COBALTACARBORANES WITH INTRAMOLECULAR MONOPHOSPHORUS BRIDGES $8,8'$-μ-$Me_2P(1,2$-$C_2B_9H_{10})_2$-3-Co, $6,6'$-μ-$Me_2P(1,7$-$C_2B_9H_{10})_2$-2-Co AND THE RESPECTIVE NON-BRIDGED TRIMETHYLPHOSPHINE DERIVATIVES (8-Me_3P-1,2-$C_2B_9H_{10}$)-3-Co-(1,2-$C_2B_9H_{11}$) AND (6-Me_3P-1,7-$C_2B_9H_{10}$)-2-Co-(1,7-$C_2B_9H_{11}$)

Andreas FRANKEN[a], Jaromir PLESEK[a], Jiri FUSEK[a] and Markus SEMRAU[b]

[a] *Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Rez near Prague, Czech Republic; e-mail: vlckova@iic.cas.cz*

[b] *Institut fur Anorganische Chemie der Christian-Albrechts-Universitat, Olshausenstr. 40, 24098 Kiel, Germany; e-mail: afr@talos.uni-kiel.de*

Received October 25, 1996
Accepted February 28, 1997

The first two cobaltacarboranes with intramolecular phoshorus bridges and two related non-bridged trimethylphosphine-cobaltacarborane derivatives are described and characterized by mass spectrometry and multinuclear NMR; all four compounds are zwitterions: $8,8'$-μ-$Me_2P(1,2$-$C_2B_9H_{10})_2$-3-Co (**1a**), $6,6'$-μ-$Me_2P(1,7$-$C_2B_9H_{10})_2$-2-Co (**2a**), (8-Me_3P-1,2-$C_2B_9H_{10}$)-3-Co-(1,2-$C_2B_9H_{11}$) (**1b**) and (6-Me_3P-1,7-$C_2B_9H_{10}$)-2-Co-(1,7-$C_2B_9H_{11}$) (**2b**). X-Ray structures of the first two and of the last compound has been established.

Key words: Cobaltacarboranes with B–P terminal bonds; B–PMe_2–B bridges; X-Ray structures; Multinuclear NMR.

A variety of single-atom-bridged cobaltacarboranes with boron atoms as bridgeheads were described earlier (Table I). Here we describe the first two analogs containing phosphorus as the bridging element: $8,8'$-μ-$Me_2P(1,2$-$C_2B_9H_{10})_2$-3-Co (**1a**) and $6,6'$-μ-$Me_2P(1,7$-$C_2B_9H_{10})_2$-2-Co (**2a**) along with two related non-bridged trimehylphosphine-cobaltacarborane by products: 8-$Me_3P(1,2$-$C_2B_9H_{10}$)-3-Co-(1,2-$C_2B_9H_{11}$) (**1b**) and 6-$Me_3P(1,7$-$C_2B_9H_{10}$)-2-Co-(1,7-$C_2B_9H_{11}$) (**2b**). The skeletal carbon atoms are adjacent in **1a** and **1b** (Fig. 1), whereas they are in mutual *meta* positions in **2a** and **2b** (Fig. 1).

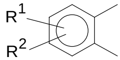
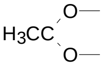
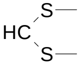
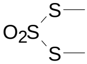
Compounds **1a**, **1b** and **2a**, **2b** were obtained *via* a classical EINS-type reaction from the isomeric parent cobaltacarborane ions with white phosphorus in benzene under $AlCl_3$ catalysis (analogy of the previously reported cobaltacarborane bridging with sulfur[7,23]) followed by methylation of the resulting mixture of intermediate anions (Eq. (*A*)).

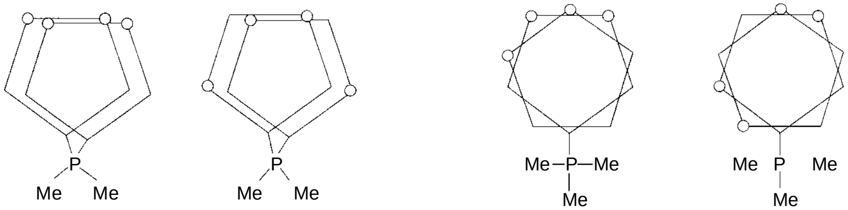
$$\underset{\mathbf{1}}{[3\text{-Co-}(1,2\text{-}C_2B_9H_{11})_2]^-Cs^+} \xrightarrow{\text{a, b}} \qquad (A)$$

$$\underset{\mathbf{1a}}{8,8'\text{-}\mu\text{-}Me_2P(1,2\text{-}C_2B_9H_{10})_2\text{-3-Co}} + \underset{\mathbf{1b}}{8\text{-}Me_3P(1,2\text{-}C_2B_9H_{10})\text{-3-Co-}(1,2\text{-}C_2B_9H_{11})}$$

a) P_4, $AlCl_3$, benzene, 80 °C, 4 h; b) Me_2SO_4, NaOH, EtOH

TABLE I
List of reported 8,8′-μ-X$(1,2\text{-}C_2B_9H_{10})_2$-3-Co bridged cobaltacarboranes with mono- to triatomic bridges between boron atoms (structures according to Fig. 2); citations in bold letters indicate X-ray structures

Number of bridging atoms	Bridge	References
1	N	**1**, 2
	O	2, **3**, **4**
	S	2, 5–7, **8**, **9**
	Se, Te	2
	I, Br	10
	–O–N(R_2)–	11
2	–S–S–	5
		7, 12–14, **15, 16, 17**
		18
3		18, 19, **20**
		**21**



1a **2a** **1b** **2b**

FIG. 1
Arrangements of the pentagonal ligand planes in the bridged **1a**, **2a** and non-bridged **1b**, **2b** phosphine-cobaltacarboranes. For clarity the rests of icosahedra and all terminal hydrogens are omitted; the central Co ion is sandwiched between the respective pairs of pentagons

Using the isomeric 2-Co-(1,7-$C_2B_9H_{11}$)$_2^-$ ion **2** the respective **2a** and **2b** analogs resulted. The non-isolated anionic precursors of both series of zwitterions were apparently the acidic phosphine derivatives, *i.e.* H–P< bridge in **1a** and **2a** precursors and with a B–PH_2 terminal arrangement at one icosahedral ligand in precursors of **1b** and **2b**. So far we have abandoned isolation of these primary reaction products due to difficulties with separation of anions having closely similar properties and because of danger of oxidation of these intermediates to the respective phosphonic acid polyanions during a long work-up.

Formation of the non-bridged zwitterions **1b** and **2b** indicates a stepwise bridge formation in both series of cobaltacarboranes. The yields of defined products **1a**, **1b** and **2a**, **2b** were rather poor because we were able to isolate only zwitterionic species resulting after the methylation step. The fate of the major part of the starting anions **1** and **2** is still obsure. An appreciable part might have been converted to the intermolecularly bridged telomeric ions, *e.g.* of the $[C_2B_9H_{11}\ .\ Co(C_2B_9H_{10}\text{-}P(R_2)\text{-}C_2B_9H_{10}\ .\ Co)_n\text{-}C_2B_9H_{11}]^-$ type; such species are out of today's isolation and identification techniques.

On the other hand, all four isolated zwitterions could be adequately characterized; they represent a new type of compounds with a B–P bond. Compounds **1a** and **2a** extend the family of known single-atom-bridged metallacarboranes. Some general characteristics of compounds **1** and **2** are shown in Table II; ^{11}B, ^{11}B-decoupled ^1H and ^{31}P NMR spectra are collected in Table III.

It was difficult to establish the respective structures by a conventional combination of mass spectroscopy and multinuclear NMR methods only; hence X-ray diffraction

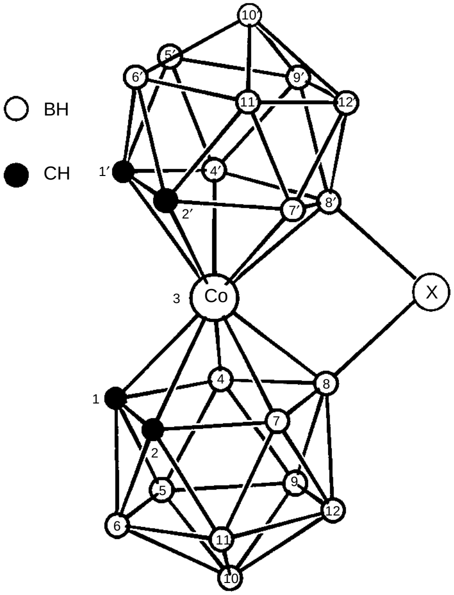


FIG. 2
Several monoatomically bridged analogs derived from the isomeric 2-Co-(1,7-$C_2B_9H_{11}$)$^-$ ion framework were described recently[22–24]

TABLE II
Some properties of compounds **1a, 1b** and **2a**, **2b**

Compound[a]	TLC[b], R_F	MS[c], m/z	^{1}H NMR (δ, ppm)	
			C–H	CH_3
1a	0.66	386	4.119	1.531
2a	0.66	386	4.097, 3.437	1.873
1b	0.34	402	4.402, 4.317	1.771
2b	0.34	402	3.626, 3.350 2.997, 2.738	2.072

[a] All compounds are deep orange solids not melting up to 250 °C; they are insoluble in water, negligibly soluble in ethanol and diethyl ether, well soluble in benzene, dichloromethane, acetonitrile, acetone and tetrahydrofuran. [b] See Experimental. [c] In agreement with calculated value for respective compounds.

TABLE III
^{11}B, [(^{11}B)-^{1}H][a] and ^{31}P NMR data on **1a** and **1b** and **2a** and **2b** in δ, ppm, [*J*, Hz] (intensity). All ^{11}B signals are doublets collapsing to singlets on ^{11}B decoupling with exception of signals marked with an asterisk, where the splitting is due to ^{31}P coupling.

Compound	^{11}B	^{31}P
1a	B(10) 1.335 [3.130] (1); B(4,7) –7.667 [3.515] (2); B(5,11) –7.667 [3.515] (2); B(8) –8.504 (1)*; B(9,12) –14.233 [1.845] (2); B(6) –20.323 [1.79] (1)	–31.25 (1, sept)
2a	B(9,9′) 1.677 [3.125] (2); B(11,11′) –3.613 [2.952] (2); B(3,3′) –8.695 [3.420] (2); B(4,4′) –10.560 (2); B(5,5′) –12.958 (2); B(10,10′,12,12′) –13.947 [1.993] (4); B(6) –15.394 (1)*; B(6′) –16.288 (1)*; B(8,8′) –16.538 (2); B(8,8′) –16.538 (2)	–47.828 (1,sept)
1b	B(8) 5.883 [3.542] (1); B(10) 4.380 [3.218] (1); B(10′) 1.563 [3.140] (1); B(8′) –1.119 (1)*; B(9,12) –4.318 [2.148] (2); B(4,7,4′,7′) –5.497 [3.053, 2.945] (4); B(9′,12′) –7.267 [1.968] (2); B(5,11) –15.203 [1.804] (2); B(5′,11′) –16.99 [1.740] (2); B(6) –20.190 (1); B(6′) –21.541 (1)	–4.8 (1, q)
2b[b]	B 4.209 [3.217] (1); B 2.267 [3.202] (1); B –1.920 [3.743] (1); B –3.214 (1); B –4.565 [2.650] (1); B –5.631 (1); B –6.340 [4.013] (1); B –7.610 [3.887] (1); B –10.389 (1)*; B –11.017 [1.858] (2); B –12.425 [1.924] (2); B –15.527 [1.864] (2); B –16.288 [1.820] (2)	–5.136 (1, q)

[a] ^{11}B decoupled ^{1}H NMR. [b] Assignment was impossible due to signals overlapping.

was used to supplement the information or to confirm the results based on the mentioned methods. Thus, mass spectroscopy along with multinuclear NMR did unequivocally reveal the constitution of **1a** and **1b** (Tables II and III); on the other hand the crystals of **1a** were "disordered", so that their X-ray investigation led only to reliable data on the inclination angle (11.6°) between both ligand planes (see Experimental). No suitable crystals could be grown from samples of **1b**.

On the other hand, it was problematic to assign all the NMR signals of the compounds **2a** and **2b** due to a too complicated pattern and also due to heavy overlaps (Table III). Fortunately, perfect crystals could be grown in both cases and the respective structures could be established directly (Figs 3 and 4). Selected bond lengths are presented in Table IV and selected angles in Table V*.

Noteworthy is the dihedral angle between both pentagonal ligand planes in **1a** (11.6°) and **2a** (8.6°). The inclination of the ligand planes in **2a** is only 74% of that observed in **1a**; exactly the same relations were found recently in the respective sulfur analogs[29] (16.5° and 12.2°, respectively). So our suspicion discussed in the previous paper seems to be confirmed. The deltahedral ligands with adjacent carbon atoms are more prone to mutal inclination during bridge formation than are those with non-adjacent carbons.

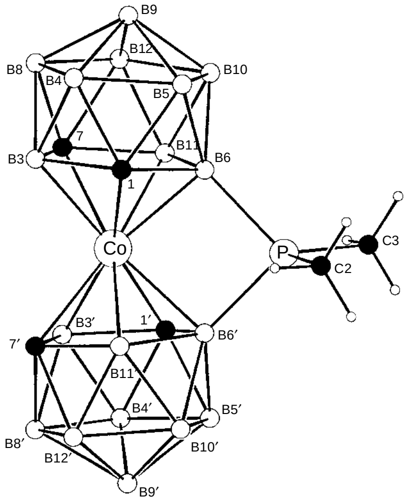


FIG. 3
Structure of **2a**

---

* Full data have been deposited at Fachinformationszentrum Karlsruhe, 76344 Eggenstein–Leopoldshafen, Germany, crysdata@fiz-karlsruhe.de (but might be also obtained on request from the authors).

EXPERIMENTAL

Apparatus and Chemicals

TLC was carried out on SILUFOL (Kavalier, Votice, Czech Republic) in toluene–hexane (1 : 1). Mass spectrum was recorded on a Finnigan MAT MAGNUM ion trap quadrupole mass spectrometer. The NMR spectra were measured in deuterioacetone using a Varian UNITY 500 spectrometer at 160.36 MHz for ^{11}B (referenced to $BF_3 . Et_2O$) and 500 MHz for ^1H (referenced to tetramethylsilane). X-Ray diffraction was carried out on CAD4, Enraf–Nonius device, MoKα radiation, λ = 0.71969 Å).

Structure solution and refinement: direct methods (SHELXS86, (ref.[25]), full-matrix least squares refinement (SHELXL90, (ref.[26]), anisotropic refinement of all non-hydrogen atoms, hydrogen atoms fixed in calculated positions. Program ORTEP (ref.[27]) was used to draw the molecules.

The bis-1,2(1,7)-dicarbollidocobaltate cesium salts were prepared according to the literature[28]. Other chemicals and solvents were analytical grade from current commercial sources and were used as purchased.

Structure Determination of **1a**, **2a** and **2b**

Crystal data of **1a**: $C_6H_{26}B_{18}CoP$, M_R 384.6, orthorhombic, space group *Pbac* (No. 61), a = 29.295(2), b = 7.012(5), c = 9.606(5) Å (based on the least squares refinement of 25 precisely centered reflections within the 16–20 θ range), V = 1 973.0(2) Å^3, Z = 4, D_c = 1.036 g cm^{-3}, μ = 0.933 mm^{-1}, $F(000)$ = 584.

Measurement: A crystal 0.3 × 0.25 × 0.3 mm in size of a total of 1 894 reflections up to 2θ = 50° within the h, k, l range of 0, 34; 0, 8; 0, 11, respectively, 1 882 reflections were regarded as "observed" according to the $I > 2\sigma(I)$ criterion. Three standard reflections which were monitored every 90 min showed no significant fluctuations (< 1.5%). Function minimized: $w(F_o^2 - F_c^2)^2$ with $w = 4F^2/[(F_o^2)]^2$, final R = 0.1462, R_w = 0.1674, R_{inst} = 0.0134, S = 1.061, $|(\Delta/\sigma)_{max}|$ = 0.052. The final difference electron density map was featureless, with extremal values of 0.916; –0.38 e Å^3 near

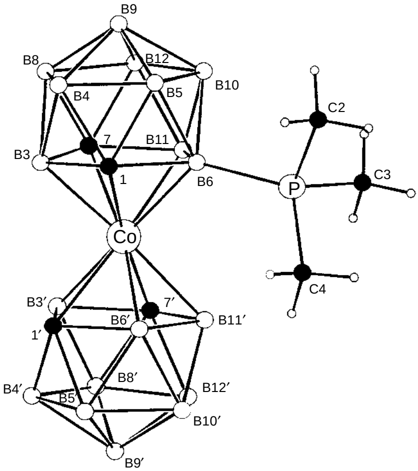


FIG. 4
Structure of **2b**

the Co atom. Program ORTEP (ref.[27]) was used to draw the molecules. The structure was disordered with two different 8,8′-μ-$Me_2P(1,2-C_2B_9H_{10})_2$-3-Co molecules. Due to this fact only the angle between the ligand planes (11.6°) was useful.

Crystal data of **2a**: $C_6H_{26}B_{18}CoP$, M_R 384.6, orthorhombic, space group *Pnca* (No. 60), a = 11.478(2), b = 12.438(6), c = 13.770(4) Å (based on the least squares refinement of 25 precisely centered reflections within the 16–20θ range), V = 1 966.0(11) $Å^3$, Z = 4, D_c = 1.280 g cm^{-3}, μ = 0.940 mm^{-1}, F(000) = 760.

TABLE IV
Selected bond lengths (Å) for the compounds **2a**, **2b**

Atoms	Distances	
	2a	**2b**
B6–C1	1.718(4)	1.697(5)
C1–B3	1.695(4)	1.719(5)
B3–C7	1.689(4)	1.687(5)
C7–B11	1.684(4)	1.695(5)
B11–B6	1.754(4)	1.800(6)
B6–Co	2.066(3)	2.106(4)
C1–Co	2.081(3)	2.057(3)
B3–Co	2.079(3)	2.049(4)
C7–Co	2.089(3)	2.080(3)
B11–Co	2.081(3)	2.080(3)
B6′–Co	2.066(3)	2.071(4)
C1′–Co	2.081(3)	2.092(3)
B3′–Co	2.079(3)	2.061(4)
C7′–Co	2.089(3)	2.072(3)
B11′–Co	2.081(3)	2.085(4)
B6′–C1′	1.718(4)	1.686(5)
C1′–B3′	1.695(4)	1.690(6)
B3′–C7′	1.689(4)	1.704(5)
C7′–B11′	1.684(4)	1.675(5)
B11′–B6′	1.754(4)	1.813(6)
B6–P	1.915(3)	1.948(4)
P–C3	1.804(3)	1.789(4)
P–C4	1.804(3)	1.790(4)
P–C5	–	1.795(4)

Measurement: A crystal 0.3 × 0.35 × 0.4 mm in size of a total of 1 759 reflections up to 2θ = 50° within the *h*, *k*, *l* range of –2, 13; –4, 14; 0, 16, respectively, 1 744 reflections were regarded as "observed" according to the $I > 2\sigma(I)$ criterion. Three standard reflections which were monitored every 90 min showed no significant fluctuations (<1.5%). Function minimized: $w(F_o^2 - F_c^2)^2$ with $w = 4F^2/[(F_o^2)]^2$, final $R = 0.0403$, $R_w = 0.0527$, $R_{int} = 0.0134$, $S = 1.092$, $|(\Delta/\sigma)_{max}| = 0.082$. The final difference electron density map was featureless, with extreme values of 0.816; –0.218 e Å^{-3} near the Co atom.

Crystal data of **2b**: $C_7H_{30}B_{18}CoP$, $M_R = 398.79$, orthorhombic, space group *Pcab* (No. 61), $a = 14.499(4)$, $b = 13.3506(12)$, $c = 21.304(4)$ Å (based on the least squares refinement of 25 precisely centered reflections within the 16–20θ range), $V = 4123.8(14)$ Å^3, $Z = 8$, $D_c = 1.285$ g cm^{-3}, $m = 0.900$ mm^{-1}, $F(000) = 1\,632$.

Measurement: A crystal 0.2 × 0.31 × 0.2 mm in size of a total of 1 919 reflections up to 2θ = 50° within the *h*, *k*, *l* range of –2, 13; –7, 12; –20, 20, respectively, 1 555 reflections were regarded as

TABLE V
Selected bond angles (°) for the compounds **2a**, **2b**

Atoms	Angles	
	2a	**2b**
B6–C1–B3	109.2(2)	112.3(3)
C1–B3–C7	107.9(2)	104.4(3)
B3–C7–B11	109.2(2)	112.2(3)
C7–B11–B6	108.0(2)	105.9(3)
B11–B6–C1	105.6(2)	104.6(3)
B6′–C1′–B3′	109.2(2)	111.8(3)
C1′–B3′–C7′	107.9(2)	104.6(3)
B3′–C7′–B11′	109.2(2)	112.8(3)
C7′–B11′–B6′	108.0(2)	104.5(3)
B11′–B6′–C1′	105.6(2)	105.6(3)
Co–B6–P	93.77(14)	125.2(2)
B6–P–B6′	90.3(2)	–
B6–P–C3	113.29(14)	108.7(2)
B6–P–C4	114.21(14)	110.9(2)
B6–P–C5	–	120.2(2)
C3–P–C4	110.4(2)	105.5(2)
C3–P–C4	–	107.0(2)
C4–P–C5	–	103.5(2)
Dihedral angle between ligand planes	8.6	–

"observed" according to the $I > 2\sigma(I)$ criterion. Three standard reflections which were monitored every 90 min showed no significant fluctuations (<1.5%). $R = 0.0296$, $R_w = 0.0315$, $R_{\text{int}} = 0.0319$, $S = 1.045$, $|(\Delta/\sigma)_{\max}| = 2.148$. The final difference electron density map was featureless, with extreme values of 0.306; –0.187 e Å^3 near the Co atom.

Synthesis and Isolation of **1** and **2**

A mixture of white phosphorus (0.55 g, 18 mmol), $AlCl_3$ (0.27 g, 2 mmol) and of [3(2)-Co-(1,2(1,7)-$C_2B_9H_{11})_2]^-$ Cs^+ salt (2.3 g, 5 mmol) in benzene (50 ml) was stirred for 24 h at 80 °C under nitrogen. Subsequently, sodium hydoxide (2 g, 50 mmol) dissolved in 50% ethanol (40 ml) was added. After addition of dimethyl sulfate (2.5 g, 62 mmol) the mixture was stirred for 1 h. The benzene layer was separated and the aqueous solution was extracted with two portions of benzene (20 ml). The combined benzene layers were washed with water (30 ml). After separation of the organic layer, the benzene was evaporated in vacuum, the residue was chromatographed on a silica gel column using 1 : 1 benzene–hexane mixture as an eluent. Yield 0.15 g (8%) of orange crystals of **1a**/**2a**, *m/z* 386 corresponds to $^{12}C_6{}^1H_{26}{}^{11}B_{18}{}^{59}Co^{31}P$ and 0.12 g (6%) of yellow crystals of **1b**/**2b**, *m/z* 402 corresponds to $^{12}C_7{}^1H_{30}{}^{11}B_{18}{}^{59}Co^{31}P$.

Crystals for X-Ray Structure Determinations

In a test tube (internal diameter 1 cm) 4 ml of a saturated solution of **1** or **2** in methylene chloride was carefully covered by a layer of hexane (12 ml), the tube was stoppered and left for one week at ambient temperature. Deep orange prisms of suitable size were obtained with **1a** and **2a**, **2b**; only useless dendrites resulted with **1b**.

We are indebted to Dr I. Cisarova (Department of Inorganic Chemistry, Charles University, Prague) for the X-ray analyses. A partial support of this work by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. 203/94/0984) is gratefully appreciated.

REFERENCES

1. Cisarova I., Maly K., Hummel L.: Acta Crystallogr., C *50*, 198 (1994).
2. Plesek J., Hermanek S., Base K., Todd L. J., Wright W. F.: Collect. Czech. Chem. Commun. *41*, 3509 (1976).
3. Petrina A., Petricek V., Maly K., Subrtova V., Linek A., Hummel L.: Z. Kristallogr. *154*, 217 (1981).
4. Subrtova V., Petricek V., Linek A., Jecny J.: Z. Kristallogr. *144*, 139 (1976).
5. Janousek Z., Plesek J., Hermanek S., Base K., Todd L. J., Wright W. F.: Collect. Czech. Chem. Commun. *46*, 2818 (1981).
6. Plesek J., Hermanek S., Janousek Z.: Chem. Ind. (London) *1974*, 108.
7. Plesek J., Hermanek S.: Collect. Czech. Chem. Commun. *43*, 1325 (1978).
8. Cisarova I., Petricek V.: Acta Crystallogr., C *42*, 663 (1986).
9. Vohlidal J., Plesek J., Sedlacek J., Cisarova I., Matejka P., Hermanek S.: Collect. Czech. Chem. Commun. *61*, 877 (1996).
10. Plesek J., Hermanek S., Stibr B.: Collect. Czech. Chem. Commun. *49*, 1492 (1984).
11. Plesek J., Rajabi F. H., Vangani V., Fusek J.: Collect. Czech. Chem. Commun. *59*, 1326 (1994).
12. Francis J. N., Jones C. J., Hawthorne M. F.: J. Am. Chem. Soc. *94*, 4878 (1972).

13. Plesek J., Hermanek S.: Czech 188 587 (1981); Czech Appl. PV 8387-76 (20.12.1976); Chem. Abstr. *96*, 143085 (1982).
14. Plesek J., Hermanek S.: Collect. Czech. Chem. Commun. *60*, 1297 (1995).
15. Shelly K., Knobler C. B., Hawthorne M. F.: New J. Chem. *12*, 317 (1988).
16. Cisarova I.: Private communication.
17. Cisarova I.: Private communication, publication pending.
18. Churchill M. R., Gold K., Francis J. N., Hawthorne M. F.: J. Am. Chem. Soc. *91*, 1222 (1969).
19. Francis J. N., Hawthorne M. F.: Inorg. Chem. *10*, 594 (1971).
20. Churchill M. R., Gold K.: Inorg. Chem. *10*, 1928 (1971).
21. Plesek J., Hermanek S., Franken A., Cisarova I., Nachtigal C.: Collect. Czech. Chem. Commun., *62*, 47 (1997).
22. Plesek J., Gruner B., Fusek J., Votavova H.: Collect. Czech. Chem. Commun. *58*, 2936 (1993).
23. Plesek J., Gruner B., Vanek T., Votavova H.: J. Chromatogr. *1993*, 633; 73.
24. Plesek J., Gruner B., Holub. J.: Collect. Czech. Chem. Commun., *62*, 884 (1997).
25. G. M. Sheldrick: *SHELXS86. Program for Crystal Structure Solution.* University of Gottingen, Gottingen 1986.
26. G. M. Sheldrick, *SHELXL93. Program for the Refinement of Crystal Structures*. University of Gottingen, Gottingen 1993.
27. C. K. Johnson: Rep. ONRL-3794. OAK Ridge National Laboratory, TN 1965.
28. Hawthorne M. F., Young D. C., Andrews T. D., Howe D. V., Pilling R. L., Pitts A. D., Reintjes M., Warren L. F., Wegner P. A.: J. Am. Chem. Soc. *90*, 879 (1968).
29. Plesek J., Franken A., Frohlich R.: Collect. Czech. Chem. Commun., *62*, 57 (1997).
30. Jelinek T., Stibr B., Mares F., Plesek J., Hermanek S.: Polyhedron *6*, 1740 (1987).