Journal of Organometallic Chemistry, 301 (1986) 349–354
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS AND STRUCTURE OF BIS(μ-CYCLOHEXENE-2-YLTHIO)-μ_4-THIODODECACARBONYLTETRAIRON

B.I. KOLOBKOV, N.S. NAMETKIN *, V.D. TYURIN **, A.I. NEKHAEV*,

A.V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the U.S.S.R., Leninskii Prospect 29, Moscow (U.S.S.R.)

G.G. ALEKSANDROV,

All-Union Scientific Research Institute of Antibiotics, Nagatinskaya st. 3a, Moscow (U.S.S.R.)

M.T. TASHEV and H.B. DUSTOV

Bukhara Technological Institute of Food and Light Industry, Leninskogo Komsomola Prospect 15, Bukhara (U.S.S.R.)

(Received August 10th, 1985)

Summary

The reaction of sulfur with cyclohexene and $Fe_3(CO)_{12}$ in the ratio $S/Fe_3(CO)_{12}$, 3/1 gives $Fe_4(CO)_{12}S(SC_6H_9)_2$ with a yield of ca. 1% along with $Fe_2(CO)_6S_2$, $Fe_3(CO)_9S_2$, $Fe_2(CO)_6(S_2C_6H_{10})$ and $Fe_2(CO)_6(SC_6H_9)_2$. The structure of the tetranuclear complex was established by X-ray analysis.

Introduction

Complexes containing the fragment $Fe_4(CO)_{12}S_3$ have been described in the literature. $Fe_4(CO)_{12}S(SCH_3)_2$ (I), the first example of these complexes, was formed as a by-product with a yield of 1% in the reaction of methylthiocyanate, CH_3SCN, with $Fe_3(CO)_{12}$ [1] and it was also isolated from the reaction of cyclooctatetraene methyl thioether $C_8H_7SCH_3$ with $Fe_2(CO)_9$ [2] or the reaction of dimethyldisulphide with $Fe_3(CO)_{12}$ [3] with yields of 13 and 1%, respectively. The compound $Fe_4(CO)_{12}S(SC_4H_9\text{-t})_2$ (II) was formed along with many other products as a result of the interaction of $t\text{-}C_4H_9SH$ with $Fe_3(CO)_{12}$ for a long period of time with a yield of 5% [4]. $Fe_4(CO)_{12}S(n\text{-}RS)_2$ (III) complexes were generated in reactions of dialkyldisulphides with the triethylammonium salt of the undecacarbonyltriferrate

---

* Deceased (November 1984)

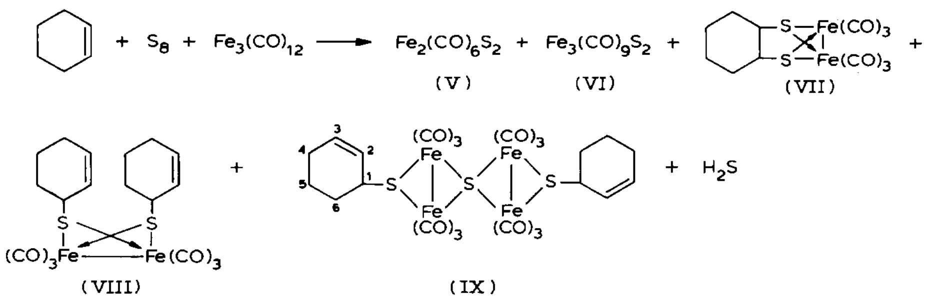
** Deceased (June 1983)

hydride $[(C_2H_5)_3NH]^+[HFe_3(CO)_{11}]^-$ (yield 2–6%), where $R = C_4H_9$, C_8H_{17}, $C_{12}H_{25}$ [5]. Finally, the dissymmetrical complex $Fe_4(CO)_{12}S(SCH_2C_5H_4 \cdot FeC_5H_5)(SCH_3)$ (IV), was synthesized with a yield of 11% from *S*-ferrocenylmethyl-*S*-methyldithiocarbonate and $Fe_2(CO)_9$ [6].

Recently, synthesis of the structural analogues of the compounds I–IV with P and As atoms as spirocentres in the reaction of PCl_3 or $AsCl_3$ with $Fe_2(CO)_9$ with yields of 11 and 41% respectively, has been reported [7].

Results and discussion

Earlier we described the results of our investigation on the interaction of elemental sulfur with cyclohexene under mild conditions (58°C) in the presence of $Fe_3(CO)_{12}$ in the ratio $S/Fe_3(CO)_{12}$, 60/1 [8]. Along with other reaction products and under a higher temperature (80°C) with the ratio $S/Fe_3(CO)_{12}$, 3/1 we have isolated the tetranuclear complex, containing a central S atom, coordinated with 4 atoms of iron, viz. bis(μ-cyclohexene-2-ylthio)-μ_4-thiododecacarbonyltetrairon (IX).



Our attempts to separate the complexes VII and VIII chromatographically on a silica gel column and by preparative thin-layer chromatography were not successful. Structure VIII has been postulated on the basis of IR (ν(C=C) 1640 cm^{-1}) and mass (m/z 426 (M^+) and 506 (M^+)) spectra of a mixture of VII and VIII, and also from structural data obtained for compound IX. Although it is known that VII is a crystalline substance [8], its mixture with VIII is a red-orange oil and complex VII is not crystallized from the mixture.

The yields relative to the initial Fe were: V, 0.8%; VI, 16.8%; VII + VIII, ca. 2%; IX, 1.3%. It should be pointed out that the reaction occurs with insignificant evolution of H_2S.

The formation of compound IX was interesting and unexpected; an unusual addition of the cyclohexene ring occurred without disturbing the olefin double bond.

The structure of compound IX was examined by X-ray analysis. The crystals of IX are triclinic, a 15.389(6), b 8.969(4), c 12.464(5), α 75.43(2), β 99.42(2), γ 103.22(2)°, V 1610.5(9) Å^3, $Z = 2$, space group $P\bar{1}$. Molecule IX (Fig. 1; Tables 1–3) consists of two doubly-bridged $Fe_2(CO)_6$ fragments bonded for a central sulfur atom. Each fragment is also bridged with the sulfur from a thiocyclohexenyl group. The molecular geometry of IX closely resembles that of the four previously reported complexes of this type, namely: I [1], IV [6], $Fe_4(CO)_{12}S(C_5H_4N)(C_5H_4NS)$ (X) [9] and $Fe_4(CO)_{12}S(CSNMe_2)(CNMe_2)$ (XI) [10].

The central sulfur atom is strongly distorted tetrahedrally coordinated: FeS(2)Fe angles vary from 68.7(1)° for the Fe(1)S(2)Fe(2) angle to 136.2(1)° for Fe(2)S(2)Fe(3).

(Continued on p. 353)

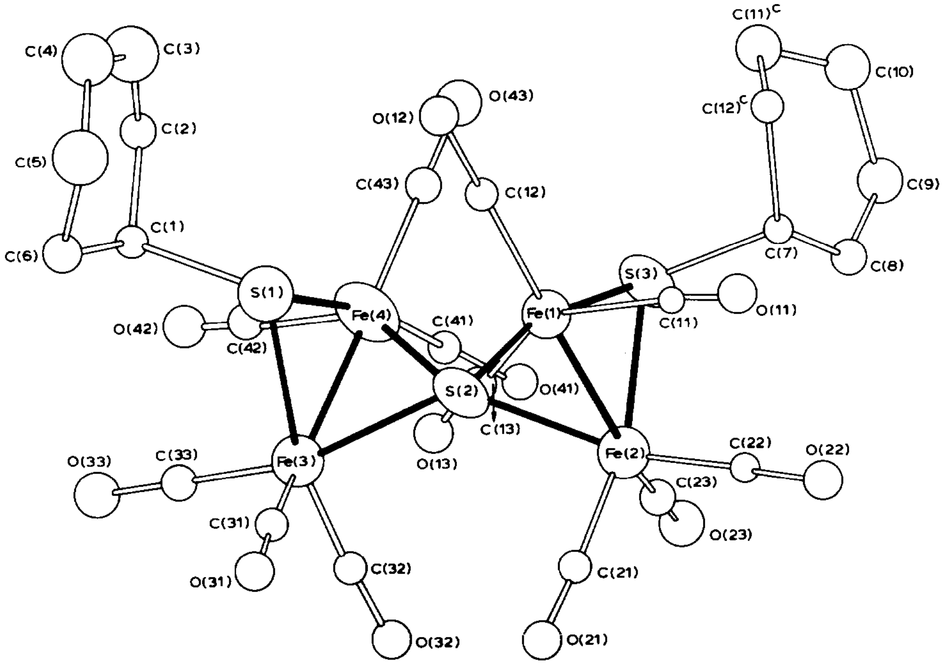


Fig. 1. The structure of $Fe_4(CO)_{12}S(SC_6H_9)_2$.

TABLE 1

ATOMIC COORDINATES ($\times 10^4$, for Fe and $S \times 10^5$) FOR COMPOUND IX

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	67257(8)	8577(14)	19928(11)	C(21)	5467(7)	3615(12)	1124(8)
Fe(2)	65487(9)	35683(15)	8773(11)	C(22)	6139(7)	3122(13)	−416(9)
Fe(3)	65327(9)	34666(15)	42295(11)	C(23)	6989(8)	5603(14)	415(10)
Fe(4)	81423(9)	38332(16)	38414(12)	C(31)	5430(7)	2353(12)	4375(8)
S(1)	74139(16)	16608(28)	49599(20)	C(32)	6231(7)	5210(12)	3441(8)
S(2)	69403(14)	29776(25)	27221(18)	C(33)	6711(8)	4215(15)	5440(10)
S(3)	78023(15)	25885(27)	10269(19)	C(41)	8368(8)	5662(13)	2913(9)
O(11)	6064(6)	−907(10)	248(7)	C(42)	8696(9)	4685(16)	4936(11)
O(12)	7821(6)	−1178(11)	2574(8)	C(43)	8982(8)	2972(14)	3544(9)
O(13)	5032(6)	−459(10)	2943(7)	C(1)	7857(7)	1423(13)	6458(9)
O(21)	4768(6)	3658(10)	1318(7)	C(2)	8763(9)	1045(17)	6621(11)
O(22)	5860(6)	2826(11)	−1281(8)	C(3)	8873(16)	−387(32)	6873(20)
O(23)	7299(7)	6936(13)	106(9)	C(4)	8237(16)	−1767(26)	7319(17)
O(31)	4693(7)	1700(11)	4480(8)	C(5)	7384(17)	−1546(28)	7173(19)
O(32)	6025(6)	6335(11)	2862(7)	C(6)	7180(10)	75(17)	7172(11)
O(33)	6815(7)	4644(12)	6259(8)	C(7)	7987(7)	2038(12)	−254(8)
O(41)	8507(6)	6875(11)	2301(8)	C(8)	8341(9)	3539(15)	−1057(10)
O(42)	9051(8)	5223(13)	5701(9)	C(9)	9232(12)	3904(21)	−1226(14)
O(43)	9522(6)	2411(11)	3359(8)	C(10)	9907(12)	2980(22)	−645(15)
C(11)	6349(7)	−220(12)	954(9)	C(11) ^{c}	9621(11)	1792(20)	354(14)
C(12)	7385(7)	−393(13)	2946(9)	C(12) ^{c}	8655(8)	886(14)	122(10)
C(13)	5707(7)	76(12)	2554(8)				

TABLE 2. BOND LENGTHS (Å) FOR COMPOUND IX

Bond		Bond		Bond	
Fe(1)-Fe(2)	2.529(2)	Fe(3)-C(33)	1.758(14)	O(33)-C(33)	1.154(18)
Fe(1)-S(2)	2.244(3)	Fe(4)-S(1)	2.268(2)	O(41)-C(41)	1.158(13)
Fe(1)-S(3)	2.267(2)	Fe(4)-S(2)	2.236(2)	O(42)-C(42)	1.175(18)
Fe(1)-C(11)	1.753(11)	Fe(4)-C(41)	1.751(10)	O(43)-C(43)	1.146(18)
Fe(1)-C(12)	1.776(11)	Fe(4)-C(42)	1.737(14)	C(1)-C(2)	1.479(19)
Fe(1)-C(13)	1.746(11)	Fe(4)-C(43)	1.778(14)	C(1)-C(6)	1.589(16)
Fe(2)-S(2)	2.238(2)	S(1)-C(1)	1.856(11)	C(2)-C(3)	1.287(32)
Fe(2)-S(3)	2.259(3)	S(3)-C(7)	1.866(12)	C(3)-C(4)	1.441(31)
Fe(2)-C(21)	1.754(11)	O(11)-C(11)	1.170(15)	C(4)-C(5)	1.350(37)
Fe(2)-C(22)	1.742(12)	O(12)-C(12)	1.151(14)	C(5)-C(6)	1.556(32)
Fe(2)-C(23)	1.776(11)	O(13)-C(13)	1.168(14)	C(7)-C(8)	1.509(14)
Fe(3)-Fe(4)	2.533(2)	O(21)-C(21)	1.150(15)	C(7)-C(12)^{c}	1.559(17)
Fe(3)-S(1)	2.269(3)	O(22)-C(22)	1.165(15)	C(8)-C(9)	1.373(22)
Fe(3)-S(2)	2.245(3)	O(23)-C(23)	1.172(15)	C(9)-C(10)	1.462(26)
Fe(3)-C(31)	1.774(10)	O(31)-C(31)	1.163(14)	C(10)-C(11)^{c}	1.475(23)
Fe(3)-C(32)	1.743(10)	O(32)-C(32)	1.159(13)	C(11)^{c}-C(12)^{c}	1.542(19)

TABLE 3. BOND ANGLES (°) FOR COMPOUND IX

Angle		Angle		Angle	
Fe(2)Fe(1)S(2)	55.5(1)	Fe(4)Fe(3)C(33)	100.1(4)	Fe(3)S(2)Fe(4)	68.8(1)
Fe(2)Fe(1)S(3)	55.9(1)	S(1)Fe(3)S(2)	76.3(1)	Fe(1)S(3)Fe(2)	67.9(1)
Fe(2)Fe(1)C(11)	100.0(3)	S(2)Fe(3)C(31)	105.8(4)	Fe(1)S(3)C(7)	114.1(3)
Fe(2)Fe(1)C(12)	149.9(3)	S(2)Fe(3)C(32)	91.1(4)	Fe(2)S(3)C(7)	115.0(3)
Fe(2)Fe(1)C(13)	104.1(4)	S(2)Fe(3)C(33)	155.1(4)	Fe(1)C(11)O(11)	177(1)
S(2)Fe(1)S(3)	76.8(1)	C(31)Fe(3)S(1)	103.3(4)	Fe(1)C(12)O(12)	179(1)
S(2)Fe(1)C(11)	155.0(3)	C(31)Fe(3)C(32)	97.3(5)	Fe(1)C(13)O(13)	179.1(9)
S(2)Fe(1)C(12)	104.2(4)	C(31)Fe(3)C(33)	98.8(5)	Fe(2)C(21)O(21)	178(1)
S(2)Fe(1)C(13)	91.6(4)	C(32)Fe(3)S(1)	158.1(4)	Fe(2)C(22)O(22)	179.6(9)
S(3)Fe(1)C(11)	94.4(3)	C(32)Fe(3)C(33)	90.0(6)	Fe(2)C(23)O(23)	178(1)
S(3)Fe(1)C(12)	100.6(3)	C(33)Fe(3)S(1)	94.1(4)	Fe(3)C(31)O(31)	176(1)
S(3)Fe(1)C(13)	160.0(4)	Fe(3)Fe(4)S(1)	56.1(1)	Fe(3)C(32)O(32)	176(1)
C(12)Fe(1)C(11)	100.4(5)	Fe(3)Fe(4)S(2)	55.8(1)	Fe(3)C(33)O(33)	177(1)
C(13)Fe(1)C(11)	89.4(5)	Fe(3)Fe(4)C(41)	105.8(4)	Fe(4)C(41)O(41)	179(1)
C(13)Fe(1)C(12)	98.0(5)	Fe(3)Fe(4)C(42)	99.7(5)	Fe(4)C(42)O(42)	178(1)
Fe(1)Fe(2)S(2)	55.8(1)	Fe(3)Fe(4)C(43)	147.1(4)	Fe(4)C(43)O(43)	179.6(9)
Fe(1)Fe(2)S(3)	56.2(1)	S(1)Fe(4)S(2)	76.5(1)	C(2)C(1)S(1)	109.3(9)
Fe(1)Fe(2)C(21)	101.2(3)	S(2)Fe(4)C(41)	92.3(4)	C(2)C(1)C(6)	112(1)
Fe(1)Fe(2)C(22)	99.2(4)	S(2)Fe(4)C(42)	154.9(5)	C(6)C(1)S(1)	108.8(7)
Fe(1)Fe(2)C(23)	151.0(4)	S(2)Fe(4)C(43)	102.4(4)	C(1)C(2)C(3)	121(2)
S(2)Fe(2)S(3)	77.0(1)	C(41)Fe(4)S(1)	161.8(4)	C(2)C(3)C(4)	127(3)
S(2)Fe(2)C(21)	89.2(3)	C(41)Fe(4)C(42)	89.7(6)	C(3)C(4)C(5)	114(2)
S(2)Fe(2)C(22)	154.4(4)	C(41)Fe(4)C(43)	98.8(6)	C(6)C(5)C(4)	121(2)
S(2)Fe(2)C(23)	106.3(4)	C(42)Fe(4)S(1)	94.5(4)	C(1)C(6)C(5)	109(1)
S(3)Fe(2)C(21)	157.4(3)	C(42)Fe(4)C(43)	102.0(6)	S(3)C(7)C(8)	107.3(8)
S(3)Fe(2)C(22)	93.6(4)	C(43)Fe(4)S(1)	97.6(3)	S(3)C(7)C(12)^{c}	106.8(7)
S(3)Fe(2)C(23)	100.0(4)	Fe(3)S(1)Fe(4)	67.9(1)	C(8)C(7)C(12)^{c}	113.6(9)
C(21)Fe(2)C(22)	91.2(5)	Fe(3)S(1)C(1)	117.8(4)	C(7)C(8)C(9)	120(1)
C(21)Fe(2)C(23)	101.0(6)	Fe(4)S(1)C(1)	113.8(3)	C(8)C(9)C(10)	125(1)
C(22)Fe(2)C(23)	98.7(5)	Fe(1)S(2)Fe(2)	68.7(1)	C(9)C(10)C(11)^{c}	114(2)
Fe(4)Fe(3)S(1)	56.0(1)	Fe(1)S(2)Fe(3)	135.0(1)	C(10)C(11)^{c}C(12)^{c}	111(1)
Fe(4)Fe(3)S(2)	55.4(1)	Fe(1)S(2)Fe(4)	126.3(1)	C(11)^{c}C(12)^{c}C(7)	111(1)
Fe(4)Fe(3)C(31)	152.9(4)	Fe(2)S(2)Fe(4)	133.7(1)		
Fe(4)Fe(3)C(32)	102.1(4)	FE(3)S(2)Fe(2)	136.2(1)		

The average Fe–S(2) bond length is 2.241(3) Å. In the dinuclear fragments the Fe atoms are bonded by normal Fe–Fe bonds (2.529(2) and 2.533(2) Å), and also with a bridging S atom of the C_6H_9 ligand (the average Fe–S bond length is 2.266(3) Å and the average angles of FeSFe and FeSC are 67.9(1) and 115.2(4)°, respectively). In addition, each Fe atom is coordinated with three terminal carbonyl groups (the average Fe–CO and C–O bond lengths are 1.76(1) and 1.16(2) Å, respectively), so that the Fe outermost electron shell, contains 18 electrons.

The cyclohexenyl fragments have the usual conformation of a distorted half-chair: in C(1)–C(6), the C(5) and C(6), but in the C(7)–C(12)^c atoms, the C(11)^c and C(12)^c are on different sides of the plane of the four atoms of an olefin system. The cyclohexenyl C(1)–C(6) ring appears to be disordered with atoms C(5) and C(6), stoichiometrically occupying two equivalent positions on different sides from the plane C(1)C(2)C(3)C(4). An analogical disordered character of the cyclohexenyl fragment has been found in benzo[*p*]-2-thiatetracyclo[7.5.3.0^{3,8}.0^{1,10}]heptadeca-3(8),15-diene for C(6) and C(7) atoms of the title compound [11].

The conformation of molecule IX may be characterized by dihedral angles between Fe_2S planes (97.4 and 96.8°) and an angle of 85.9° between Fe_2S planes in the Fe_4S tetrahedron. From the data listed in Tables 2 and 3 we conclude that the $Fe_4(CO)_{12}S_3$ framework is very similar to that in compounds I [1] and IV [6].

Experimental

The IR spectra were recorded in CCl_4 on a UR-20 spectrophotometer. The PMR spectrum was recorded on a Varian T-60 (60 MHz) spectrometer in $CDCl_3$ (10% concentration of IX) with TMS as the internal standard. The ^{13}C NMR spectrum was carried out with a Bruker WP-80 spectrometer at an operating frequency on ^{13}C nuclei of 20.115 MHz. The spectrum of a 30% solution of XI was measured under standard conditions in $CDCl_3$ with TMS as the internal standard. The mass spectra were obtained on a LKB-2091 instrument with direct inlet into the ion source at 50°C (VII + VIII) and 100°C (IX) and an ionization energy of 70 eV. An X-ray diffraction study was performed on a Syntex-P$\bar{1}$ diffractometer (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$-scanning, $3 \leqslant 2\theta \leqslant 48°$, 3600 reflections with $F^2 \geqslant 2\sigma$. The structure of complex IX was solved by direct method and refined by the least-squares method in anisotropic (Fe, S)–isotropic full matrix approximation to $R = 0.075$.

Synthesis of IX

A mixture of 9.6 g (0.3 g-atom) of sulfur, 50.4 g (0.1 mol) of $Fe_3(CO)_{12}$, 100 ml of cyclohexene in 1 l of n-heptane was stirred under argon for 9 h at 80°C. The H_2S evolved was led into a saturated aqueous solution of $CdCl_2$. Excesses cyclohexene and n-heptane were removed in vacuo. The residue was Soxhlet-extracted with pentane, then with ether until the colour no longer changed. The pentane and ether extracts were evaporated and the residue was dissolved in hexane and cooled to −78°C. The resulting precipitate contained unreacted $Fe_3(CO)_{12}$ and VI. The hexane solution was rotary evaporated to the minimum volume and chromatographed on a silica gel column (hexane as eluent). Isolated: first fraction V, m.p. 45°C; second fraction VI, m.p. 114°C (cf. ref. 12); third fraction a mixture of VII and VIII; fourth fraction IX, dark-red crystals. Obtained: 0.43 g (0.8%) of V, 8.15 g (16.8%) of VI, 1.4 g (ca. 2%) of VII + VIII, 0.2 g (0.4%) of $Fe_3(CO)_{12}$, 0.8 g (1.3%) of IX.

For IX: M.p. 165°C (dec.)(hexane). IR spectrum (ν, cm^{-1}): 2087, 2060, 2048, 2012, 1996, 1980(C≡O), 3036(CH), 2950, 2870, 2840 (CH_2), 1640 (C=C). Mass spectrum (m/z): 818 (M^+), 482 (M^+ −12CO), 320 ($M^+ - 12CO - 2C_6H_9$), 264 ($Fe_3S_3{}^+$), 232 ($Fe_3S_2{}^+$), 176 ($Fe_2S_2{}^+$), 144 (Fe_2S^+), 112 (Fe_2^+), 81 ($C_6H_9{}^+$), 56 (Fe^+). PMR spectrum (δ, ppm): 5.4–6.0 (2H, CH=CH), 3.10 (1H, SCH), 1.2–2.4 (6H). ^{13}C NMR spectrum ($\delta(^{13}C)$, ppm): 208.5 (C≡O); 47.8 C(1); 131.4 C(2); 128.8 C(3); 31.9 C(4); 24.9 C(5); 19.7 C(6). Found: C, 35.18; H, 2.28; Fe, 27.19; S, 11.63. $C_{24}H_{18}Fe_4O_{12}S_3$ calcd.: C, 35.24; H, 2.22; Fe, 27.31; S, 11.76%.

References

1 J.M. Coleman, A. Wojcicki, P.J. Pollick and L.F. Dahl, Inorg. Chem., 6 (1967) 1236.
2 S.C. Carleton, F.G. Kennedy and S.A.R. Knox, J. Chem. Soc. Dalton Trans., (1981) 2230.
3 C. Glidewell and A.R. Hyde, Inorg. Chim. Acta, 87 (1984) L15.
4 J.A. De Beer and R.J. Haines, J. Organomet. Chem., 24 (1970) 757.
5 N.S. Nametkin, V.D. Tyurin, I.P. Podol'skaya and B.I. Kolobkov, IX Intern. Symp. Organosulfur Compounds Chemistry, Abstracts, Riga, U.S.S.R., 1980, p. 326.
6 H. Patin, G. Mignani, C. Mahe, J.-Y. Le Marouille, A. Benoit and D. Grandjean, J. Organomet. Chem., 210 (1981) C1.
7 G. Huttner, G. Mohr, B. Pritzlaff, J. v. Seyerl and L. Zsolnai, Chem. Ber., 115 (1982) 2044.
8 N.S. Nametkin, V.D. Tyurin, G.G. Aleksandrov, I.V. Petrosyan, B.I. Kolobkov, A.M. Krapivin and Yu.T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1981) 2572.
9 G. Le Borgne and D. Grandjean, J. Organomet. Chem., 92 (1975) 381.
10 W.K. Dean and D.G. Vanderveer, J. Organomet. Chem., 146 (1978) 143.
11 G.G. Aleksandrov, A.A. Shcherbakov, Yu.T. Struchkov and V.G. Kharchenko, Cryst. Struct. Commun., 9 (1980) 625.
12 W. Hieber and J. Gruber, Z. Anorg. Allg. Chem., 296 (1958) 91.