

INTERACTION OF VINYLGERMANES WITH IRON CARBONYLS. X-RAY CRYSTAL STRUCTURE OF THE $\text{Ge}[\text{Fe}(\text{CO})_4]_4$ COMPLEX

A.S. BATANOV *, L.V. RYBIN, M.I. RYBINSKAYA, Yu.T. STRUCHKOV

Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences of the U.S.S.R., 28 Vavilov Str., Moscow B-334 (U.S.S.R.)

I.M. SALIMGAREEVA and N.G. BOGATOVA

Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the U.S.S.R., 71 October Ave., Ufa 54 (U.S.S.R.)

(Received January 25th, 1983)

Summary

The reaction between vinylgermanes and iron carbonyls yields, besides π -olefin complexes, the cluster compound $\text{Ge}[\text{Fe}(\text{CO})_4]_4$ (I), characterized here by X-ray crystallography. The presence of an unsaturated substituent at the Ge atom plays an important role in the formation of I.

Introduction

As we have reported previously [1], vinylgermanes and hexavinyl digermane react with nonacarbonyldiiron in hydrocarbon solvents at 35–40°C (like their Si analogues [2]) forming π -olefin complexes with the $\text{Fe}(\text{CO})_4$ group coordinated by the vinyl C=C bond of the germane, while under more severe conditions we obtained a dark red crystalline substance (I) containing C, Fe and Ge, but no hydrogen. In the present paper we describe the preparation of I in more detail and report its molecular structure determined by an X-ray single crystal structural study.

Results and discussion

Complex I (yield ca. 4%) was obtained by boiling tetravinylgermane with $\text{Fe}_3(\text{CO})_{12}$ in benzene or toluene. The same reaction with $\text{Fe}_2(\text{CO})_9$ gave a slightly smaller yield, and the reaction between hexavinyl digermane and $\text{Fe}_3(\text{CO})_{12}$ gave ca. 2% of I. The formation of I obviously proceeds through elimination of all the vinyl groups from the Ge atom. We found that such an elimination of all organic radicals under heating with iron carbonyls also took place in the case of alkenyl-alkylgermanes. Thus boiling of $\text{Et}_3\text{Ge}(\text{CH}=\text{CH}_2)$ with $\text{Fe}_3(\text{CO})_{12}$ in toluene gives I, while

heating of GeEt_4 with $\text{Fe}_3(\text{CO})_{12}$ in toluene or with $\text{Fe}_2(\text{CO})_9$ in benzene does not. Therefore we propose that the reaction passes through intermediate formation of $(\eta^2\text{-vinylgermane})\text{Fe}(\text{CO})_4$ complexes, as reported earlier [1]. The coordination of iron by a vinyl group directly bound to the Ge atom should labilize the other Ge–C bonds (as observed in cyclogermapentadiene iron complexes [3]) and hence promote the formation of I.

Complex I belongs to a rather poorly investigated class of carbonyliron clusters containing non-transition elements, which now rouse considerable interest [4–7].

TABLE 1
INTERATOMIC DISTANCES (Å)

Fe(A)–Fe(B)	2.825(1)	Fe(A)···Fe(C)	4.380(1)	Fe(B)···Fe(C)	4.371(1)
Fe(C)–Fe(D)	2.821(1)	Fe(A)···Fe(D)	4.374(1)	Fe(B)···Fe(D)	4.327(1)
	A		B		C
	D		C		D
Fe–Ge	2.388(1)	2.407(1)	2.406(1)	2.398(1)	
Fe–C(1)	1.820(5)	1.849(5)	1.825(5)	1.833(5)	
Fe–C(2)	1.778(6)	1.779(5)	1.805(5)	1.801(5)	
Fe–C(3)	1.783(5)	1.807(5)	1.810(5)	1.803(5)	
Fe–C(4)	1.794(6)	1.801(5)	1.812(5)	1.799(5)	
C(1)–O(1)	1.139(6)	1.127(6)	1.138(7)	1.134(7)	
C(2)–O(2)	1.140(7)	1.139(7)	1.138(6)	1.134(7)	
C(3)–O(3)	1.161(7)	1.142(6)	1.142(7)	1.148(6)	
C(4)–O(4)	1.140(7)	1.144(7)	1.137(6)	1.138(6)	

TABLE 2
BOND ANGLES (°)

Fe(A)GeFe(B)	72.20(3)	Fe(A)GeFe(C)	132.04(3)	Fe(B)GeFe(C)	130.56(3)
Fe(C)GeFe(D)	71.94(3)	Fe(A)GeFe(D)	132.16(3)	Fe(B)GeFe(D)	128.52(3)
	A		B		C
	D		C		D
GeFeFe	54.21(2)	53.60(2)	53.90(2)	54.16(2)	
GeFeC(1)	151.4(2)	144.2(2)	151.6(2)	143.8(2)	
GeFeC(2)	104.7(2)	111.3(2)	103.4(2)	111.4(2)	
GeFeC(3)	86.3(2)	85.0(2)	90.1(2)	83.8(2)	
GeFeC(4)	85.4(2)	85.8(2)	83.2(2)	83.2(2)	
FeFeC(1)	97.4(2)	90.6(2)	98.7(2)	89.7(2)	
FeFeC(2)	158.3(2)	164.7(2)	156.3(2)	165.4(2)	
FeFeC(3)	86.0(2)	93.7(2)	85.3(2)	92.6(2)	
FeFeC(4)	92.1(2)	89.5(2)	92.2(2)	87.6(2)	
C(1)FeC(2)	103.9(2)	104.6(2)	104.5(2)	104.7(2)	
C(1)FeC(3)	95.1(2)	98.0(2)	95.3(2)	99.8(2)	
C(1)FeC(4)	94.0(2)	95.8(2)	91.5(2)	96.4(2)	
C(2)FeC(3)	88.0(2)	86.3(2)	88.2(2)	87.2(2)	
C(2)FeC(4)	90.6(3)	87.0(2)	91.5(2)	88.5(2)	
C(3)FeC(4)	170.9(2)	165.7(2)	173.0(2)	163.8(2)	
FeC(1)O(1)	179.5(5)	178.1(4)	177.3(5)	178.6(5)	
FeC(2)O(2)	177.2(5)	179.6(5)	177.2(4)	179.1(5)	
FeC(3)O(3)	176.5(5)	174.8(5)	175.1(5)	175.4(4)	
FeC(4)O(4)	177.6(5)	175.0(5)	176.3(4)	175.1(4)	

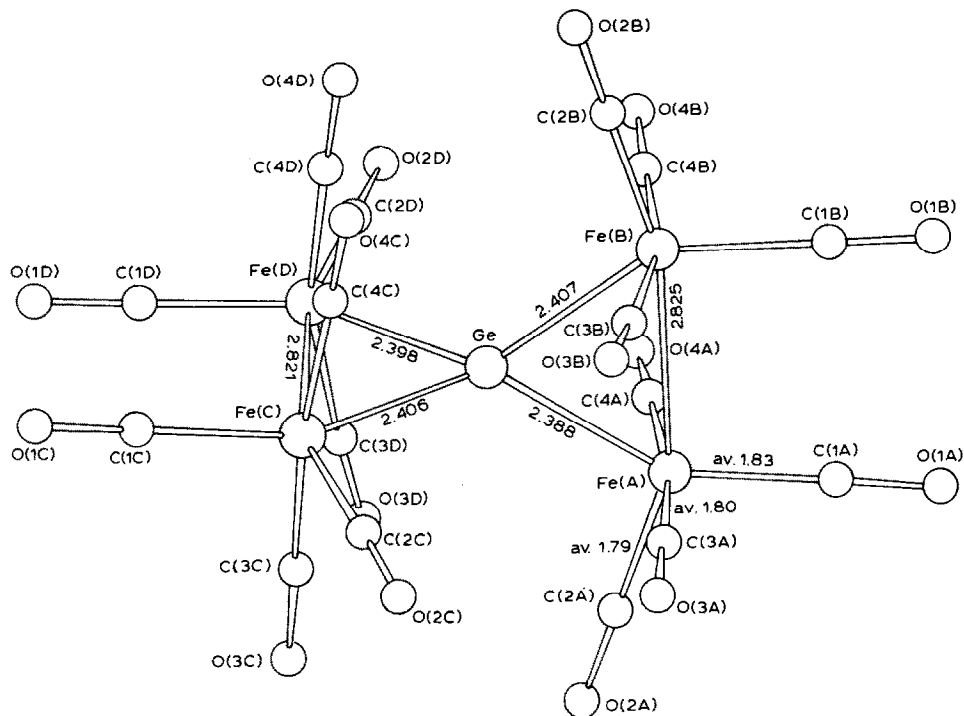


Fig. 1. Molecular structure of $\text{Ge}[\text{Fe}(\text{CO})_4]_4$ (I) with selected bond lengths.

This feature and also the formation of I in reactions of various vinylgermanes with iron carbonyls merits the unequivocal structural characterization of I.

Elemental analysis of I established only the percentage of carbon (25.8%) and the total content of Fe and Ge. The ratio Fe:Ge was difficult to determine and this ambiguity led to the incorrect assignment of I in [1]. The IR spectrum of I in heptane contains four bands of terminal carbonyls with $\nu(\text{C}=\text{O})$ 2078, 2050, 2030

(Continued on p. 324)

TABLE 3
GEOMETRIES OF Ge-BRIDGED ORGANOIRON COMPLEXES

Complex	Average bond length (Å)		Average FeGeFe angle (°)	Ref.
	Fe-Ge	Fe-Fe		
I $\text{Ge}[\text{Fe}(\text{CO})_4]_4$	2.40(1)	2.823(2)	72.1(1)	This work
II $[\text{Fe}(\text{CO})_4]_2\text{Ge}(\text{Cl})\text{CH}_2\text{SiMe}_2\text{CH}_2\text{Cl}$	2.370(8)	2.814(8)	72.7(2)	9
III $[\text{Fe}(\text{CO})_3]_2(\mu\text{-GePh}_2)_2(\mu\text{-CO})$	2.422(15)	2.666(3)	66.8(1)	10
IV $[\text{Fe}(\text{CO})_3]_2(\mu\text{-GeMe}_2)_3$	2.398(4)	2.750(11)	70.0(2)	11
V $[\text{Fe}(\text{CO})_4]_2(\text{GeEt}_2)_2$	2.492(6)	—	104.5	12
VI $[\text{Fe}(\text{CO})_4]_2[\text{Ge}(\text{Cl})\text{CH}_2\text{SiMe}_2\text{CH}_2\text{Cl}]_2$	2.444(2)	—	103.73(7)	9
VII $[\text{Fe}(\text{C}_3\text{H}_5)(\text{CO})]_2(\mu\text{-GeMe}_2)(\mu\text{-CO})$	2.346(1)	2.628(1)	68.15(3)	13
VIII $[\text{Fe}(\text{C}_3\text{H}_5)(\text{CO})_2]_2(\mu\text{-GeCl}_2)$	2.357(4)	—	128.4(2)	14

TABLE 4

ATOMIC COORDINATES (FOR Fe AND Ge $\times 10^5$, FOR C and O $\times 10^4$) AND ANISOTROPIC THERMAL FACTORS IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{*2} + \dots + 2B_{12}hka^*b^* \dots)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ge	70202(5)	24082(4)	38713(2)	0.93(2)	1.03(2)	1.18(2)	-0.09(1)	0.28(1)	0.02(2)
Fe(A)	72950(7)	22455(6)	50362(3)	1.51(3)	1.48(3)	1.19(3)	-0.21(2)	0.23(2)	0.04(2)
Fe(B)	47109(7)	26611(6)	41957(3)	1.14(2)	1.13(3)	1.48(3)	-0.05(2)	0.53(2)	-0.04(2)
Fe(C)	77676(7)	12134(6)	30438(3)	1.05(2)	1.11(3)	1.52(3)	0.05(2)	0.36(2)	-0.07(2)
Fe(D)	81849(7)	35724(6)	31628(3)	1.08(2)	1.12(3)	1.51(3)	-0.17(2)	0.40(2)	0.09(2)
C(1A)	6591(5)	2327(4)	5807(2)	2.4(2)	1.0(2)	1.7(2)	-0.2(2)	-0.1(2)	0.2(2)
C(2A)	9109(6)	1857(5)	5275(3)	2.4(2)	3.5(3)	2.0(2)	-0.3(2)	0.1(2)	0.8(2)
C(3A)	6898(6)	781(4)	4903(2)	2.3(2)	2.0(2)	1.3(2)	0.5(2)	0.7(2)	0.3(2)
C(4A)	7781(6)	3713(5)	5044(3)	3.2(3)	2.1(2)	1.5(2)	-0.9(2)	0.2(2)	-0.2(2)
C(1B)	3731(5)	2679(4)	4904(2)	1.8(2)	0.7(2)	2.1(2)	-0.2(1)	0.5(2)	0.0(2)
C(2B)	3393(5)	2960(5)	3509(3)	1.4(2)	2.5(2)	2.2(2)	0.3(2)	0.5(2)	0.0(2)
C(3B)	4439(5)	1189(4)	3976(2)	1.2(2)	2.0(2)	1.7(2)	-0.4(2)	0.7(2)	-0.1(2)
C(4B)	5118(5)	4151(5)	4217(3)	1.8(2)	1.9(2)	2.5(2)	0.0(2)	1.2(2)	-0.2(2)
C(1C)	8365(5)	1006(4)	2253(3)	1.9(2)	1.5(2)	2.4(2)	0.3(2)	0.5(2)	0.4(2)
C(2C)	7407(5)	-196(4)	3313(2)	1.3(2)	1.7(2)	1.7(2)	0.2(2)	0.2(2)	-0.2(2)
C(3C)	9526(5)	1104(4)	3521(3)	1.9(2)	1.4(2)	3.4(3)	0.1(2)	0.3(2)	-0.3(2)

C(4C)	5937(5)	1388(4)	2655(2)	2.0(2)	1.2(2)	1.2(2)	1.2(2)	1.2(2)	0.0(2)	0.5(2)	-0.2(2)
C(1D)	9080(5)	3555(4)	2436(3)	1.9(2)	1.2(2)	1.2(2)	1.2(2)	2.1(2)	-0.3(2)	0.5(2)	0.1(2)
C(2D)	8159(5)	5041(5)	3394(3)	1.7(2)	1.9(2)	1.9(2)	1.9(2)	2.7(3)	-0.3(2)	0.6(2)	0.0(2)
C(3D)	9708(5)	3413(4)	3793(2)	1.5(2)	1.4(2)	1.4(2)	1.4(2)	1.9(2)	-0.2(2)	0.6(2)	-0.2(2)
C(4D)	6404(5)	3742(4)	2730(2)	2.1(2)	1.2(2)	1.2(2)	1.2(2)	1.5(2)	0.0(2)	0.4(2)	0.1(2)
O(1A)	6161(4)	2378(3)	6292(2)	4.0(2)	2.5(2)	2.5(2)	2.5(2)	1.7(2)	0.0(2)	1.2(1)	-0.3(1)
O(2A)	10258(4)	1565(5)	5418(2)	1.7(2)	7.3(3)	7.3(3)	7.3(3)	4.7(3)	0.4(2)	0.0(2)	2.4(2)
O(3A)	6714(5)	-184(3)	4829(2)	4.9(2)	1.6(2)	1.6(2)	1.6(2)	2.4(2)	0.0(2)	1.3(2)	0.3(1)
O(4A)	8135(5)	4636(4)	5062(2)	6.0(3)	2.7(2)	2.7(2)	2.7(2)	3.1(2)	-1.9(2)	0.0(2)	-0.4(2)
O(1B)	3111(4)	2714(3)	5328(2)	2.5(2)	1.9(2)	1.9(2)	1.9(2)	2.4(2)	-0.3(1)	1.4(1)	-0.3(1)
O(2B)	2543(4)	3152(4)	3071(2)	1.9(2)	4.9(2)	4.9(2)	4.9(2)	2.6(2)	0.8(2)	0.2(1)	0.7(2)
O(3B)	4191(4)	285(3)	3800(2)	3.0(2)	1.7(2)	1.7(2)	1.7(2)	3.1(2)	-0.7(1)	1.5(2)	-0.6(1)
O(4B)	5280(5)	5110(5)	4205(2)	3.9(2)	1.4(2)	1.4(2)	1.4(2)	5.1(3)	-0.2(1)	2.0(2)	-0.2(2)
O(1C)	8708(4)	838(4)	1757(2)	3.6(2)	3.4(2)	3.4(2)	3.4(2)	2.8(2)	1.0(2)	2.0(2)	0.2(2)
O(2C)	7237(4)	-1090(3)	3489(2)	2.5(2)	1.6(2)	1.6(2)	1.6(2)	2.4(2)	0.0(1)	0.0(1)	0.5(1)
O(3C)	10627(4)	953(4)	3818(3)	1.9(2)	2.6(2)	2.6(2)	2.6(2)	6.4(3)	0.4(1)	-1.1(2)	-0.8(2)
O(4C)	4785(4)	1436(3)	2406(2)	1.5(1)	1.9(2)	1.9(2)	1.9(2)	2.1(2)	-0.1(1)	-0.1(1)	-0.1(1)
O(1D)	9621(4)	3565(4)	1983(2)	3.3(2)	3.5(2)	3.5(2)	3.5(2)	2.7(2)	-0.6(2)	1.7(2)	0.2(2)
O(2D)	8159(4)	5963(3)	3545(2)	3.0(2)	1.7(2)	1.7(2)	1.7(2)	5.1(3)	-0.3(1)	0.8(2)	-0.8(2)
O(3D)	10654(4)	3378(3)	4212(2)	1.6(1)	2.7(2)	2.7(2)	2.7(2)	2.7(2)	-0.3(1)	0.0(1)	-0.3(1)
O(4D)	5277(4)	3924(3)	2476(2)	1.8(1)	1.8(2)	1.8(2)	1.8(2)	2.7(2)	0.2(1)	-0.2(1)	0.6(1)

and 2015 cm^{-1} but no bands of bridging carbonyl, and essentially coincides with the spectrum of $\text{Ge}[\text{Fe}(\text{CO})_4]_4$, whose existence was briefly reported [8] without any details concerning its synthesis and properties.

The molecular structure of I was determined by an X-ray structural study. This structure is shown in Fig. 1, bond lengths and angles are listed in Tables 1 and 2. The metal framework of molecule I consists of two GeFe_2 cycles, joined in a *spiro* system via the Ge atom, which has a distorted tetrahedral environment. The planes of the metallocycles form a dihedral angle of 88.8° , i.e. they are almost perpendicular to each other. Each Fe atom is coordinated by four linear terminal carbonyl groups, and the Fe–Fe and Fe–Ge covalent bonds complete the distorted octahedral coordination and the 18-electron outer shell of this atom. All four $\text{Fe}(\text{CO})_4$ groups, referred to as A, B, C and D, have essentially the same geometry.

All structurally studied Ge-bridged organoiron complexes (see Table 3) can be divided into three groups: (a) carbonyliron complexes I–IV with a Ge-bridged Fe–Fe bond; (b) carbonyliron complexes V and VI containing four-membered Ge_2Fe_2 cycles without direct Fe–Fe bonds; (c) η -cyclopentadienyliron complexes VII and VIII. The Fe–Ge bond distances differ significantly between these groups, decreasing in the order $b > a > c$. The contraction of Fe–Ge bonds in complexes c is due to the change of the oxidation state of iron from 0 in a and b to +1 in c (regarding Fe–Ge bonds as non-polar due to the similar electronegativities of Fe and Ge [15]), which results in the decrease of the Fe covalent radius*.

The difference in Fe–Ge bond lengths between complexes a and b is due to steric factors. The relationship of the Ge and Fe covalent radii (according to Pauling, 1.22 [17] and 1.24 Å [18], respectively) imposes severe strain in the GeFe_2 cycle, manifesting itself in I–IV by small (cf. normal tetrahedral) FeGeFe angles and lengthened Fe–Fe bonds. Thus the length of the triply CO-bridged Fe–Fe bond in $\text{Fe}_2(\text{CO})_9$ is 2.523 Å [19], while in complexes III and IV, where two and three carbonyl bridges, respectively, are replaced by $\mu\text{-GeR}_2$ groups, the Fe–Fe distances are longer by 0.14 and 0.23 Å. In I and II the Fe–Fe bonds of 2.823 and 2.814 Å (average) are considerably longer than the usual values (2.4–2.7 Å [20]), though still short enough for covalent bonding. The latter feature is illustrated by comparison with the non-bridged Fe–Fe bond of 2.787 Å in the $\text{Fe}_2(\text{CO})_8^{2-}$ anion [21] and the Fe–Fe distance of 2.821 Å in the $\text{Fe}_2(\text{CO})_6(\mu\text{-P}(\text{CF}_3)_2)_2$ molecule, in which the existence of a metal–metal bond was predicted by MO calculations [22]. Thus the effective shortening of the Fe–Ge bonds in I–IV may be explained by the ring strain (in terms of “bent bonds” as in cyclopropane). Actually, the Fe–Ge bonds in unstrained Ge_2Fe_2 cycles are longer (averaging 2.47 Å in better agreement with the sum of Pauling covalent radii of 2.46 Å).

The $\text{Ge}[\text{Fe}(\text{CO})_4]_4$ moieties in the molecule I have essentially the same geometry as in complex II, containing one such moiety. Complex I contains three types of structurally non-equivalent CO groups, with Ge, Fe and CO as *trans* ligands and slightly different Fe–CO distances, averaging 1.83(1), 1.79(1) and 1.80(1) Å, respectively.

The molecular structure of I is very similar to that of $\text{Sn}[\text{Fe}(\text{CO})_4]_4$ (III) [23], although the crystals of I and III are not isomorphous. The Fe–Sn bonds in III are

* According to Creswick et al. [16], ligands can affect metal–metal bond lengths also by direct interaction with antibonding orbitals of these bonds.

longer than the Fe–Ge bonds in I (average 2.54 vs. 2.40 Å). As a consequence, the Fe–Fe bonds in III are also longer (2.87 vs. 2.823 Å) and the FeSnFe angles are smaller than the FeGeFe angles in I (69 vs. 72.1°).

Experimental

IR spectrum of I in heptane was measured with a UR-20 spectrophotometer. An X-ray diffraction experiment was carried out with a Syntex P2₁ four circle autodiffractometer (graphite monochromated Mo-K_α radiation, data collection at –120°C). Structure determination and refinement was carried out using an Eclipse S/200 computer with programmes [24].

Crystal data of I: C₁₆Fe₄GeO₁₆, monoclinic, at –120°C $a = 9.494(2)$, $b = 11.818(2)$, $c = 20.652(4)$ Å, $\beta = 98.74(2)^\circ$, $V = 2290.2(7)$ Å³, $Z = 4$, $d_{\text{calcd.}} = 2.16$ cm⁻³, space group $P2_1/c$.

Intensities of 4574 independent reflections with $I \geq 2\sigma$ were measured by the $\theta/2\theta$ scan technique ($2\theta \leq 62.5^\circ$). The structure was solved by an direct method and refined by the block-diagonal least squares procedure to $R = 0.039$ and $R_w = 0.038$ using reflection weights $w = \sigma_F^{-2}$ and anisotropic thermal factors for all atoms. Final atomic parameters are listed in Table 4.

Synthesis of I

a) A mixture of 5 g (10 mmol) of Fe₃(CO)₁₂ and 1.8 g (10 mmol) of Ge(CH=CH₂)₄ in 50 ml of toluene was refluxed under stirring for 6 hours. The reaction mixture was chromatographed on a silica gel column using pentane as eluent. The yellow band, after evaporation to ca. 1/3 volume and freezing at –78°C yielded 0.17 g (ca. 4%) of brick-red crystalline I, m.p. 98°C (dec., from heptane). Found: C, 25.84%. C₁₆Fe₄GeO₁₆ calcd: C, 25.82%.

b) A mixture of 5 g (10 mmol) of Fe₃(CO)₁₂ and 1.5 g (5 mmol) of hexavinyl-digermane in 50 ml of toluene was refluxed for 5 hours and then treated as above, giving 0.10 g (2%) of I.

c) From 2.5 g (5 mmol) of Fe₃(CO)₁₂ and 0.9 g (5 mmol) of GeEt₃(CH=CH₂) by the same procedure was obtained 0.05 g (ca. 2%) of I.

References

- 1 I.M. Salimgareeva, N.G. Bogatova, O.Zh. Zhebarov, L.V. Rybin, A.A. Pogrebnyak, M.I. Rybinskaya and V.P. Yur'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1982) 1161.
- 2 M.I. Rybinskaya, L.V. Rybin, A.A. Pogrebnyak, G.V. Nurtdinova and V.P. Yur'ev, *J. Organometal. Chem.*, 217 (1981) 373.
- 3 P. Jutzi and A. Karl, *J. Organometal. Chem.*, 128 (1977) 57.
- 4 G. Schmid, *Angew. Chem. Int. Ed. Engl.*, 17 (1978) 392.
- 5 J.L. Vidal, *Inorg. Chem.*, 20 (1981) 243 and references therein.
- 6 R.A. Croft, D.N. Duffy and B.K. Nicholson, *J. Chem. Soc., Dalton Trans.*, (1982) 1023.
- 7 D.N. Duffy, K.M. Mackay, B.K. Nicholson and R.A. Thomson, *J. Chem. Soc. Dalton Trans.*, (1982) 1029.
- 8 J.D. Cotton, S.A.R. Knox, I. Paul and F.G.A. Stone, *J. Chem. Soc., A*, (1967) 264.
- 9 A.L. Bykovets, O.V. Kuz'min, V.M. Vdovin, A.Ya. Sideridu, G.G. Aleksandrov and Yu.T. Struchkov, *Izv. Akad. Nauk. SSSR. Ser. Khim.*, (1981) 490.
- 10 M. Elder, *Inorg. Chem.*, 8 (1969) 2703.
- 11 M. Elder and D. Hall, *Inorg. Chem.*, 8 (1969) 1424.
- 12 J.-C. Zimmer and M. Huber, *Compt. Rend., Ser. C*, 267 (1968) 1685.

- 13 R.D. Adams, M.D. Brice and F.A. Cotton, *Inorg. Chem.*, 13 (1974) 1080.
- 14 M.A. Bush and P. Woodward, *J. Chem. Soc., A*, (1967) 1833.
- 15 S.S. Batsanov, *Uspekhi Khimii*, 51 (1982) 1201.
- 16 M. Creswick, I. Bernal, B. Reiter and W.A. Herrmann, *Inorg. Chem.*, 21 (1982) 645.
- 17 L. Pauling, *The Nature of the Chemical Bond*, 3rd. ed., Cornell Univ. Press: Ithaca, New York, 1960, p. 246.
- 18 L. Pauling, *Proc. Nat. Acad. Sci. USA*, 72 (1975) 3799.
- 19 F.A. Cotton and J. Troup, *J. Chem. Soc. Dalton Trans.*, (1974) 800.
- 20 B.P. Biryukov and Yu.T. Struchkov, *Itogi Nauki, Ser. Kristallokhimiya*, 7 (1971) 142 (Russian).
- 21 H.B. Chin, M.B. Smith, R.D. Wilson and R. Bau, *J. Amer. Chem. Soc.*, 96 (1974) 5285.
- 22 W. Clegg, *Inorg. Chem.*, 15 (1976) 1609.
- 23 P.F. Lindley and P. Woodward, *J. Chem. Soc., A*, (1967) 382.
- 24 R.G. Gerr, A.I. Yanovskii and Yu.T. Struchkov, *Kristallografiya*, in press.