

SYNTHESIS AND MOLECULAR STRUCTURE OF THE NIOBOCENE SULPHIDE DIMER

Yu.V. SKRIPKIN, I.L. EREMENKO, A.A. PASYNSKII*

N.S. Kurnakov Institute of General and Inorganic Chemistry, Academy of Sciences of the U.S.S.R., 31 Leninskii Prospect, Moscow V-71 (U.S.S.R.)

Yu.T. STRUCHKOV and V.E. SHKLOVER

A.N. Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., 28 Vavilova St., Moscow V-312 (U.S.S.R.)

(Received January 24th, 1984)

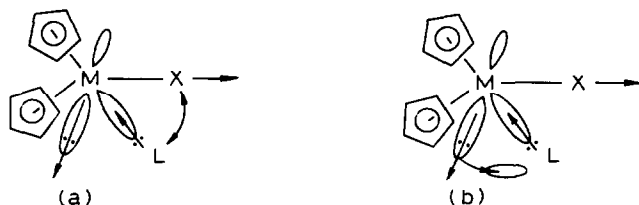
Summary

The reaction of Cp_2NbBH_4 in benzene in the presence of Et_3N and PhSH results in a green, crystalline, diamagnetic complex, $[\text{Cp}_2\text{NbSPh}]_n$ (I), which probably has a polymer structure. The reaction of Cp_2NbBH_4 under the same conditions with *t*-BuSH or $(\text{CpCrSCMe}_3)_2\text{S}$ yields a red, crystalline, diamagnetic complex, $[\text{Cp}_2\text{NbS}]_2$ (II), whose structure was established by X-ray analysis. In II, the Nb atom belongs to the niobocene fragment, whose inclined rings (dihedral angle 47.25°) are in a staggered conformation ($\text{Nb}-\text{C}_{\text{Cp(av)}}$ 2.452(7), $\text{C}-\text{C}_{\text{Cp(av)}}$ 1.40(1) Å). Moreover, each Nb atom forms two equivalent short bonds, Nb–S (2.429(2) and 2.427(2) Å), and the angles Nb–S–Nb ($83.51(5)^\circ$) are coequal, as are the S–Nb–S angles ($96.49(6)^\circ$). The Nb–Nb distance (3.2343(8) Å) is evidently bond-forming. The molecule on the whole resembles C_{2v} in symmetry.

Introduction

One of the main problems of modern coordination chemistry is the formation of transition-metal sandwich compounds with groups containing valence n - and π -electron pairs. For instance, according to the Alcock, Green and Hoffmann models [1], the fragment Cp_2MX (where $\text{Cp} = \pi\text{-C}_5\text{H}_5$, $\text{M} = \text{Nb}^{\text{III}}$ or V^{III} , and X is a one-electron σ -bonded ligand) has three orbitals in the bisector plane of the angle between the rings. One of them ($2a_1$ symmetry) is occupied by the electron pair of the M–X bond, the other ($1a_1$ symmetry) is occupied by the lone electron pair of the M atom, while the third (symmetry b_2) remains vacant. Further coordination of the L ligands is governed by the superposition of the stabilizing factor of the M–L donor–acceptor interaction and the destabilizing steric effect that repels L from X and the

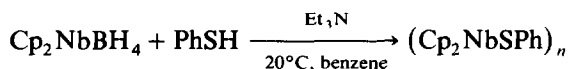
cyclopentadienyl groups. The relative importance of these effects evidently depends on whether L has vacant orbitals for interaction with the lone electron pair of M (structures a and b, respectively):



For instance, Cp_2VSR ($\text{R} = \text{Me}, \text{Ph}$) is a monomer with two unpaired electrons [2,3] due to the absence of low-level vacant orbitals in the SR groups, which should lead to an a-type structure ($\text{X} = \text{SR}$; L is the other Cp_2VSR molecule by way of the SR bridges). Nevertheless, these complexes easily attract the CO molecule which is capable of accepting the vanadium atom lone electron pair (b-type) [2]. The formation of a-type structures is much easier when only one electron is present in the $1a_1$ orbital (electronic configuration d^1). Thus, a diamagnetic dimer $(\text{Cp}_2\text{TiSPh})_2$ with SPh bridges [3,4] and a mononuclear complex $\text{Cp}_2\text{V}(\text{SR})_2$ with a single unpaired electron [5] are known. As there the mononuclear complex $\text{Cp}_2\text{Nb}(\text{SR})_2$ ($\text{R} = \text{Me}, \text{Ph}$) exists [6], it appeared interesting to synthesize and study the properties of Cp_2NbSR ($\text{R} = \text{Ph}, t\text{-Bu}$) (electronic configuration d^2). Up to now, only one niobium sandwich monothiolate complex, $\text{Cp}_2\text{Nb}(\text{CO})\text{SH}$, has been described [7].

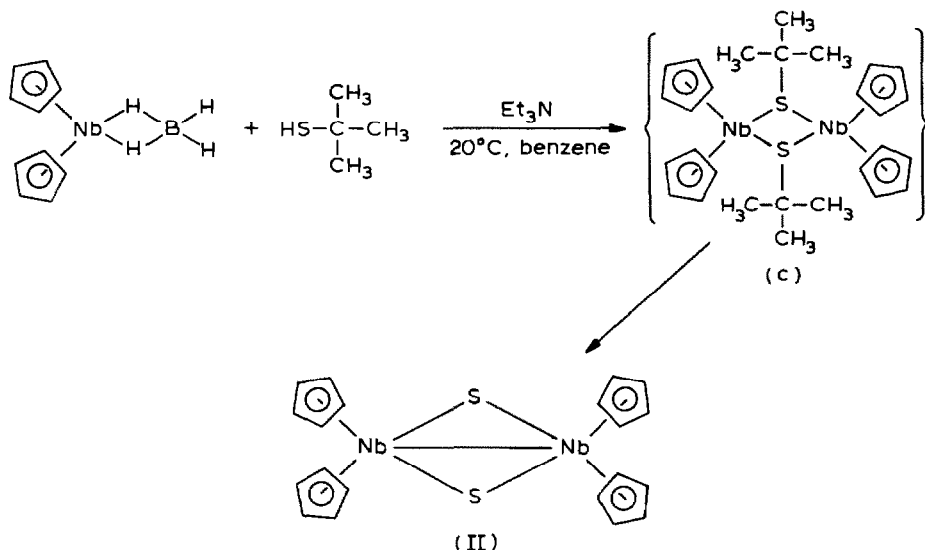
Results and discussion

To synthesize the Cp_2NbSR -type compounds, the so-called “boron hydride method” was used (treating Cp_2NbBH_4 with proton donors). This method was previously used to obtain the carboxylate derivatives $\text{Cp}_n\text{Nb}(\text{OOCR})_m$ ($n = 0$ or 2 ; $m = 1-5$) [8]. The final result of the mercaptane reaction with the $\text{Cp}_2\text{NbBH}_4/\text{Et}_3\text{N}$ system turned out to be greatly dependent on the nature of R. Thus, in the reaction with thiophenol, a Cp_2NbSPh complex is formed:

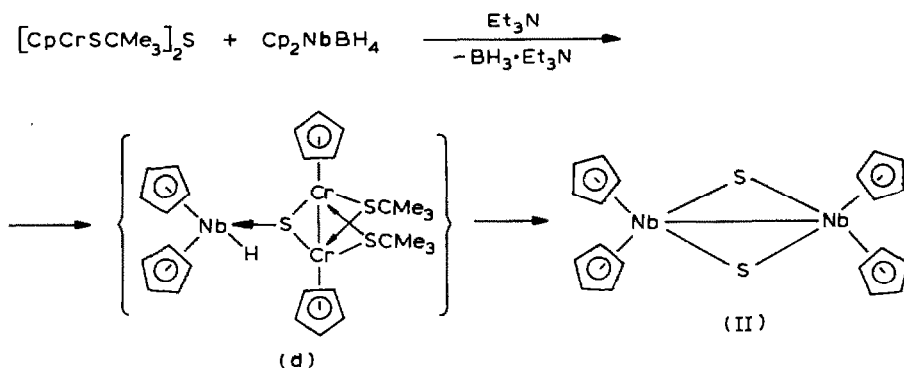


Complex I is a green, diamagnetic, crystalline substance, m.p. (decomp.) $263-265^\circ\text{C}$, which, unlike Cp_2VSPH , is insoluble in organic solvents, which interferes with molecular weight determination and the growing of crystals needed for X-ray structural analysis. The mass spectrum of I contains a molecular ion $[\text{Cp}_2\text{NbSPh}]^+$ (m/z 332), and a fragment $[\text{Cp}_2\text{Nb}]^+$ (m/z 223). Complex L evidently has a dimer or polymer structure due to the formation of thiolate bridges without additional Nb–Nb bonds. The difference from the mononuclear Cp_2VSPH evidently lies in the larger covalent radius of Nb (1.66 \AA) [9], as compared to 1.49 \AA for V [9].

On the other hand, attempts to synthesize a more soluble analogue by substituting the phenyl group for a t-butyl group lead to a split-up of the t-butyl groups and the formation of the niobocene sulphide dimer $[\text{Cp}_2\text{NbS}]_2$ (II):



The loss of *t*-butyl radicals can probably be explained by the short contacts between the cyclopentadienyl ligands and the CMe_3 groups in the intermediate binuclear complex (c). Complex II is also formed in the reaction of $\text{Cp}_2\text{NbBH}_4/\text{Et}_3\text{N}$ with the dinuclear $(\text{CpCrSCMe}_3)_2\text{S}$ complex [10], according to the scheme which includes the sterically overloaded intermediate d (the chromium-containing residue was not analysed):



Complex II is a red, diamagnetic, crystalline substance, which decomposes without melting at temperatures above 300°C , is poorly soluble in THF, and is insoluble in benzene and heptane. The mass spectrum of II includes a molecular ion, $[\text{Cp}_2\text{NbS}]_2^+$ (m/z 510), its fragmentation products with stepwise split-up of the four cyclopentadienyl ligands (m/z 445, 380, 315 and 250, respectively), as well as mononuclear dimer dissociation products, beginning with $[\text{Cp}_2\text{NbS}]^+$ (m/z 255). The structure of complex II has been unambiguously determined by X-ray analysis (cf. Figs. 1 and 2). The atomic coordinates, main bond lengths and angles are listed in Tables 1, 2 and 3, respectively. The dinuclear molecules $[\text{Cp}_2\text{NbS}]_2$ are structural units in the crystals of complex II. In these molecules, the Nb atom in the niobocene fragment with a staggered ring conformation ($\text{Nb}-\text{C}_{5,\text{H}_5(\text{av})}$ 2.452(7), $\text{C}-\text{C}_{(\text{av})}$ 1.40(1)

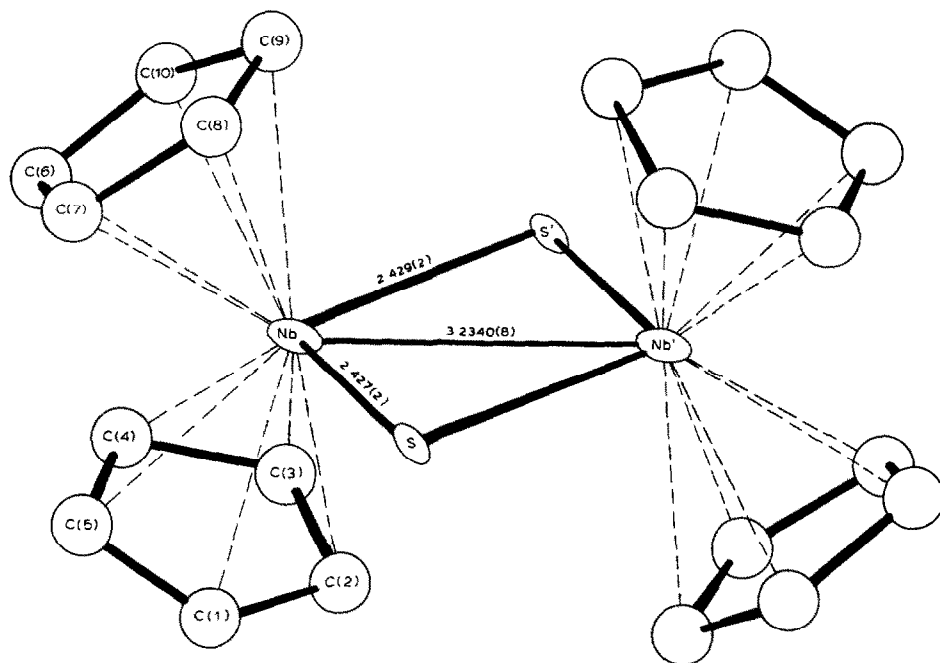


Fig. 1. Molecular structure of complex II.

Å) forms almost equivalent short bonds with the two sulphur atoms: Nb–S (2.429(2) and 2.427(2) Å). The Nb–S–Nb angles are coequal (83.5(5)°), as are the S–Nb–S angles (96.49(6)°). On the whole, the molecule, is like C_{2v} in symmetry. The Nb–Nb bond length (3.2340(8) Å) is similar to the value 3.314 Å recorded for the Nb–Nb bond in $[\text{Cp}(\text{C}_5\text{H}_4)\text{NbH}]_2$ [11], and also to the sum of the covalent Nb atom radii (1.66 + 1.66 = 3.32 Å). It seems that strong exchange interactions along the direct

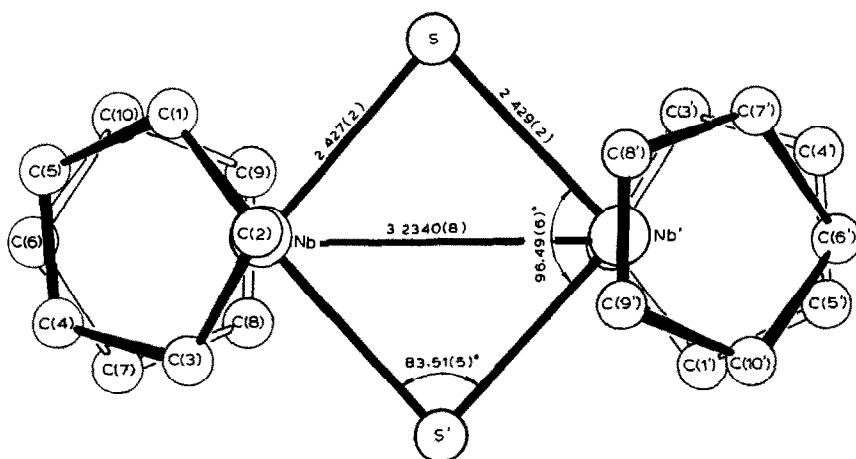


Fig. 2. Molecular structure of complex II.

Nb–Nb bond determines the diamagnetism of complex II. At the same time, short contacts, $S \cdots C_{C_5H_5}$ (2.9–3.1 Å), in complex II hamper further shortening of the Nb–Nb bond. It is of interest to compare the lengths of the Nb–Nb and Nb–S bonds in II with those found in the dinuclear complex $[CpNb(CO)_2]_2(\mu-SCH_3)_2$ (III) and in the two complexes [12] which the authors believe to have the formulae $[CpNb(CO)_2]_2(\mu-S)_2$ (IV) and $[CpNb(CO)_2]_2(\mu-S)_3$ (V). These compounds have

TABLE 1

ATOMIC COORDINATES FOR COMPLEX II ($\times 10^5$ for Nb and S; $\times 10^4$ for C)

Atom	x	y	z
Nb	58251(4)	14508(7)	–4966(7)
S	41498(12)	15607(20)	9675(20)
C(1)	7374(6)	783(9)	768(10)
C(2)	6599(6)	926(10)	2037(9)
C(3)	6271(5)	2609(9)	2127(8)
C(4)	6835(6)	3473(10)	886(9)
C(5)	7526(5)	2336(10)	66(9)
C(6)	6433(6)	3464(10)	–2576(8)
C(7)	5428(6)	3904(9)	–2094(9)
C(8)	4801(6)	2607(9)	–2619(9)
C(9)	5413(6)	1367(10)	–3372(8)
C(10)	6448(6)	1874(9)	–3336(9)

TABLE 2

BOND LENGTHS d (Å)

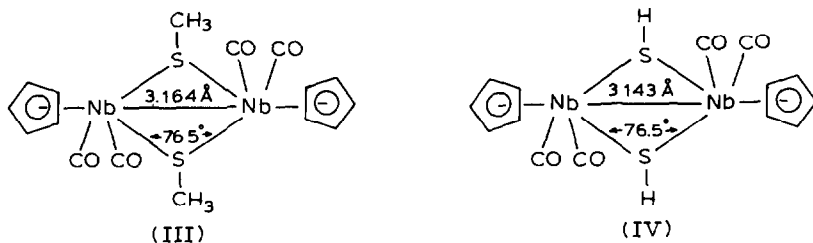
Bond	d	Bond	d
Nb–Nb'	3.2340(8)	Nb–C(9)	2.480(7)
Nb–S	2.427(2)	Nb–C(10)	2.427(7)
Nb–S'	2.429(2)	C(1)–C(2)	1.39(1)
Nb–C(1)	2.455(8)	C(1)–C(5)	1.39(1)
Nb–C(2)	2.445(7)	C(2)–C(3)	1.41(1)
Nb–C(3)	2.470(7)	C(3)–C(4)	1.39(1)
Nb–C(4)	2.443(7)	C(4)–C(5)	1.41(1)
Nb–C(5)	2.448(7)	C(6)–C(7)	1.40(1)
Nb–C(6)	2.427(7)	C(6)–C(10)	1.41(1)
Nb–C(7)	2.441(7)	C(8)–C(9)	1.39(1)
Nb–C(8)	2.488(7)	C(9)–C(10)	1.43(1)

TABLE 3

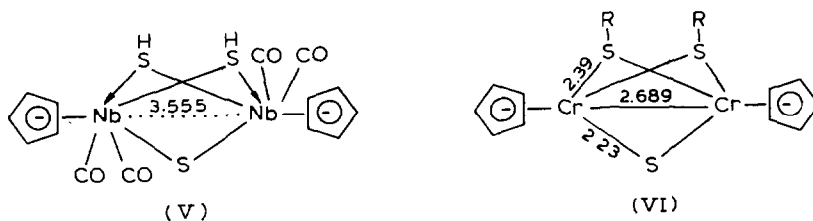
BOND ANGLES, ω (°)

Angle	ω	Angle	ω
SNbS'	96.49(6)	C(1)C(5)C(4)	108.2(7)
NbS'Nb'	83.51(5)	C(7)C(6)C(10)	108.8(7)
C(2)C(1)C(5)	107.5(7)	C(6)C(7)C(8)	107.5(7)
C(1)C(2)C(3)	109.5(7)	C(7)C(8)C(9)	108.6(6)
C(2)C(3)C(4)	106.9(6)	C(8)C(9)C(10)	108.1(7)
C(3)C(4)C(5)	108.2(7)	C(6)C(10)C(9)	106.8(6)

been obtained from $\text{CpNb}(\text{CO})_3 \cdot \text{THF}$ and MeSH or H_2S , respectively. Although structural analysis [12] failed to determine hydrogen atoms at the sulphide bridges in the diamagnetic complexes IV and V, a close resemblance of the structures of complexes IV and III, which has methylthiolate bridges, allows us to suppose that IV has two hydrosulphide, rather than sulphide, bridges:



The Nb-S distance is practically the same as that of Nb-SH (2.54 Å) in $\text{Cp}_2\text{Nb}(\text{CO})\text{SH}$ [7]. At the same time, in $[\text{Cp}_2\text{NbS}]_2$ (II), the Nb-S bonds are much shorter (av. 2.428(2) Å). A similar difference in the M-S and M-SR linkages was observed in the structure of the above-mentioned dinuclear complex $(\text{CpCrSCMe}_3)_2\text{S}$ (VI) ($\text{Cr}-\text{SCMe}_{3\text{av.}} = 2.39(1)$, $\text{C}-\text{S}_{\text{av.}} = 2.23(1)$ Å) [10]:



In complex V, the length of the four Nb-S bonds (av. 2.640(3) Å) is radically increased compared to the other two Nb-S bond lengths (2.525(2) Å). We may therefore assume that V has two hydrosulphide and one sulphide bridges. This, given the absence of a Nb-Nb bond (Nb...Nb distance is 3.555 Å), provides for 18 electrons around the niobium atom and explains the diamagnetism of V.

Experimental

All procedures during the synthesis and isolation of complexes I and II were carried out in a pure argon atmosphere using pure, absolute solvents saturated with argon. Cp_2NbBH_4 was synthesized according to the method of ref. 13, and $(\text{CpCrS}(\text{CMe}_3)_2\text{S})$ according to that of ref. 10. The commercial reagents PhSH and $t\text{-BuSH}$ were distilled before use, and Et_3N was distilled over Na. IR spectra were obtained using KBr pellets in a UR-20 spectrometer. Melting points were determined in a vacuum-sealed capillary and are uncorrected. Mass spectra were obtained using a DS-50 spectrometer. Experimental data for the X-ray structural study were collected on a Syntex P2₁ autodiffractometer ($\lambda(\text{Mo-K}_\alpha)$, $\theta-2\theta$ scanning, $2^\circ \leq 2\theta \leq 56^\circ$, $T = -120^\circ\text{C}$). The structure was solved by a direct method using a modified MULTAN program*, and refined in a full-matrix anisotropic approxima-

* The program was modified by R.G. Herr and A.I. Yanovsky at the Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R.

tion for all non-hydrogen atoms up to $R = 0.059$ and $R_w = 0.071$ for 1256 independent reflections with $I \geq 2\sigma$. Lattice cell parameters: a 13.260(10), b 7.964(7), c 8.230(10) Å, β 95.41(8)°, $Z = 2$, space group $P2_1/n$, V 865.2 Å³. Hydrogen atoms were localized by difference Fourier synthesis and refined in an isotropic approximation. The C–H distances in the C₅H₅ ligands varied from 0.71(8) to 1.05(9) Å.

[Cp₂NbSPh]_n

10 ml of Et₃N was added to a dark-green solution of 1.8 g (7.5 mmol) of Cp₂NbBH₄ in 30 ml of benzene; the solution then assumed a brownish hue. A solution of 0.825 g (7.5 mmol) of PhSH in 10 ml of benzene was then added dropwise at room temperature and the mixture turned red. After gas elimination, the precipitated dark-green crystals were separated from the solution, washed with a mixture of benzene and heptane (1/1), and dried in vacuo. Yield 0.92 g (36%). M.p. (decomp.) 263–265°C. Found: C, 57.60; H, 4.73; S, 8.70; Nb, 27.60. C₁₆H₁₅NbS calcd.: C, 57.83; H, 4.55; S, 9.64; Nb, 27.96%. IR spectrum (cm⁻¹): 745w, 625w, 695m, 742s, 828s, 882w, 1012m, 1030m, 1440m, 1474m, 3100m.

[Cp₂NbS]₂

(a) From Cp₂NbBH₄ and *t*-BuSH. 10 ml of Et₃N was added to a dark-green solution of 1.5 g (6.3 mmol) of Cp₂NbBH₄ in 40 ml of benzene (the solution assumed a brownish hue). A solution of 0.57 g (6.3 mmol) of Me₃CSH in 10 ml of benzene was then added dropwise at room temperature. The reaction mixture turned brownish-yellow in colour. After 1 h, the precipitated dark-red crystals were separated from the solution, washed with a mixture of benzene and heptane (1/1), and dried in vacuo. Yield 0.91 g (53%). $T_{\text{decomp.}} > 300^\circ\text{C}$. Found: C, 48.20; H, 4.10; S, 11.30; Nb, 36.30. C₁₀H₁₀NbS₂ calcd.: C, 47.06; H, 3.95; S, 12.56; Nb, 36.41%. IR spectrum (cm⁻¹): 400w, 605w, 627w, 685w, 815s, 850m, 900w, 950w, 1019m, 1372w, 1440m, 3072w, 3100w, 3130w.

(b) From (CpCrSCMe₃)₂S and Cp₂NbBH₄. A solution of 0.4 g (1.68 mmol) of Cp₂NbBH₄ in a mixture of 20 ml of benzene and 10 ml of THF was added to a violet solution of 0.9 g (2.02 mmol) of (CpCrSCMe₃)₂S in 15 ml of benzene. The reaction mixture was boiled for 2.5 h, during which 1.5 ml of Et₃N was added. The precipitated needle-like crystals were separated from the solution by decantation, washed with THF and benzene, and dried in a high vacuum. Yield 0.26 g.

Acknowledgements

The authors thank Dr. D.V. Zagorevsky and Dr. Yu.S. Nekrasov for the mass spectra.

References

- 1 J.W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, **98** (1976) 1729.
- 2 G. Fachinetti, S. Del Nero and C. Floriani, *J. Chem. Soc., Dalton Trans.*, (1976) 203.
- 3 A.A. Pasyanskii, I.L. Eremenko, Yu.V. Skripkin and V.T. Kalinnikov, *Koord. Khim.*, **3** (1977) 1511.
- 4 M.F. Lappert and A.R. Sanger, *J. Am. Chem. Soc.*, **A**, (1971) 1314.
- 5 G. Fachinetti and C. Floriani, *J. Chem. Soc., Dalton Trans.*, (1974) 2433.
- 6 W.E. Douglas, M.L.H. Green, C.K. Prout and G.V. Rees, *J. Chem. Soc., Chem. Commun.*, (1971) 896.
- 7 N.I. Kirilova, A.I. Gusev, A.A. Pasyanskii and Yu.T. Struchkov, *Zh. Strukt. Khim.*, **14** (1973) 868.

- 8 A.A. Pasynskii, Yu.V. Skripkin and V.T. Kalinnikov, *J. Organomet. Chem.*, 150 (1978) 51.
- 9 V.G. Andrianov, B.P. Biryukov and Yu.T. Struchkov, *Zh. Strukt. Khim.*, 10 (1969) 1129.
- 10 A.A. Pasynskii, I.L. Eremenko, Yu.V. Rakitin, V.M. Novotortsev, V.T. Kalinnikov, G.G. Aleksandrov and Yu.T. Struchkov, *J. Organomet. Chem.*, 165 (1979) 57.
- 11 L.G. Guggenberger, *Inorg. Chem.*, 12 (1973) 294.
- 12 W.A. Herrmann, H. Biersack, M.L. Ziegler and B. Balbach, *J. Organomet. Chem.*, 206 (1981) 35.
- 13 C.R. Lukas and M.L.H. Green, *J. Chem. Soc., Chem. Commun.*, (1972) 1005.