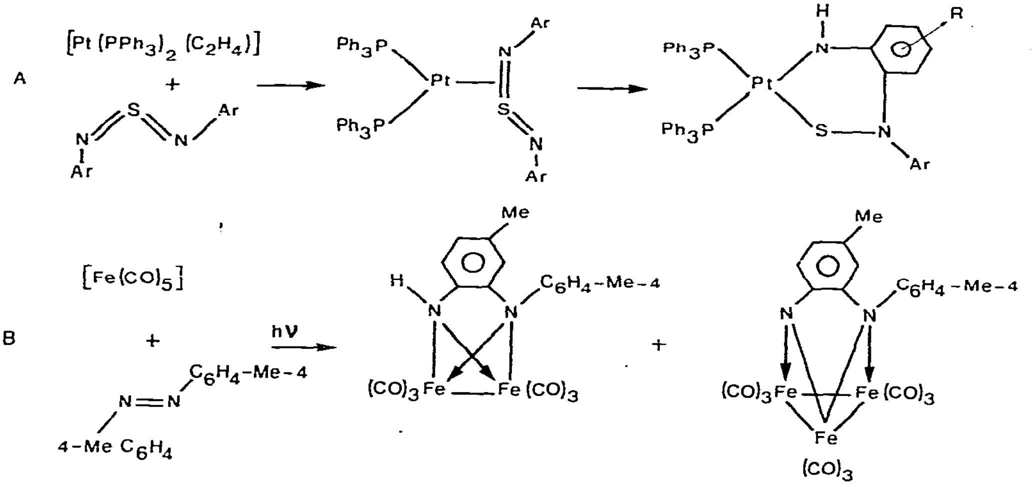

Fig. 1. (A) Reaction of Ar—N=S=N—Ar with [$Pt(PPh_3)_2(C_2H_4)$]; (B) reaction of Ar—N=N—Ar with [$Fe(CO)_5$].

In the light of our knowledge of the behaviour towards metal atoms of N=S bonds in N=S=O and N=S=N molecules it seemed worthwhile to study the reaction of iron carbonyls with sulfurdiimines in much greater detail in order to find out which other fragments in addition to RNS can be captured by metal atoms, since in principle S atoms and nitrene fragments could also be formed. Furthermore, the occurrence of rearrangements such as those observed in the reaction of azobenzene with iron carbonyls should be possible in our reactions by cleavage of N=S bonds in a sulfurdiimine.

The presence of a nitrene fragment in polynuclear metal compounds has already been established by Otsuka et al. [9,10] and Gall et al. [11] in the reactions of [CpNi(CO)$_2$] (Cp = cyclopentadiene) and [Fe(CO)$_3$(NO)]$_2$Hg with di-t-butylsulfurdiimine (DBSD), which result in [(CpNi)$_3$N-t-C$_4$H$_9$)] and [Fe$_4$(NO)$_4$(N-t-C$_4$H$_9$)$_2$S$_2$], respectively. In both cluster compounds a nitrene fragment is linked to three metal atoms.

We describe below the full details * reported for the reaction of [Fe$_2$(CO)$_9$] with R—N=S=N—R (R = t-C$_4$H$_9$ and 4-MeC$_6$H$_4$); we show not only that RNS, RN and S fragments can be captured, but also that rearrangements between the various polynuclear species take place leading to novel iron clusters **.

Experimental

All reactions were carried out under dry oxygen-free nitrogen. Solvents were dried over sodium wire and distilled under N$_2$ before use. The preparations of R—N=S=N—R, R = t-C$_4$H$_9$ (DBSD) [14] and R = 4-MeC$_6$H$_4$ (DTSD) [15], [Fe$_2$(CO)$_9$] and [Fe$_3$(CO)$_{12}$] [16] have been described.

Reaction a: DBSD with [Fe$_2$(CO)$_9$]

A mixture of 14.3 mmol of [Fe$_2$(CO)$_9$] and about 14.3 mmol of DBSD in 100 ml hexane (or benzene) was stirred at room temperature with exclusion of light for 3 days. The resulting red solution was filtered and poured on to a silica gel column (diameter: 0.05 m, length 0.6 m). n-Hexane was used as an eluent. The various fractions were concentrated to small volumes in vacuum and set aside at —30°C. Crystals were obtained of [Fe$_2$(CO)$_6$(RNS)] (IIa), [Fe$_3$(CO)$_9$(RNS)S] (VIIa) and of a mixture of [Fe$_2$(CO)$_6$S$_2$] (Va) and [Fe$_3$(CO)$_9$S$_2$] (VIa). Further purification by sublimation in vacuum at 45°C was carried out for IIa. Va and VIa could not be separated by sublimation. Analytically pure VIa was obtained by repeated crystallization in hexane. VIIa decomposed in vacuum. When crystallization did not occur, the fractions were concentrated to dryness. Subsequent sublimation of the resulting residues afforded [Fe$_2$(CO)$_7$(RNS)] (Ia) and an oily mixture of Ia and [Fe$_2$(CO)$_6${RNC(O)S}] (IIIa), respectively. All complexes were unstable in CHCl$_3$. Yields calculated with respect to iron: Ia 0.02 mmol (0.1%), IIa 1 mmol (7%), IIIa not isolated, Va not isolated pure, VIa 0.15 mmol (1.5%) and VIIa 0.1 mmol (1%).

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* Some of the results were described in a preliminary communication [12].

** M.O. calculations and U.P.S. spectroscopy results of these compounds will be published [13].

Reaction b: DTSD with [Fe$_2$(CO)$_9$]

The conditions described for reaction *a* were used, except that the reaction was performed on a larger scale, involving 71.5 mmol of each compound. The various fractions from column chromatography gave crystals for IIIb, IVb, and [Fe$_3$(CO)$_9$(RN)S] (VIIIb), which were further purified by sublimation at 45°C in vacuum. Ib and IIb were studied only in solution. Yields calculated with respect to iron: IIIb 0.2 mmol (0.3%), IVb 0.2 mmol (0.3%), and VIIIb 2.2 mmol (4.5%).

Spectroscopic measurements and analytical data

The ^{1}H NMR spectra were recorded on Varian A60 (C.W.) and XL 100 (F.T.) spectrometers. The IR and Raman spectra were recorded on Beckman IR 4250 and Jobin Yvon Ramanor HG 2 S spectrophotometers, respectively. The 70 eV E.I. mass spectra were recorded with a Varian MAT 711 mass spectrometer; the samples were introduced into the ion source (200°C) with a direct insertion probe at ca. 100°C. Elemental analyses (Table 1) were carried out by the elemental analytical section of the Institute for Organic Chemistry TNO, Utrecht. Analytical data for sulfur are less accurate because of the presence of iron in the complexes.

Crystal data

From single crystal diffractometry: IIIb: *a* 7.301(1), *b* 29.845(2), *c* 7.960(1) Å, β 90.20(1)°, *Z* 4, monoclinic, space group $P2_1/n$; VIIa: *a* 11.039(1), *b* 11.525(1), *c* 15.996(1) Å, β 96.241(6), *Z* 4, monoclinic, space group $P2_1/n$; VIIIb: *a* 8.917(1), *b* 15.641(1), *c* 15.868(2) Å, α 79.34(1), β 74.53(1), γ 85.43(1)°, *Z* 4, triclinic, space group $P\bar{1}$.

Intensity data, structure determination and refinement

[Fe$_2$(CO)$_6${4-MeC$_6$H$_4$NC(O)S}] (IIIb). 2629 independent reflections were measured on a Nonius CAD 4 automatic four circle diffractometer (Cu-K_α,

TABLE 1

ANALYTICAL DATA AND MASS SPECTRA

Compound		Found (calcd.) (%)					*m/e*
		C	H	N	O	S	
(IIa)	[Fe$_2$(CO)$_6$(t-C$_4$H$_9$NS)]	31.30 (31.37)	2.33 (2.37)	3.67 (3.66)	24.96 (25.07)	7.97 (8.37)	383 (383)
(IIIb)	[Fe$_2$(CO)$_6${4-MeC$_6$H$_4$NC(O)S}]	38.75 (37.79)	1.84 (1.59)	3.29 (3.15)		6.34 (7.21)	
(IVb)	(4-MeC$_6$H$_4$N)$_2$	79.25 (79.97)	6.65 (6.71)	13.14 (13.32)			210 (210)
(VIa)	[Fe$_3$(CO)$_9$S$_2$]	22.77 (22.35)			28.65 (29.76)	10.40 (13.26)	484 (484)
(VIIa)	[Fe$_3$(CO)$_9$(t-C$_4$H$_9$NS)S]	28.60 (28.14)	1.91 (1.63)	2.52 (2.52)	25.47 (25.95)	8.21 (11.56)	667 (555)
(VIIIb)	[Fe$_3$(CO)$_9$(4-MeC$_6$H$_4$N)S]	34.64 (31.51)	1.38 (1.27)	2.59 (2.52)		6.09 (5.76)	558 (557)

$\theta - 2\theta$ scan), 1655 of which were below the 2σ level and were treated as unobserved. The structure was solved by locating the two Fe atoms from an E^2-Patterson synthesis. After two difference Fourier syntheses, all nonhydrogen atoms could be located. Block-diagonal least squares refinement, anisotropic for Fe and S and isotropic for O, C and N, converged to an R index of 13.9%. Anisotropic least squares refinement for all non-hydrogen atoms reduced R to 7.1% for the 974 observed reflections. No absorption correction was applied.

[$Fe_3(CO)_9(t$-$C_4H_9NS)S$] (VIIa). 3671 independent reflections were measured on a Nonius CAD 4 automatic four circle diffractometer (Cu-K_α, $\theta - 2\theta$ scan), 1980 of which were below the 2.5σ level and were treated as unobserved. The structure was solved by locating the three Fe and two S atoms by SIMPEL, an interactive program system for direct methods [17]. After three difference Fourier syntheses, all non-hydrogen atoms were located. Block-diagonal least squares refinement, anisotropic for Fe and S and isotropic for O, C and N, converged to an R index of 12.6%. After correction for absorption, anisotropic least squares refinement for all non-hydrogen atoms reduced R to 6.7% for the 1637 observed reflections.

[$Fe_3(CO)_9(4$-$MeC_6H_4N)S$] (VIIIb). A crystal, approximately 0.40 × 0.40 × 0.15 mm, was mounted on a glass fiber and aligned with [110] coincident with the diffractometer ϕ axis. 4276 independent reflections were measured on a Nonius CAD 4 automatic four circle diffractometer (Cu-K_α, $\theta - 2\theta$ scan), 1648 of which were below the 2σ level and were treated as unobserved. The structure was solved by locating the six Fe and two S atoms by SIMPEL [17]. After three difference Fourier syntheses, all non-hydrogen atoms were located. Block-diagonal least squares refinement, anisotropic for Fe and S and isotropic for O, C and N, converged to an R index of 14.3%. After correction for absorption ($\mu = 192.0$ cm^{-1}) block diagonal least squares refinement reduced R to 9.5% for the 2628 observed reflections.

Results

The scheme in Fig. 6 shows the various reaction products, which were identified by elemental analysis, ^{1}H NMR, mass, IR and Raman spectroscopy (Tables 1—3). The structures of IIIb, VIIa and VIIIb were established by single crystal X-ray diffraction, the results of which will be described first. The characterization of other products present in the reaction mixtures will then be described.

The molecular structure of [$Fe_2(CO)_6\{4$-$MeC_6H_4NC(O)S\}$] (IIIb)

The atomic coordinates, bond distances and bond angles are listed in Table 4, 5 and 6, respectively. The molecular structure (Fig. 2) consists of two $Fe(CO)_3$ groups bonded to each other by a single metal—metal bond. The atoms are bridged by both the nitrogen and the sulfur atoms, which are connected to each other by a carbonyl group. The Fe—Fe distance of 2.431(4) Å, Fe—S distances of 2.270(5) and 2.279(5) and Fe—N distances of 2.02(1) Å are consistent with values observed for similar complexes [18,19]. The averaged Fe—C and C—O distances are 1.82(4) and 1.11(3) Å, respectively. The Fe—C—O angles do not deviate significantly from 180°.

TABLE 2

VIBRATIONAL FREQUENCIES

Compound		ν(CO) [a] (cm^{-1})	ν(FeS)/ν(FeN) [b, c] (cm^{-1})	ν(FeFe) [b] (cm^{-1})
Ia	$[Fe_2(CO)_7(t\text{-}C_4H_9NS)]$	2084s, 2046vs, 2012vs, 2006vs, 1703m; (1688s in KBr)		
Ib	$[Fe_2(CO)_7(4\text{-}MeC_6H_4NS)]$	2082s, 2046vs, 2010vs, 2007vs, 1970w, 1718s		
IIa	$[Fe_2(CO)_6(t\text{-}C_4H_9NS)]$	2077s, 2032vs, 2000sh, 1966vs, 1986sh, 1979sh, 1954w	360s [d], 314m, 260w	208s
IIb	$[Fe_2(CO)_6(4\text{-}MeC_6H_4NS)]$	2078s, 2042vs, 2003vs		
IIIa	$[Fe_2(CO)_6\{t\text{-}C_4H_9NC(O)S\}]$	2982s, 2043vs, 2007vs, 1720s		
IIIb	$[Fe_2(CO)_6\{4\text{-}MeC_6H_4NC(O)S\}]$	2088s, 2051vs, 2012vs, 1747s; (1722s in KBr)	302m, 276w	220m
Va	$[Fe_2(CO)_6S_2]$	2087s, 2045vs, 2008vs		
VIa	$[Fe_3(CO)_9S_2]$	2064vs, 2045vs, 2023vs, 1992w	291m	219m, 170m
VIIa	$[Fe_3(CO)_9(t\text{-}C_4H_9NS)S]$	2078m, 2061s, 2033vs, 2017s, 2005s, 1997s, 1974w, 1866w		
VIIIb	$[Fe_3(CO)_9(4\text{-}MeC_6H_4N)S]$	2090w, 2060vs, 2039vs, 2017vs, 1997m, 1977m		

[a] From hexane solutions in IR. [b] From benzene solutions in Raman. [c] vs = very strong, s = strong, m = medium, w = weak and sh = shoulder. [d] Strong in IR.

TABLE 3

^{1}H NMR DATA [a]

Compound		Solvent	ppm relative to TMS		
(Ia)	$[Fe_2(CO)_7(t\text{-}C_4H_9NS)]$	C_7D_8			0.96(s)
(IIa)	$[Fe_2(CO)_6(t\text{-}C_4H_9NS)]$	C_7D_8			0.68(s)
		$CDCl_3$			1.15(s)
(IIIa)	$[Fe_2(CO)_6\{t\text{-}C_4H_9NS(O)S\}]$	C_7D_8			1.08(s)
(IVb)	$[(4\text{-}MeC_6H_4N)_2]$	$CDCl_3$	7.80(d)	7.30(d)	1.42(s)
(VIIIb)	$[Fe_3(CO)_9(4\text{-}MeC_6H_4N)S]$	C_7D_8	6.80(d)	6.47(d)	1.87(s)
		$CDCl_3$	7.10(d)	6.80(d)	2.58(s)

[a] d = doublet, s = singlet.

Except for the phenyl group, the molecule has a mirror plane, within the limits of accuracy; this passes through N, S, C(8), O(8) and the point midway between the Fe atoms. The dihedral angle between this mirror plane and the plane through the phenyl group is 81°.

Disregarding the Fe-Fe bonding the local coordination about each iron atom (see Fig. 3) may be described as a distorted tetragonal pyramid having the two carbonyl ligands and the two bridging N and S atoms located in the basal plane with the carbonyl ligand at the axial site. The Fe—Fe bond is actually bent, and lies approximately along the extrapolation of the two Fe—(CO) (axial) bonds [20]. The N—C(8)—S angle is 102(1)°, the Fe(1)—N—Fe(2) angle is 74.0(4)° and the Fe(1)—S—Fe(2) angle is 64.6(1)°, which are small both for an sp^2 and sp^3 hybridisation. They are, however, rather similar to those found

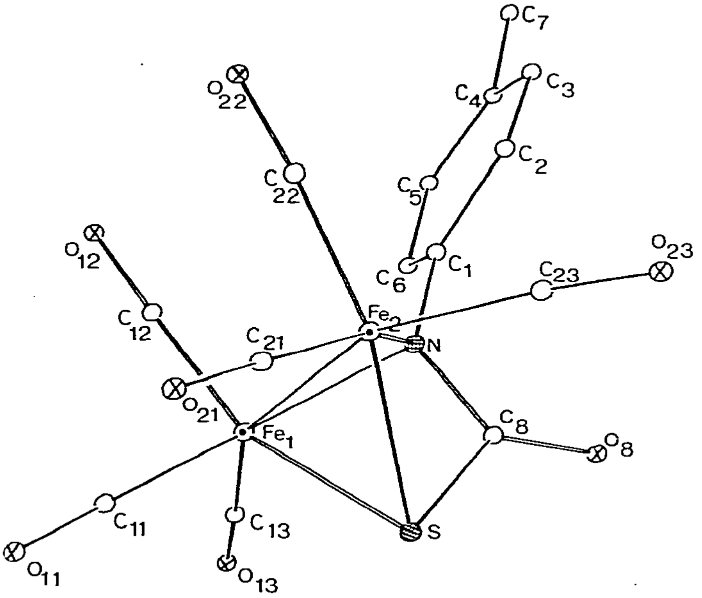

Fig. 2. Molecular structure of $[Fe_2(CO)_6\{4\text{-}MeC_6H_4NC(O)S\}]$ (IIIb).

TABLE 4

ATOMIC COORDINATES (WITH STANDARD DEVIATIONS)

Compound IIIb				Compound VIIa			Compound VIIIb′			Compound VIIIb″		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Fe(1)	—0,0083(4)	0.1328(1)	—0,0859(3)	0,9517(3)	0,2814(3)	0,3181(2)	0.9356(5)	0,4242(2)	0,3594(2)	0,4896(5)	0,2781(2)	0,7385(2)
Fe(2)	0.1862(4)	0.1890(1)	—0,2156(4)	0,8893(3)	0,3549(3)	0,1229(2)	1.0319(5)	0,4282(2)	0.1956(2)	0,4436(5)	0.1941(3)	0,8935(2)
Fe(3)				0,7015(3)	0,2557(3)	0,1795(2)	0,7510(5)	0,3906(2)	0,2226(3)	0,1900(5)	0,1748(2)	0,8578(3)
S(1)	0,2322(6)	0,1642(1)	0,0520(5)	0,8624(4)	0,1473(4)	0,2320(3)	0,8279(8)	0,5078(4)	0,2598(4)	0,2880(8)	0,3037(4)	0,8513(4)
S(2)				0,8125(4)	0,4018(4)	0,2422(3)						
N	0,223(2)	0,122(1)	—0,220(2)	0,979(1)	0,226(1)	0,198(1)	0.901(2)	0,345(1)	0,287(1)	0,403(2)	0,163(1)	0,789(1)
C(1)	0,257(2)	0,091(1)	—0,351(2)	1,094(2)	0,163(2)	0,182(1)	0,926(3)	0,248(2)	0,308(2)	0,454(3)	0,091(2)	0,745(2)
C(2)	0,349(2)	0,107(1)	—0,498(2)	1,085(2)	0,135(3)	0,086(1)	0,853(3)	0,209(2)	0,392(2)	0,444(4)	0,093(2)	0,661(2)
C(3)	0,382(3)	0,078(1)	—0,632(2)	1,204(2)	0,238(2)	0,208(2)	0,871(4)	0,114(2)	0,412(2)	0,498(4)	0,018(2)	0,618(2)
C(4)	0,322(3)	0,034(1)	—0,621(3)	1,107(2)	0,041(2)	0,228(2)	0,957(4)	0,072(2)	0,347(2)	0,551(3)	—0,058(2)	0,666(2)
C(5)	0,230(3)	0,020(1)	—0,476(3)				1,024(3)	0,113(2)	0,264(2)	0,556(3)	—0,060(2)	0,749(2)
C(6)	0,202(3)	0,048(1)	—0,346(3)				1,012(3)	0,205(2)	0,242(2)	0,508(3)	0,012(2)	0,794(2)
C(7)	0,358(3)	0,001(1)	—0,767(3)				0,972(5)	—0,034(3)	0,372(3)	0,602(4)	—0,136(2)	0,616(2)
C(8)	0,338(2)	0,122(1)	—0,076(2)									
C(11)	—0,182(3)	0,166(1)	0,018(3)	0,857(3)	0,299(2)	0,408(1)	1,059(3)	0,354(2)	0,414(2)	0,667(3)	0,239(2)	0,671(2)
C(12)	—0,155(2)	0,120(1)	—0,266(3)	1,052(2)	0,195(2)	0,384(1)	1,009(3)	0,520(2)	0,382(2)	0,571(3)	0,383(2)	0,738(2)
C(13)	—0,054(3)	0,084(1)	0,036(3)	1,048(2)	0,404(2)	0,335(1)	0,777(3)	0,422(2)	0,453(2)	0,403(3)	0,312(2)	0,651(2)
C(21)	0,074(3)	0,239(1)	—0,163(2)	0,874(2)	0,270(2)	1,023(1)	1,211(3)	0,373(2)	0,207(2)	0,641(3)	0,157(2)	0,871(2)
C(22)	0,081(3)	0,192(1)	—0,431(3)	0,804(2)	0,468(2)	0,074(1)	1,026(3)	0,403(1)	0,098(1)	0,358(4)	0,114(2)	0,978(2)
C(23)	0,416(3)	0,212(1)	—0,256(3)	1,022(2)	0,437(2)	0,116(1)	1,128(4)	0,531(2)	0,144(2)	0,473(4)	0,251(2)	0,968(2)
C(31)				0,658(2)	0,152(2)	0,103(1)	0,722(3)	0,291(2)	0,187(2)	0,140(4)	0,061(2)	0,875(2)
C(32)				0,586(2)	0,347(2)	0,135(1)	0,579(3)	0,378(2)	0,313(2)	0,096(3)	0,210(2)	0,773(2)
C(33)				0,607(2)	0,219(2)	0,260(2)	0,657(3)	0,450(2)	0,139(2)	0,034(4)	0,195(2)	0,949(2)
O(8)	0,477(2)	0,100(1)	—0,050(2)									
O(11)	—0,282(2)	0,188(1)	0,079(3)	0,800(2)	0,312(2)	0,458(1)	1,139(2)	0,305(1)	0,449(1)	0,780(2)	0,217(1)	0,625(1)
O(12)	—0,240(2)	0,114(1)	—0,379(2)	1,114(2)	0,143(1)	0,433(1)	1,061(2)	0,580(1)	0,393(1)	0,519(2)	0,446(1)	0,739(1)
O(13)	—0,083(2)	0,051(1)	0,107(2)	1,106(2)	0,488(2)	0,364(1)	0,666(2)	0,422(1)	0,511(1)	0,342(2)	0,339(1)	0,594(1)
C(21)	—0,007(3)	0,272(1)	—0,138(2)	0,853(2)	0,228(1)	—0,039(1)	1,325(2)	0,337(1)	0,214(1)	0,767(2)	0,128(1)	0,853(1)
O(22)	0,024(3)	0,193(1)	—0,554(3)	0,745(2)	0,547(1)	0,046(1)	1,032(2)	0,390(1)	0,025(1)	0,314(3)	0,056(2)	1,039(2)
O(23)	0,556(2)	0,225(1)	—0,277(2)	1,105(1)	0,498(1)	0,112(1)	1,182(3)	0,596(1)	0,116(1)	0,501(3)	0,301(2)	1,011(2)
O(31)				0,634(2)	0,085(2)	0,050(1)	0,693(2)	0,231(1)	0,165(1)	0,109(3)	—0,011(1)	0,886(2)
O(32)				0,508(2)	0,404(2)	0,105(1)	0,474(2)	0,374(1)	0,371(1)	0,042(3)	0,234(1)	0,715(1)
O(33)				0,550(2)	0,197(2)	0,314(1)	0,620(2)	0,493(1)	0,084(1)	—0,073(3)	0,206(2)	1,003(2)

TABLE 5

BOND DISTANCES (Å) (WITH STANDARD DEVIATIONS)

	IIIb	VIIa	VIIIb′	VIIIb″
Fe(2)—Fe(1)	2.431(4)		2.50(1)	2.51(1)
Fe(2)—Fe(3)		2.614(4)	2.52(1)	2.53(1)
Fe(1)—S(1)	2.270(5)	2.227(5)	2.23(2)	2.23(2)
Fe(1)—S(2)	—	2.314(6)		
Fe(2)—S(1)	2.279(5)	—	2.24(2)	2.24(1)
Fe(2)—S(2)	—	2.237(6)		
Fe(3)—S(1)	—	2.259(5)	2.24(1)	2.24(1)
Fe(3)—S(2)	—	2.253(6)		
Fe(1)—N	2.02(1)	2.08(1)	1.92(2)	1.95(2)
Fe(2)—N	2.02(1)	2.09(1)	1.94(2)	1.94(2)
Fe(3)—N			1.91(2)	1.94(2)
N—S(1)	—	1.70(2)		
Fe(1)—C(11)	1.81(2)	1.87(2)	1.77(3)	1.81(3)
Fe(1)—C(12)	1.83(2)	1.75(2)	1.82(3)	1.85(3)
Fe(1)—C(13)	1.79(2)	1.77(2)	1.75(3)	1.72(3)
Fe(2)—C(21)	1.76(2)	1.86(2)	1.79(3)	1.77(3)
Fe(2)—C(22)	1.88(2)	1.75(2)	1.69(2)	1.72(3)
Fe(2)—C(23)	1.85(2)	1.76(2)	1.83(3)	1.69(4)
Fe(3)—C(31)	—	1.74(2)	1.81(3)	1.82(3)
Fe(3)—C(32)	—	1.74(2)	1.79(3)	1.75(3)
Fe(3)—C(33)	—	1.80(2)	1.74(3)	1.77(3)
C(11)—O(11)	1.10(3)	1.09(3)	1.17(3)	1.14(3)
C(12)—O(12)	1.11(3)	1.16(3)	1.13(4)	1.11(4)
C(13)—O(13)	1.14(3)	1.17(3)	1.16(3)	1.17(4)
C(21)—O(21)	1.15(3)	1.11(3)	1.14(4)	1.17(4)
C(22)—O(22)	1.06(3)	1.18(3)	1.20(3)	1.19(4)
C(23)—O(23)	1.11(3)	1.16(3)	1.13(4)	1.21(5)
C(31)—O(31)	—	1.17(3)	1.14(4)	1.15(4)
C(32)—O(32)	—	1.15(3)	1.13(3)	1.15(4)
C(33)—O(33)	—	1.15(3)	1.19(4)	1.13(4)
C(8)—O(8)	1.24(2)	—		
N—C(1)	1.42(2)	1.51(2)	1.51(3)	1.42(3)
N—C(8)	1.42(2)	—		
S—C(8)	1.79(2)	—		
C(1)—C(2)	1.43(2)	1.56(3)	1.37(3)	1.36(4)
C(1)—C(3)	—	1.51(3)		
C(1)—C(4)	—	1.59(3)		
C(1)—C(6)	1.35(2)	—	1.37(4)	1.45(4)
C(2)—C(3)	1.40(2)	—	1.46(4)	1.45(5)
C(3)—C(4)	1.41(3)	—	1.35(4)	1.42(5)
C(4)—C(5)	1.40(3)	—	1.35(4)	1.32(4)
C(4)—C(7)	1.54(3)	—	1.64(5)	1.56(5)
C(5)—C(6)	1.35(3)	—	1.42(4)	1.42(4)

in similar complexes [18,19]. The coordination about C(8) is planar, whereas the coordination about N is a distorted tetrahedron.

The molecular structure of [$Fe_3(CO)_9(t\text{-}C_4H_9NS)S$] (VIIa)

The atomic coordinates, bond distances, bond angles and dihedral angles are listed in Tables 4, 5, 7 and 8. The molecular structure (Fig. 4) consists of three $Fe(CO)_3$ groups with one single metal—metal bond, a t-C_4H_9NS fragment with a single N—S bond and a sulfur atom. The RNS fragment and the sulfur atom

TABLE 6

BOND ANGLES OF IIIb (deg) (WITH STANDARD DEVIATIONS)

Fe(2)—Fe(1)—N	52.9(4)	C(11)—Fe(1)—C(12)	93(1)
Fe(2)—Fe(1)—S	57.9(1)	C(11)—Fe(1)—C(13)	94(1)
N—Fe(1)—S	71.0(4)	C(12)—Fe(1)—C(13)	98(1)
Fe(1)—Fe(2)—N	53.1(3)	C(11)—Fe(1)—N	156(1)
Fe(1)—Fe(2)—S	57.5(1)	C(12)—Fe(1)—S	156(1)
N—Fe(2)—S	70.9(4)	C(13)—Fe(1)—Fe(2)	155(1)
Fe(1)—S—Fe(2)	64.6(1)	C(21)—Fe(2)—C(22)	90(1)
Fe(1)—S—C(8)	76.8(5)	C(21)—Fe(2)—C(23)	98(1)
Fe(2)—S—C(8)	75.9(5)	C(22)—Fe(2)—C(23)	101(1)
N—C(8)—S	102(1)	C(21)—Fe(2)—N	155(1)
N—C(8)—O(8)	128(2)	C(22)—Fe(2)—S	158(1)
S—C(8)—O(8)	130(1)	C(23)—Fe(2)—Fe(1)	150(1)
Fe(2)—N—Fe(1)	74.0(4)	C(1)—N—Fe(1)	130(1)
Fe(2)—N—C(8)	93.3(9)	C(1)—N—Fe(2)	133(1)
Fe(1)—N—C(8)	93.9(9)	C(1)—N—C(8)	120(1)

each bridge the three Fe atoms in such a way that the skeleton, formed by the three Fe, two S and one N atoms, has an approximate prismane configuration. The only significant deviation from this configuration is the difference in lengths of the N—S (1.70 Å) and of the Fe(2)—Fe(3) (2.614 Å) bonds. The average dihedral angle between the three prism faces is 60°, whereas the average

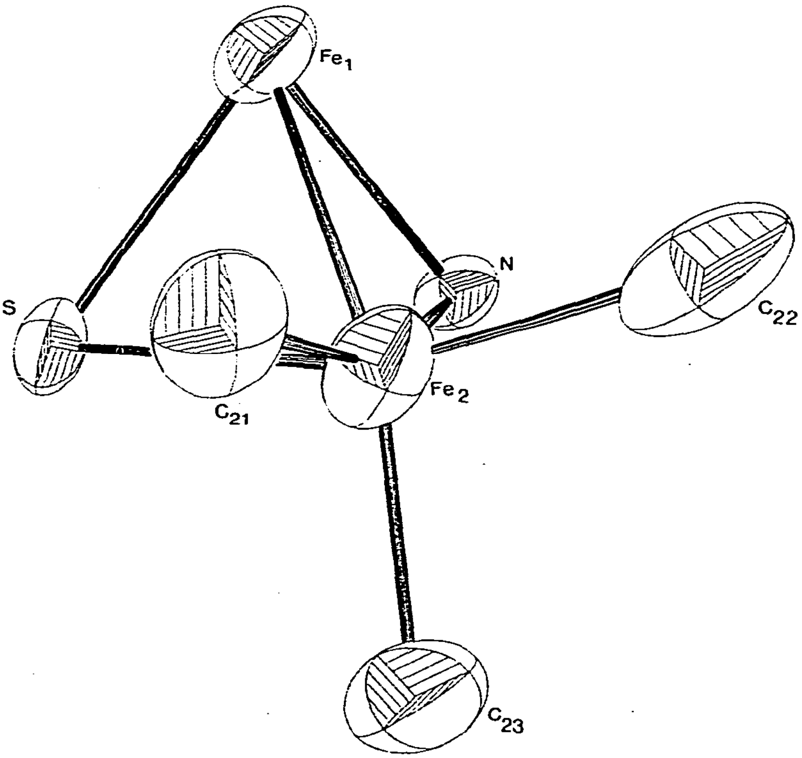

Fig. 3. Coordination about Fe in [Fe$_2$(CO)$_6${4-MeC$_6$H$_4$NC(O)S}] (IIIb).

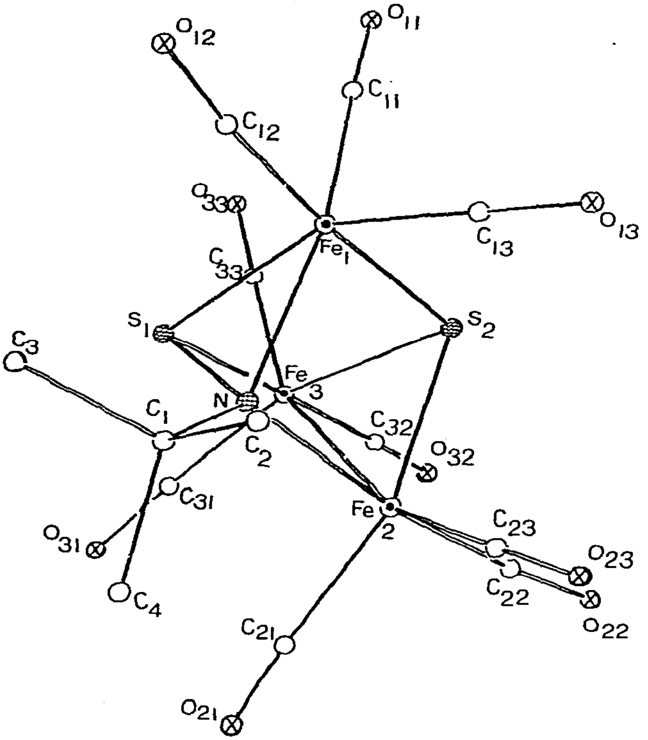

Fig. 4. Molecular structure of [$Fe_3(CO)_9(t\text{-}C_4H_9NS)S$] (VIIa).

TABLE 7

BOND ANGLES OF VIIa (deg) (WITH STANDARD DEVIATIONS)

S(1)—Fe(1)—N	46.5(4)
S(1)—Fe(1)—S(2)	82.4(2)
N—Fe(1)—S(2)	81.6(4)
C(11)—Fe(1)—C(12)	88(1)
C(11)—Fe(1)—C(13)	100(1)
C(12)—Fe(1)—C(13)	92(1)
C(11)—Fe(1)—N	153(1)
C(12)—Fe(1)—S(2)	175(1)
C(13)—Fe(1)—S(1)	150(1)
N—Fe(2)—Fe(3)	80.3(4)
Fe(3)—Fe(2)—S(2)	54.7(2)
N—Fe(2)—S(2)	83.1(4)
C(21)—Fe(2)—C(22)	91(1)
C(21)—Fe(2)—C(23)	104(1)
C(22)—Fe(2)—C(23)	89(1)
C(21)—Fe(2)—S(2)	148(1)
C(22)—Fe(2)—N	171(1)
C(23)—Fe(2)—Fe(3)	163(1)
S(1)—Fe(3)—Fe(2)	75.5(2)
S(1)—Fe(3)—S(2)	83.1(2)
S(2)—Fe(3)—Fe(2)	54.1(2)
C(31)—Fe(3)—C(32)	90(1)
C(31)—Fe(3)—C(33)	102(1)
C(32)—Fe(3)—C(33)	89(1)
C(31)—Fe(3)—S(2)	157(1)
C(32)—Fe(3)—S(1)	175(1)
C(33)—Fe(3)—Fe(2)	154(1)
Fe(1)—S(1)—N	62.2(5)
Fe(1)—S(1)—Fe(3)	97.1(2)
Fe(3)—S(1)—N	100.2(5)
Fe(1)—S(2)—Fe(2)	90.7(2)
Fe(1)—S(2)—Fe(3)	94.8(2)
Fe(2)—S(2)—Fe(3)	71.2(2)
S(1)—N—Fe(2)	103.7(7)
S(1)—N—Fe(1)	71.4(5)
Fe(1)—N—Fe(2)	101.8(6)
N—C(1)—C(2)	108(2)
N—C(1)—C(3)	111(2)
N—C(1)—C(4)	112(2)
C(2)—C(1)—C(3)	111(2)
C(2)—C(1)—C(4)	105(2)
C(3)—C(1)—C(4)	110(2)
C(1)—N—S(1)	119(1)
C(1)—N—Fe(1)	121(1)
C(1)—N—Fe(2)	126(1)

TABLE 8

DIHEDRAL ANGLES OF VIIa BETWEEN PLANES

Plane	Atoms defining the plane	Dihedral angles (deg)			
1	Fe(2), Fe(3), S(1), N	1—2	61.8	2—4	89.2
2	Fe(1), Fe(2), S(2), N	1—3	59.2	2—5	87.9
3	Fe(1), Fe(3), S(1), S(2)	1—4	89.6	3—4	82.6
4	Fe(2), Fe(3), S(2)	1—5	84.9	3—5	89.3
5	Fe(1), S(1), N	2—3	59.6	4—5	7.1

dihedral angle between the two triangles and the prism faces is 87° (see Table 8).

The NS double bond, which is 1.53 Å in the free ligand [21], is lengthened in VIIa to 1.70 Å, which is the distance found for a single N—S bond [6]. The Fe—Fe distance of 2.614(4) Å, the Fe—S distances of 2.227(5)—2.314(6) Å and the Fe—N distances of 2.08(1) and 2.09(1) are consistent with values observed for other complexes [18,19]. The average Fe—C and the average C—O distances are 1.78(5) and 1.15(3) Å, respectively.The Fe—C—O angles do not deviate significantly from 180°.

The coordination around both iron atoms is similar, and approximately octahedral. The four atoms around Fe(1) (S(1), N, C(11) and C(13) lie in one plane, which is perpendicular to the approximately linear C(12)—Fe(1)—S(2) axis. This is also found for the four atoms around Fe(2) (C(21), C(23), S(2) and Fe(3)) with respect to the N—Fe(2)—C(22) axis and for the four atoms around Fe(3) (C(31), C(33), S(2) and Fe(2)) with respect to the C(32)—Fe(3)—S(1) axis. In all these three planes a deviation from the ideal octahedral geometry is found for the angle involved in the prismane skeleton. The average value for this angle is 52(4)°, whereas the average of the other angles in these planes is 103(4)°. Just as with IIIb, it is assumed that the Fe—Fe bond is, in fact, bent and lies approximately along the extrapolation of the Fe(2)—C(23) and Fe(3)—C(33) bonds [20].

The molecular structure of [$Fe_3(CO)_9(4\text{-}MeC_6H_4N)S$] (VIIIb)

There are two molecules in the asymmetric unit, VIIIb′ and VIIIb″. Their atomic coordinates, bond distances and bond angles are listed in Tables 4, 5 and 9, respectively. The molecular structure (Fig. 5) consists of three $Fe(CO)_3$ groups with two single metal—metal bonds, while an RN fragment and an S atom both bridge the three iron atoms. The local coordination about Fe(1) and Fe(3) is similar to that for Fe(1) and Fe(2) in [$Fe_2(CO)_6\{4\text{-}MeC_6H_4NC(O)S\}$] (IIIb) (see Fig. 3). So, for VIIIb the same remarks concerning the Fe—Fe bonds could be made as for IIIb. The central iron atom, Fe(2), has a seven-coordinate geometry. Compound VIIIb is isostructural with [$Fe_3(CO)_9S_2$], [$Fe_3(CO)_9Se_2$], [$Fe_3(CO)_9\{(C_6H_5)_2C{=}N_2\}_2$] and [$Fe_3(CO)_9(CH_3N)_2$] [19,27,35]. The Fe—Fe distances of 2.50(1)—2.53(1) Å, Fe—N distances of 1.91(2)—1.94(2) Å and Fe—S distances of 2.23(2)—2.24(2) Å are consistent with values observed for similar complexes [18,19,27,35]. The averaged Fe—C and C—O distances are 1.77(5) and 1.16(3) Å resp.

TABLE 9

BOND ANGLES OF VIIIb (deg) (WITH STANDARD DEVIATIONS)

	VIIIb′	VIIIb″		VIIIb′	VIIIb″
Fe(1)—S—Fe(2)	68.0(2)	68.4(2)	N—Fe(3)—Fe(2)	49.7(5)	49.5(6)
Fe(2)—S—Fe(3)	68.7(2)	68.8(2)	S—Fe(1)—C(11)	165(1)	164(1)
Fe(1)—S—Fe(3)	91.1(3)	90.7(3)	N—Fe(1)—C(12)	156(1)	157(1)
Fe(1)—N—Fe(2)	80.6(7)	80.3(7)	Fe(2)—Fe(1)—C(13)	148(1)	144(1)
Fe(2)—N—Fe(3)	81.7(7)	81.1(6)	S—Fe(2)—C(21)	145(1)	142(1)
Fe(1)—N—Fe(3)	112.5(9)	109.5(8)	S—Fe(2)—C(22)	115(1)	117(1)
Fe(1)—N—C(1)	123(2)	122(1)	S—Fe(2)—C(23)	87(1)	89(1)
Fe(2)—N—C(1)	128(1)	132(2)	N—Fe(2)—C(21)	95(1)	96(1)
Fe(3)—N—C(1)	119(2)	121(1)	N—Fe(2(—C(22)	106(1)	104(1)
S—Fe(1)—N	75.7(6)	76.9(5)	N—Fe(2)—C(23)	157(1)	163(1)
S—Fe(1)—Fe(2)	56.2(2)	56.0(2)	Fe(1)—Fe(2)—C(21)	92(1)	91(1)
N—Fe(1)—Fe(2)	50.1(5)	49.7(6)	Fe(1)—Fe(2)—C(22)	154(1)	153(1)
S—Fe(1)—N	75.0(5)	76.8(5)	Fe(1)—Fe(2)—C(23)	109(1)	114(1)
S—Fe(2)—Fe(1)	55.8(2)	55.6(2)	Fe(3)—Fe(2)—C(21)	138(1)	142(1)
S—Fe(2)—Fe(3)	55.6(2)	55.6(2)	Fe(3)—Fe(2)—C(22)	77(1)	77(1)
N—Fe(2)—Fe(1)	49.3(6)	49.9(5)	Fe(3)—Fe(2)—C(23)	130(1)	128(1)
N—Fe(2)—Fe(3)	48.6(6)	49.4(5)	S—Fe(3)—C(31)	171(1)	168(1)
Fe(1)—Fe(2)—Fe(3)	78.8(2)	78.2(2)	N—Fe(3)—C(33)	159(1)	158(1)
S—Fe(3)—N	75.7(6)	76.9(6)	Fe(2)—Fe(3)—C(32)	138(1)	140(1)
S—Fe(3)—Fe(2)	55.7(2)	55.7(2)			

Reaction a, $R = t\text{-}C_4H_9$

Otsuka et al. [17] have described the reaction of DBSD with $[Fe(CO)_5]$ in hexane at ambient temperature under irradiation with diffuse sunlight, which yielded only IIa (Fig. 6). In contrast, we have studied the reaction of DBSD

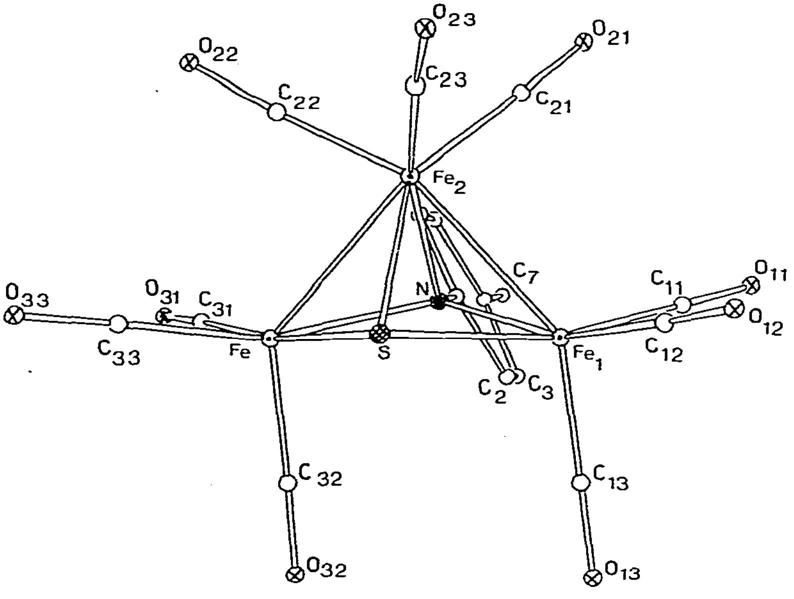

Fig. 5. The molecular structure of $[Fe_3(CO)_9(4O\text{-}MeC_6H_4N)S]$ (VIIIb).

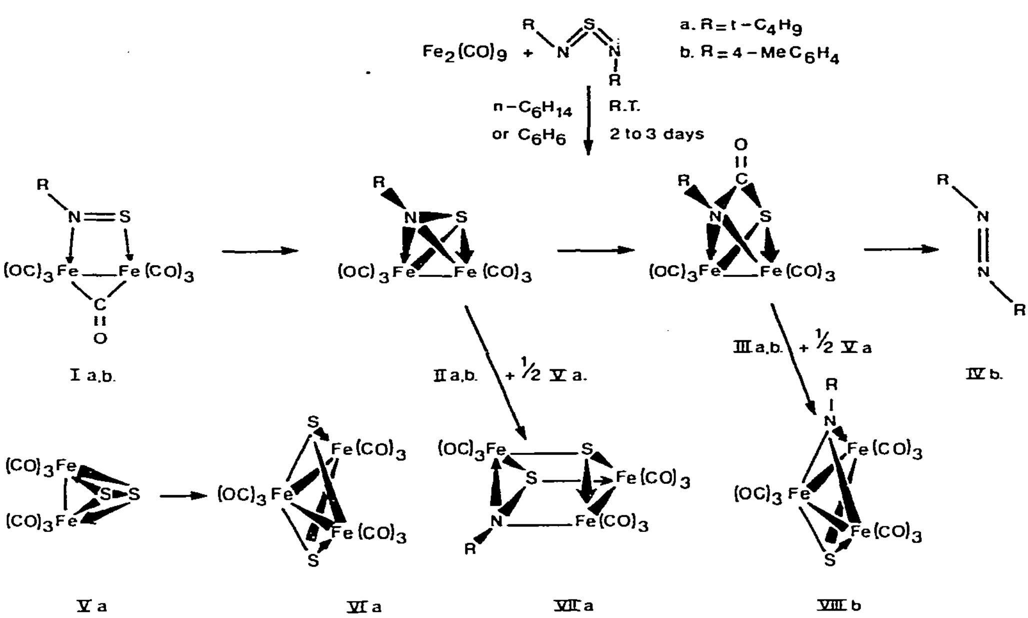

Fig. 6. The different reaction products from the reaction of $[Fe_2(CO)_9]$ with R—N=S=N—R (R = $t\text{-}C_4H_9$, $4\text{-}MeC_6H_4$).

with $[Fe_2(CO)_9]$ in hexane and benzene at ambient temperature. Our reaction yielded six different complexes, of which IIa was the main product. The proposed structure of this compound consists of an RNS fragment bound to a dinuclear $[Fe_2(CO)_6]$ entity. The presence of a single Fe—Fe bond is confirmed by the occurrence of a strong polarized band at 208 cm^{-1} in the Raman spectrum, in agreement with previously reported data [22], and supported by the fact that the intensity of this band is enhanced by a factor of two with respect to the solvent (benzene) at 606 cm^{-1} when the exitation line is changed from 6471 to 5145 Å [23]. Other bands in this low frequency region of the Raman spectrum at 360, 314 and 260 cm^{-1} are tentatively assigned to Fe—S and Fe—N stretching modes, by analogy with reported data for ν(FeS) [22] (see Table 2).

Since IIIa and IIIb appear to have almost identical carbonyl stretching frequencies, the structure of IIIa, which was studied only in solution, is assumed to be similar to IIIb, for which the structure has been established by X-ray diffraction.

When the reaction was followed by ^1H NMR spectroscopy (Table 3) it was found that Ia is the main product and IIa is a by-product, formed in a 7/1 molar ratio. The other products could not be detected by ^1H NMR. Only IIa could be isolated in substantial amount though sufficient Ia was obtained to give an IR spectrum. The stretching frequencies of the terminal carbonyl groups are similar to those of IIa and IIIa, whereas the stretching frequencies of the bridging carbonyl groups differ by only 17 cm^{-1}. In the region between 650 and 1350 cm^{-1} the IR spectrum of Ia differs from that of IIa, which indicates the presence of a differently bonded NS fragment. From these observations, and by analogy with similar diiron complexes involving cyclic azo compounds

[24,25], structure Ia, shown in Fig. 6, is proposed. An alternative structure involves an end-on coordinated RNS group, which bridges the two Fe atoms via the S atom.

The well known compounds Va [26] and VIa [27] were difficult to isolate pure from the reaction mixture. After repeated crystallization only VIa was obtained pure. In the Raman spectrum of VIa shows three bands in the metal-metal stretching frequency region at 170, 197 and 219 cm^{-1}. The two strongest bands are tentatively assigned to ν(Fe—Fe), whereas the third band could arise from a δ(C—Fe—C) [22,23]. A band at 297 cm^{-1} is tentatively assigned to ν(FeS).

The mass spectrum of VIIa (Table 1) shows a parent peak at *m/e* 667 as well as fragments resulting from the successive loss of eleven carbonyl groups. This points to the overall formula $[Fe_4(CO)_{11}(RNS)S]$. This means that for VIIa a $Fe(CO)_2$ fragment is added to the original compound. From U.P.S. experiments it has been shown that VIIa is unstable in vacuum.

Reaction b, R = 4-MeC$_6$H$_4$

Just as in reaction *a* (with DBSD), the products Ib, IIb and IIIb are formed. Ib and IIb have only been studied in solution. The values for ν(CO) of Ia with respect to Ib, and IIa with respect to IIb are almost similar (Table 2). In contrast with reaction *a*, only a small trace of IIb is found, while IIIb is the only isolated dinuclear iron complex. In the Raman spectrum of IIIb at 220 cm^{-1} a band is found which is tentatively assigned to ν(Fe—Fe) and bands at 276 and 302 cm^{-1} to ν(FeS) by analogy with IIa and by comparison with other data [22] (Table 2).

The formation of azotoluene (IVb) is probably caused by decomposition of IIIb, because it is also formed when solid IIIb is heated under nitrogen in a thermoanalyser. Otsuka et al. [7] isolated only azobenzene and a trace of aniline from the reaction of $[Fe_2(CO)_9]$ with Ph—N=S=N—Ph, whereas IIb was prepared from a reaction between $[Fe_2(CO)_9]$ and Ph—N=S=O.

Discussion

(A) Structural aspects

For $[Fe_2(CO)_7(RNS)]$ (I) a structure containing a bridging carbonyl group is proposed. Assuming that each of the iron atoms fulfills the 18 electron rule, this implies that the RNS ligand, which is positioned parallel to the Fe—Fe axis, must act as a four-electron donor, and so an NS double bond must also be present.

In $[Fe_2(CO)_6(RNS)]$ (II) the RNS fragment is rotated by 90° with respect to the Fe—Fe bond, so that the sulfur and nitrogen bridge the two iron atoms. In this structure the RNS ligand acts as a six-electron donor and thus has a single NS bond. The structural features of this complex are similar to those of $[Fe_2(CO)_6(S_2)]$ (V), for which the structure has been established by X-ray diffraction [26], and to those of $[Fe_2(CO)_6(N—N)]$ [24,25,28—31].

$[Fe_2(CO)_6RNC(O)S]$ (III) has an RNC(O)S fragment, which is bonded to the $[Fe_2(CO)_6]$ entity via a N and S atom positioned similarly as the RNS fragment in II and likewise a six-electron donor. III is the first example of a compound in which a carbonyl group is inserted into an NS bond. A few examples of similar insertion processes in N—N bonds have been reported for [$Fe_2(CO)_6$-(RNNR)] [28—30, 32, 33)]. Such an inserted carbonyl group has also been found in [$(CpCo)_2$ {t-C_4H_9NC(O)N-t-C_4H_9}], which was prepared from DBSD and [CpCo$(CO)_2$] [9,34]. Accordingly, upon reaction with Co^I DBSD gives an R—N—C(O)—N—R fragment, whereas with Fe^0 an R—N—C(O)—S fragment is obtained.

In [$Fe_3(CO)_9$(RNS)S] (VIIIb) a triply bridging four-electron donor nitrene (RN) and a triply bridging four-electron donor S atom are each linked to the [$Fe_3(CO)_9$] entity, which contains two Fe—Fe bonds. The structural features of this complex are very similar to [$Fe_3(CO)_9S_2$] (VIa) [27] and to [$Fe_3(CO)_9$-$(RN)_2$] [28—30,35,36].

The most interesting product, however, is [$Fe_3(CO)_9$(RNS)S] (VIIa), not only because the skeleton, formed by the three iron, two sulfur and one nitrogen atoms, has a prismane structure, which is novel in cluster chemistry, but also because only one Fe—Fe bond is present in the trinuclear iron complex. Previously two types of triiron clusters containing ligands which are bonded via hetero atoms were known: (i) clusters containing two Fe—Fe bonds and two triply bridging ligands each acting as a four-electron donor such as VIIIb [28—30, 35—37]; (ii) clusters containing three Fe—Fe bonds are one ligand, bridging the three iron atoms and acting as a six-electron donor [7,25,38]. In VIIa both a triply bridging four-electron donor sulfur and a bridging six-electron donor RNS ligand are present. This results in a total of 52 valence electrons for the cluster, which means that only one Fe—Fe bond is necessary to give an 18 electron configuration on each of the iron atoms.

(B) Some aspects of the reaction route

The present work is to our knowledge the first attempt to study in detail the products obtained by the cleavage of the R—N=S=N—R molecule and rearrangement of the fragments on iron centers. At this stage of our study there is no direct evidence for the sequences by which the products are formed. However, on the basis of the structures of the isolated compounds and by analogy with information from the literature some conclusions about the course of the reaction can be drawn. In particular the product ratio of the various complexes seemed to be dependent on R.

Conversions of I into II involves the loss of a two-electron donor carbonyl ligand with concomitant rotation of the four-electron donor RNS ligand, which then becomes a six-electron donor ligand via bridging N and S atoms. This process necessarily weakens the NS bond, which formally has a double bond character in I but a single bond character in II. In this respect it seems plausible to assume that III is formed from II by insertion of CO into the weakened NS bond. The overall reaction from I → II → III thus illustrates how an NS bond can become activated on a metal—metal center towards an insertion reaction. The suggested processes have been observed for the reactions of similar cycloazo compounds with [$Fe_2(CO)_9$] (I → II) [24,25] and for the reaction of RN_3, RNCO or RNO_2 with [$Fe_2(CO)_9$] (II → III) [28—30]. The fact that for R = 4-MeC_6H_4 compound IIIb and for R = t-C_4H_9 compound IIa is the main product may be due to electronic, kinetic, a steric effects. It is not clear which effect dominates in the insertion reaction of a carbonyl group in the NS bond.

The difference between reactions *a* and *b* with respect to the yields of product II and III has consequences for the formation of further products. A possible route for the formation of the trinuclear complexes is a reaction of the dinuclear species with another iron carbonyl complex or fragment. For example $[Fe_2(CO)_6(S_2)]$ (Va) decomposes in $[Fe_3(CO)_9S_2]$ (VIa), which is in agreement with previous observations [28]. In reaction *b* the dinuclear complex IIIb is present in relatively large amounts, and it seems likely that this dinuclear species reacts with another iron carbonyl fragment to give VIIIb. This process is similar to that for $[Fe_2(CO)_6\{RNC(O)NR\}]$, which gives a dinitrene complex of the type $[Fe_3(CO)_9(NR)_2]$ [28—30]. The same applies for the conversion of IIa into VIIa in reaction *a*. In this case, however, the RNS fragment remains intact, which is in agreement with the conversion of similar complexes $[Fe_2(CO)_6(N{-}N)]$ into $[Fe_3(CO)_9(N{-}N)]$ (Fig. 1) [7,25,38], in which the cyclic-azo group remains unaltered. An obvious difference from the present reaction is that in VIIIa a triply bridged S atom is also present. This can be rationalised by a reaction of $[Fe_2(CO)_6(S_2)]$ (Va) giving $[Fe_3(CO)_9(RNS)S]$ (VIIa), in which Va provides a $[Fe(CO)_3S]$ fragment.

It is noteworthy that in the reaction *b* ($R = 4\text{-}MeC_6H_4$), IIIb is a minor product while VIIIb is the major product. The fact that in this reaction $[Fe_2(CO)_6(S_2)]$ and $[Fe_3(CO)_9S_2]$ are essentially absent suggests that Va is highly reactive towards either IIIb or an intermediate which is formed from IIIb by elimination of an OCS fragment. The yield of VIIa is low, indicating that IIa is somewhat inert towards Va and thus in reaction *a* Va and VIa are also present.

The formation of azotoluene (IVb) from IIIb is another interesting aspect of the reaction. In a separate experiment it was shown that azotoluene is produced by heating the solid carbonyl-inserted product IIIb. Elimination of a nitrene species occurs, and this dimerizes to give an azo compound. The residual product, which must be a dinuclear iron species containing a carbonyl sulfide ligand, has not been scanned.

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