column chromatographic workup on silica gel. The NMR data might correspond to $[\{W(CO)_5\}_2(\mu,\eta^1:\eta^1\text{-}P_2Cl_4)]$, for which a molecular ion peak at *m*/*z* (%) 851.7 (3) was found in the mass spectrum (EI-MS (70 eV, 50 °C)) of the crude reaction mixture. The analogous Cr derivative $[\{Cr(CO)_5\}_2(\mu,\eta^1:\eta^1\text{-}P_2Cl_4)]$ (**5**) has been synthesized and structurally characterized in reference [17].

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[15] Data of the X-ray structure analysis of **3**: Stoe STADI IV diffractometer (ω scan), $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), empirical absorption correction (Psi scans). The structure was solved by direct methods using SHELXS-86,[22a] and refined by full-matrix-least-squares on F^2 using SHELXL-93,[22b] with anisotropic displacement for all atoms. **3**: $C_{15}Cl_2O_{15}P_2W_3$, $M_r = 1104.54$, crystal dimensions $0.30 \times 0.19 \times 0.03$ mm^3, monoclinic, space group $P2_1/c$ (no. 14); $a = 14.650(3)$, $b = 13.304(3)$, $c = 13.646(4)$ Å, $\beta = 98.68(3)^\circ$, $T = 200(2)$ K, $Z = 4$, $V = 2629.2(9)$ Å^3, $\rho_{calcd} = 2.790$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 13.485$ mm^{-1}, 5919 independent reflexes ($2\theta_{max} = 55^\circ$), 4159 observed with $F_o = 4\sigma(F_o)$; 352 parameters, $R_1 = 0.0498$, $wR_2 = 0.1162$. X-ray structure analyses have been carried out for several crystals of **3** obtained from different reactions, but in every case the two phosphorus atoms were found to be disordered. They occupy two different positions in a ratio of 80:20. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151480. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[21] In the solid-state Raman spectrum of **3**, nine absorptions were found in the region for terminal CO ligands. This number agrees with the number of bands of the calculated spectrum. At lower wavenumbers, it was possible to assign the P – P and symmetric P – Cl stretching frequencies at 434 and 313 cm^{-1}, respectively, as well as the asymmetric P – Cl stretching frequency at 269 cm^{-1}.

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Crystal Structures from a Building Set: The First Boridecarbides of Niobium**

Harald Hillebrecht* and Knuth Gebhardt

Dedicated to Professor Gerhard Thiele
on the occasion of his 65th birthday

Borides and carbides of the "early" transition metals are distinguished by high chemical stability and unique physical properties such as high melting points (NbB_2: 3036 °C, NbC_{1-x}: 3600 °C), great hardness (NbB_2: 33 GPa, TiC: 27 GPa), and metallic conductivity. The development of methods to generate high temperatures[1] has enabled the syntheses of these compounds. Structure analyses revealed that carbides can be describes as interstitial compounds with carbon atoms in the octahedral holes of a close-packed array of metal atoms.[2] NaCl-type structures prevail, frequently combined with a significant variation in the carbon content and a number of stacking and ordering variants have been described.[3] In contrast, in borides the boron atoms usually prefer a trigonal prismatic coordination. Different compositions are given by connecting the prisms in different manners through the rectangular faces. According to the degree of condensation zigzag chains result (monoborides MB), single (M_3B_4) or double chains (M_2B_3) of boron hexagons, or graphite-like layers of hexagons (diborides MB_2, AlB_2-type). Without exception the boron – boron separations at around 1.8 Å are in the region of single bonds (e.g. V_3B_4, Nb_3B_4, CoB).[4, 5]

An increase of these unique properties, or their modification, may be possible in ternary compounds M/B/C (M = metal atom). Numerous investigations by conventional means (direct reaction of the elements at high temperatures, melting in an arc furnace followed by annealing) only gave Mo_2BC, which is known since 1963.[6, 7]

We suppose the main reason for the unsuccessful syntheses of further transition metal boridecarbides is that in the temperature region in which the desired compounds are themodynamically stable product formation is impossible because of kinetic reasons. Our earlier investigations have shown that the use of molten metals as a reaction medium, as in an "auxiliary bath technique" (Lebeau[8]), leads to single crystals of new compounds, which are not accessible by other means.[9]

For transition metal borides the use of aluminum as an auxiliary metal is well established.[10] But aluminum is not suitable for the synthesis of analogous carbides because the formation of Al_4C_3 dominates. The same is true in attempts to prepare boridecarbides as carbon again reacts to give Al_4C_3.[5] With copper, which forms neither borides (exception $CuB_{\sim 24}$) nor carbides,[11] as an auxiliary metal single crystals of boron

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carbide B_4C[5, 12] are formed but no boridecarbides are produced. The starting point of our experiments was to try and vary the ratio of Al:Cu to assure a sufficient high reactivity of the transition metal towards boron and carbon on the one hand and to avoid the formation of Al_4C_3 and B_4C on the other.[5] In the system Nb/B/C this concept led, for the first time, to the successful synthesis of a series of boridecarbides (see Experimental Section). The compounds Nb_3B_3C, $Nb_4B_3C_2$, $Nb_7B_4C_4$, and $Nb_7B_6C_3$ were yielded as single crystals and their structures determined.[13]

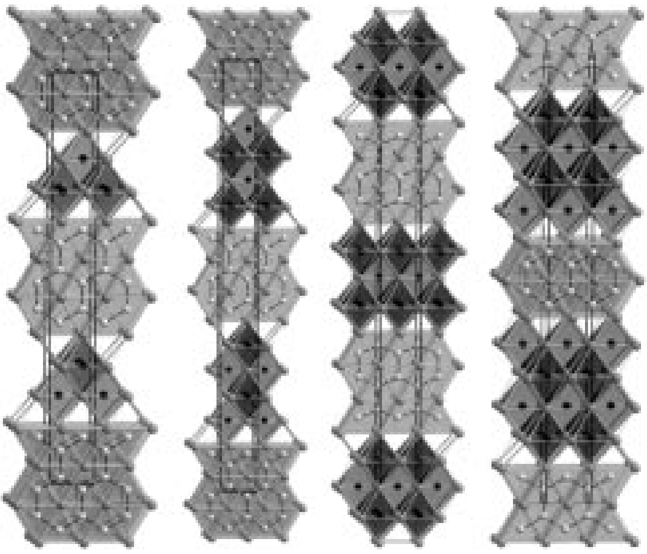

Figure 1. Crystal structure of (from left to right) Nb_3B_3C (view in [100]), $Nb_4B_3C_2$ (view in [100]), $Nb_7B_6C_3$ (view in [010]), and $Nb_7B_4C_4$ (view in [001]). Atoms: Nb grey, B white, C black; polyhedra: Nb_6C octahedra dark, Nb_6B trigonal prisms light.

All the four crystal structures (see Figure 1) are characterized by a separation into two partial structures with a layerlike arrangement. In the boride partial structure, boron atoms are trigonal prismatically coordinated by niobium. These trigonal prisms are interconnected by the rectangular faces forming boron–boron bonds. Thus the boron atoms build up hexagons which are connected to chains ($Nb_7B_4C_4$) or double chains (Nb_3B_3C, $Nb_4B_3C_2$, $Nb_7B_6C_3$). A junction to layers is made by joining the trigonal faces; the same structural motif is found in Nb_3B_4 and Nb_2B_3. The carbide partial structure represents a fragment of an NaCl-type (100)-layer, that is, a cubic close packing of Nb atoms with carbon atoms in octahedral holes. The thickness of these layers varies, resulting in different compositions: $(NbC)_2$ in Nb_3B_3C; $(NbC)_3$ in $Nb_7B_6C_3$; $(NbC)_4$ in $Nb_4B_3C_2$ and $Nb_7B_4C_4$.

Therefore the crystal structures of the four ternary compounds can be reduced to well-known fragments of binary phases by a combination of layers with different thickness: $Nb_3B_3C = (Nb_2B_3)_2(NbC)_2$, $Nb_4B_3C_2 = (Nb_2B_3)_2(NbC)_4$, $Nb_7B_6C_3 = (Nb_2B_3)_2(NbC)_3$, $Nb_7B_4C_4 = Nb_3B_4(NbC)_4$. Because of this close relationship the distances between the atoms are comparable to those in the binary compounds (Nb–Nb: 3.05–3.17 Å, Nb–C: 2.11–2.27 Å, Nb–B: 2.34–2.50 Å, B–B: 1.80–1.85 Å). The separation into two partial structures avoids boron–carbon bonds, which are known from the boridecarbides of alkali earth metals,[14] rare earth metals,[15] and aluminum.[9c] A significant substitution, that of boron for carbon, which is discussed in literature,[3, 4] seems to be impossible because of the fundamentally different coordination spheres.

The free combination of boride and carbide layers is possible because both partial structures are based on a quadratic net of Nb atoms (4^4 net according to Schläfli). The different coordination polyhedra result from different ways of stacking the layers. For the carbide partial structure the next layer of Nb atoms is placed above and below the center of the square forming an octahedral hole. In the boride partial structure subsequent layers are placed identically above and below an edge of the square. Boron atoms are in trigonal prismatic holes above and below the square planes. Because there are twice as many boron atoms as Nb atoms in the 4^4 nets an NbB_2 composition results. The partial structures are linked because they share the "outer" 4^4 net of the layers. The different sizes of partial structures are described by the general formula $(NbB)_2(NbB_2)_n(NbC)_m$: Nb_3B_3C ($n=2$, $m=2$), $Nb_4B_3C_2$ ($n=2$, $m=4$), $Nb_7B_4C_4$ ($n=1$, $m=4$), and $Nb_7B_6C_3$ ($n=2$, $m=3$). The example of Nb_3B_3C and $Nb_4B_3C_2$ shows the space group remains unchanged if the value of n is changed by two (or any other even number). Independent of the n value the same is true for the values of m. So all members of the series $Nb_xB_yC_z$ can be reduced to one of four basic types, depending on whether m and n have odd or even values (see Table 1). Three of the four different combinations, leading to four different space groups, could be identified experimentally by us. Only for the case where n and m are odd (space group *Pmmm*) have we been unable to find a niobium boridecarbide.

Table 1. Classification of phases $Nb_xB_yC_z$ and related compounds according to a building-set principle $[(NbB)_2(NbB_2)_n](NbC)_m$.

m even n even	m even n odd	m odd n even	m odd n odd
Cmcm	*Immm*	*Cmmm*	*Pmmm*
Nb_3B_3C $n=2, m=2$ $Nb_4B_3C_2$ $n=2, m=4$	$Nb_7B_4C_4$ $n=1, m=4$	$Nb_7B_6C_3$ $n=2, m=3$	–
Mo_2BC/Nb_2BN $n=0, m=2$	Nb_3B_4 $n=1, m=0$	Cr_2AlB_2[a] $n=0, m=1$	Cr_3AlB_4[a] $n=1, m=1$

[a] Ordering and defect variant, because C positions are empty and there are two kinds of metal atoms.

On the basis of this building-set principle it is not only possible to specify the different space groups for the four different variants but one can also predict lattice constants and positional parameters of each atom. Furthermore several other compounds with close structural relationships can be arranged into this scheme. Binary borides can be included by setting $m=0$ ($n=0$: NbB; $n=1$: Nb_3B_4; $n=2$: Nb_2B_3; $n \rightarrow \infty$: NbB_2). The structure of Mo_2BC can also be classified ($n=0$ and $m=2$), where the boride fragment (zigzag chain) corresponds to the monoboride MoB. Crystal structure arrangements of ternary borides are yielded if the carbon positions are empty and the metal positions were occupied in an ordered way by two different metals (see Table 1).

In general it should be possible to synthesize boridecarbides of other transition metals by following the modified auxiliary metal bath technique. Their crystal structures should fit the building-set principle outlined above. The fact that despite many attempts the synthesis of compounds analogous to Mo_2BC failed[16] shows that besides geometrical reasons electronic factors also determine the field of stability and existence of transition metal boridecarbides. The existence of Nb_2BN,[17] which is isotypical to Mo_2BC, suggests that the same considerations are valid for M/B/N systems too. Experimental work in this field has been started. Further investigations on physical properties (electrical conductivity, magnetic properties) and band-structure calculations on niobium boridecarbides are in progress.

Experimental Section

Syntheses were carried out in corundum crucibles with argon as the inert atmosphere. The temperature program for a horizontal tube furnace was: RT to 1600 °C with 400 °C h^{-1}, 24 h holding, cooling to 1500 °C with 100 °C h^{-1}, cooling to 1100 °C with 1 °C h^{-1}, cooling to RT with 150 °C. Molar ratios Cu:Al:B:C:Nb were chosen as: Nb_3B_3C: 20:5:2:1:4, $Nb_4B_3C_2$: 20:5:0.2:0.1:0.2, $Nb_7B_6C_3$: 20:5:2:1:2, $Nb_7B_4C_4$: 20:5:0.1:0.1:0.2. Single crystals were yielded as irregularly shaped polyhedra after dissolving the metal excess in half conc. HNO_3. A comparison of calculated and observed X-ray powder diagrams revealed that in all cases only one ternary compound was the main product with, in each case, microcrystalline NbC as a by-product. By means of energy dispersive X-ray spectroscopy (EDX) Nb was detected as the only metal, that is, the auxiliary metals Cu and Al were not incorporated significantly.

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