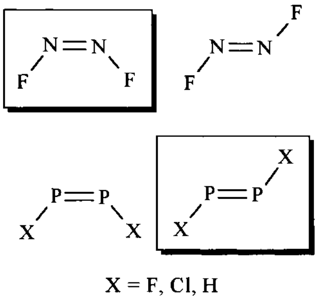
Complex Chemical Stabilization of Dichlorodiphosphene[**]

Ulf Vogel, Gregor Stößer, and Manfred Scheer[*]

Dedicated to Professor Hansgeorg Schnöckel on occasion of his 60th birthday

Small molecules with multiple bonds between main group elements have always been a fascinating field. For example, N_2F_2, the *cis* configuration **I** of which is 12.6 kJ mol^{-1} more stable than the *trans* configuration **II**, has been known for a long time (Scheme 1).[1] Although the phosphorus analogues P_2X_2 have not yet been obtained experimentally, ab initio-SCF calculations for X = F show that the *trans* configuration **II** is 5.9 kJ mol^{-1} more stable than the *cis* configuration **I** as the ground state for such a singlet molecule.[2] For diphosphene, P_2H_2, which was detected during the pyrolysis of diphosphane, P_2H_4,[3] the *trans* configuration **II** is 15 kJ mol^{-1} more stable than the corresponding *cis* configuration **I**.

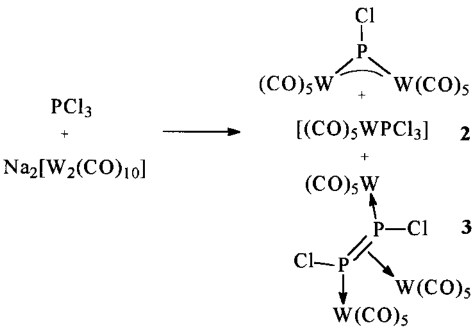


I II

Scheme 1. *cis* and *trans* isomers of N_2F_2 and P_2X_2 (the thermodynamically favored configuration is marked by a frame).

Our CCSD(T) calculations[4] regarding the stability of dichlorodiphosphene, P_2Cl_2, show a similar result: here, the *trans* arrangement (C_{2h} symmetry, d(P–P) = 2.066 Å, d(P–Cl) = 2.100 Å, $\sphericalangle$(Cl-P-P) = 97.5°) is more stable than the *cis* arrangement (C_{2v} symmetry, d(P–P) = 2.072 Å, d(P–Cl) = 2.073 Å, $\sphericalangle$(Cl-P-P) = 108.7) by 7 kJ mol^{-1}. As there has been no experimental proof for the existence of the dihalogenodiphosphenes until now, we report herein on the stabilization of dichlorodiphosphene in the coordination sphere of tungsten carbonyl complexes.

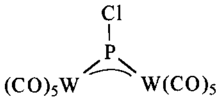
The extraction of the solid product from the reaction between $Na_2[W_2(CO)_{10}]$ and PCl_3 in THF with *n*-pentane/CH_2Cl_2 yields a deep purple colored solution. According to its ^{31}P NMR spectrum, this solution contains the chlorophosphinidene complex **1** as the main component, along with some **2**[5] and the dichlorodiphosphene complex **3** [Eq. (1)].[6] Whereas **1** and **2** decompose upon column chromatographic workup on silica gel, **3** can be isolated as a red solid in 17% yield.



(1)

The ^{31}P NMR spectrum of **1** shows a singlet at $\delta = 868$ with a $^{183}W,^{31}P$ coupling constant of 200 Hz, which is in accordance with the NMR data of phosphinidene complexes with organic substituents. The ^{31}P NMR shifts of these compounds are generally found at very low field (e.g. $[MesP\{W(CO)_5\}_2]$: $\delta = 961$, $^1J_{W,P} = 176$ Hz;[7] Mes = 2,4,6-$Me_3C_6H_2$). This feature along with the $\pi-\pi^*$ transitions at long wavelengths in the visible spectra of these compounds are interpreted as an electron delocalization in a 3c–4πe$^-$ system (structure **III**).[8] This is supported by the crystal structure of $[MesP\{Cr(CO)_5\}_2]$, which shows equidistant P–Cr bonds (2.263(1) Å).[7] Our CCSD(T) calculations[4] of **1** show also that the symmetric structure **III** represents an energy minimum (C_s symmetry, d(P–Cl) = 2.120 Å, d(P–W1) = 2.449 Å, d(P–W2) = 2.442 Å, $\sphericalangle$(Cl-P-W1) = 109.9°, $\sphericalangle$(Cl-P-W2) = 112.0°, $\sphericalangle$(W-P-W) = 138.1°).

The red dichlorodiphosphene complex **3** is insoluble in *n*-hexane, slightly soluble in toluene, and readily soluble in CH_2Cl_2. In the IR spectrum, CO stretching frequencies are found for terminal CO ligands. The mass spectrum of **3** shows the molecular ion peak, as well as characteristic fragment ion peaks.



III

The ^{31}P NMR spectrum of **3** shows a singlet at $\delta = 39.9$ with three tungsten satellites of similar intensity ($^{183}W,^{31}P$ coupling constants 26.0, 121.2, and 166.1 Hz, respectively). The ^{31}P NMR signal of the structurally related phenyl-substituted diphosphene complex **4a** ($\delta(^{31}P) = -16.6$,[9] -20.6[10]), which was synthesized by Huttner et al. as well as by Mathey et al., is found in a comparable chemical shift region. In contrast, however, signals of uncoordinated diphosphenes are shifted strongly downfield (e.g. RP=PR, $\delta(^{31}P) = 492.2$ (R = 2,4,6-$tBu_3C_6H_2$)[11]), and the resonance is shifted to high field if the molecule is side-on coordinated to a transition metal fragment (cf. $[\eta^1{:}\eta^1\text{-}P_2Ph_2\{Cr(CO)_5\}_2]$ ($\delta(^{31}P) = 927$[12]) and **4b** ($\delta(^{31}P) = 97$[9])). The largest $J_{W,P}$ coupling of **3** can be assigned to the coupling of the phosphorus atoms to the terminal pentacarbonyl tungsten units. Thus, for the complex $[R^1P{=}PR^2\{W(CO)_5\}]$ (R^1 = 2,4,6-$tBu_3C_6H_2$, R^2 = 2,4,6-$Me_3C_6H_2$), in which the $[W(CO)_5]$ fragment is coordinated through only one lone pair of electrons on phosphorus, a $^1J_{W,P}$ value of 238 Hz is found,[13] which is slightly larger than that in **3**. The two other $^{183}W,^{31}P$ coupling constants of **3** should be

$[M(CO)_5(\mu,\eta^2{:}\eta^1{:}\eta^1\text{-}P_2Ph_2\{M(CO)_5\}_2)]$ **4** (M = W (**a**), Cr (**b**))

---

[*] Prof. Dr. M. Scheer, Dipl.-Chem. U. Vogel, Dipl.-Chem. G. Stößer
Institut für Anorganische Chemie der Universität Karlsruhe
76128 Karlsruhe (Germany)
Fax: (+49) 721-661921
E-mail: mascheer@achibm6.chemie.uni-karlsruhe.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

assigned to ${}^2J_{W,P}$ coupling to the terminal $[W(CO)_5]$ group and to the coupling to the tungsten atom that bridges the P=P double bond.[14]

Compound **3** crystallizes from dichloromethane as red platelets. The central structural feature of **3**[15] (Figure 1) is a P_2Cl_2 unit which is coordinated side-on to a $[W(CO)_5]$ fragment. The two phosphorus atoms coordinate through their lone pairs additionally to two $[W(CO)_5]$ moieties. The two phosphorus atoms are disordered (ratio 80:20). The bonding features of the molecule with the major occupancy are hereafter discussed. The P=P bond length (2.140(6) Å) is significantly shorter than the single bond in white phosphorus (2.21 Å)[16] or in the tetrachlorodiphosphane complex **5**

$[\{Cr(CO)_5\}_2(\mu,\eta^1:\eta^1\text{-}P_2Cl_4)]$ **5**

(2.268(3) Å);[17] however, it is significantly longer than the P=P bond in the free diphosphene RP=PR (R = 2,4,6-tBu$_3$C$_6$H$_2$, 2.034(6) Å).[11] For the structurally similar complex **4a**, Huttner et al. and Mathey et al. reported P=P lengths of 2.14(1)[9] and 2.162(3) Å,[10] respectively; these values correspond well to the distance observed in **3**. The lengthening of the formal P=P double bond in **3** can be accounted for in terms of the electronic effects of η^2-coordination to the $[W(CO)_5]$ fragment.[18] All P–W bonds in **3** are found to be slightly shorter (bridging, 2.582(4) and 2.573(5) Å; terminal, 2.484(5) and 2.479(4) Å) than those in **4a** (2.604 Å (av) and 2.535 Å (av),[9]), which can be attributed to the more electronegative chlorine atoms as well as to the larger steric demand of the phenyl groups in **4a**. The difference in the torsion angle W2-P2-P1-W1 between **3** (115.04°) and **4a** (123.6°) also supports this explanation. The P–Cl bonds in **3** (2.084 Å (av)) are slightly longer than those in PCl_3 (2.030 Å)[19] as well as those in the tetrachlorodiphosphane complex **5** (2.0435 Å (av)).[17]

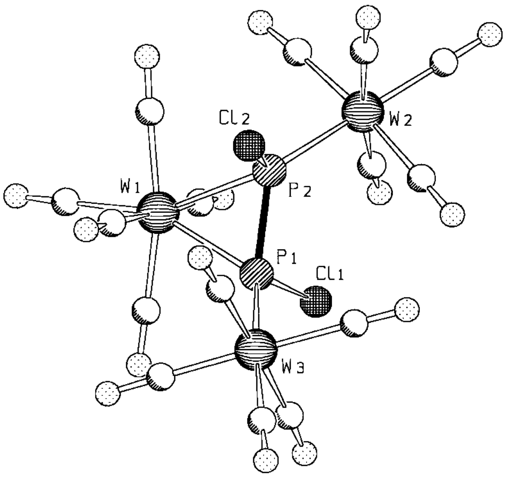


Figure 1. Molecular structure of $[W(CO)_5(\mu,\eta^2:\eta^1:\eta^1\text{-}P_2Cl_2\{W(CO)_5\}_2)]$ (**3**). Selected bond lengths [Å] and angles [°]: P1-P2 2.140(6), P1-Cl1 2.089(6), P2-Cl2 2.079(6), W1-P1 2.582(4), W1-P2 2.573(4), W2-P2 2.484(5), W3-P1 2.479(4); P1-W1-P2 49.1(1), P1-P2-W1 65.7(2), P2-P1-W1 65.2(2), Cl1-P1-P2 98.7(3), Cl2-P2-P1 98.9(3), W3-P1-P2 132.3(2), W2-P2-P1 126.7(2), Cl1-P1-W3 115.7(2), Cl2-P2-W2 117.1(2); torsion angles Cl1-P1-P2-Cl2 155.92, W2-P2-P1-W3 115.04.

Good agreement was found between the X-ray structural data of **3** and values calculated for a C_2-symmetric structure.[4, 20] For example, a P=P of 2.175 Å (exp. 2.140(6) Å) and a P–Cl distance of 2.119 Å (exp. 2.089(6) and 2.079(6) Å) were obtained. The calculated vibrational spectrum of **3** also shows good agreement with the experimentally obtained IR and Raman spectra in the solid state, in which, for example, the symmetrical P–P stretching frequency is found at 434 cm^{-1}.[21]

Experimental Section

PCl_3 (0.33 mL, 3.8 mmol) was added dropwise at ambient temperature to a solution of $Na_2[W_2(CO)_{10}]$ (2.63 g, 3.8 mmol) in THF (25 mL). The color changed from yellow to reddish violet. All volatiles were immediately removed at reduced pressure, and the residue was extracted with a mixture of n-pentane/CH_2Cl_2 (100 mL; 1/1). This solution was filtered over celite and washed twice with the same mixture (2 × 25 mL). After removal of the solvent, the residue was separated by chromatography on a silica gel column (Merck 60, 2 × 20 cm). A red fraction, containing **3**, was eluted with n-hexane/toluene (5/1). Recrystallization from CH_2Cl_2 yielded **3** (150 mg; 17 %) as red crystals.

1: ${}^{31}P\{{}^1H\}$ NMR (101.256 MHz, [D$_6$]benzene, 298 K, 85 % H_3PO_4 ext.): $\delta = 868.2$ (${}^1J$(W,P) = 200 Hz); EI-MS (70 eV; 50 °C): m/z (%): 713.8 (4) [M^+], 657.8 (2) [$M^+ - 2CO$], 629.8 (1) [$M^+ - 3CO$].

2: ${}^{31}P\{{}^1H\}$ NMR (101.256 MHz, [D$_6$]benzene, 298 K, 85 % H_3PO_4 ext.): $\delta = 98.4$ (${}^1J$(W,P) = 427.2 Hz); EI-MS (70 eV; 50 °C): m/z (%): 461.8 (23) [M^+], 433.8 (4) [$M^+ - CO$], 426.8 (22) [$M^+ - Cl$].

3: ${}^{31}P\{{}^1H\}$ NMR (101.256 MHz, [D$_6$]benzene, 298 K, 85 % H_3PO_4 ext.): $\delta = 39.3$ (J(W,P) = 166.3, 121.2, 26.0 Hz); IR (KBr): $\tilde{\nu}$(CO) = 2114 (m), 2076 (vs), 2041 (m), 2018 (s), 2003 (s), 1950 (sh), 1932 (vs, br); Raman (solid state): $\tilde{\nu}$ = 2112 (s), 2078 (s), 2065 (m), 2042 (m), 2003 (s), 1991 (m), 1969 (w), 1942 (m), 1929 (m), 569 (w), 539 (w), 468 (w), 434 (s), 372 (w), 313 (m), 269 (m), 220 (w), 120 (m, br); EI-MS (70 eV; 70 °C): m/z (%): 1103.6 (4) [M^+], 1007.6 (0.2) [$M^+ - 2Cl$], 1004.7 (1) [$M^+ - 2Cl - CO$], 920.6 (0.5) [$M^+ - 2Cl - 4CO$], 851.7 (10) [$M^+ - 9CO$], 779.6 (2) [$M^+ - W(CO)_5$], 767.6 (13) [$M^+ - 12CO$], 744.7 (34) [$M^+ - W(CO)_5 - Cl$], 35.5 (16) [Cl^+], 28.0 (100) [CO^+].

Received: November 2, 2000 [Z16030]

---

[1] A. F. Hollemann, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, 101 ed., de Gruyter, Berlin, **1995**, p. 688.

[2] S. Jin, B. T. Colegrove, H. F. Schaefer III, *Inorg. Chem.* **1991**, *30*, 2969–2977.

[3] a) Y. Wada, R. W. Kiser, *Inorg. Chem.* **1964**, *3*, 174; b) T. P. Fehlner, *J. Am. Chem. Soc.* **1967**, *89*, 6477–6482; T. P. Fehlner, *Adv. Chem. Ser.* **1968**, *72*, 181–190; c) for a general discussion compare: W. W. Schoeller in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, p. 16.

[4] The quantum-chemical calculations were carried out with the RIDFT module (BP-86 Functional) of the program package TURBOMOLE using SV(P) basis sets; a) TURBOMOLE: O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346–354; b) BP-86 Functional: A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822; c) RIDFT: K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652–660; K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119–124.

[5] For the synthesis of $[(CO)_5WPCl_3]$ (**2**): H. Meinert, H. Vogt, B. Pahnke, G. Schulenburg, *Z. Chem.* **1980**, *20*, 110–111, for spectroscopic details: R. Poilblanc, M. Bigorgne, *Bull. Soc. Chim. Fr.* **1962**, *29*, 1301–1325.

[6] Furthermore, in the ${}^{31}P$ NMR spectrum a singlet is found at $\delta = 138.2$, which reveals two different $J_{W,P}$ coupling constants of 121.1 and 247.9 Hz, respectively. This compound also decomposes during the

column chromatographic workup on silica gel. The NMR data might correspond to [{W(CO)$_5$}$_2$(μ,η^1:η^1-P$_2$Cl$_4$)], 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)$_5$}$_2$(μ,η^1:η^1-P$_2$Cl$_4$)] (**5**) has been synthesized and structurally characterized in reference [17].

[7] H. Lang, O. Orama, G. Huttner, *J. Organomet. Chem.* **1985**, *291*, 293–309.

[8] a) G. Huttner, K. Evertz, *Acc. Chem. Res.* **1986**, *19*, 406–413, and references therein; b) G. Huttner, H. Lang in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, pp. 48–54.

[9] G. Huttner, J. Borm, L. Zsolnai, *J. Organomet. Chem.* **1986**, *304*, 309–321.

[10] A. Marinetti, C. Charrier, F. Mathey, J. Fischer, *Organometallics* **1985**, *4*, 2134–2138.

[11] M. Yoshifuji, I. Shima, N. Inamoto, *J. Am. Chem. Soc.* **1981**, *103*, 4587–4589.

[12] J. Borm, L. Zsolnai, G. Huttner, *Angew. Chem.* **1983**, *95*, 1018; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 977.

[13] M. Yoshifuji, K. Shibayama, T. Hashida, K. Toyota, T. Niitsu, I. Matsuda, T. Sato, N. Inamoto, *J. Organomet. Chem.* **1986**, *311*, C63–C67.

[14] In general, the magnitude of a ^1J coupling constant increases with the s character of the bond (P. S. Pregosin, R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, Springer, Berlin, **1979**, p. 16). In **3**, the bond between phosphorus and the terminal [W(CO)$_5$] units should possess more s character than the bond to the bridging [W(CO)$_5$] moiety.

[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, $\beta = 98.68(3)°$, $T = 200(2)$ K, $Z = 4$, $V = 2629.2(9)$ Å^3, $\rho_{calcd} = 2.790$ Mg m^{-3}, μ(Mo$_{K\alpha}$) = 13.485 mm^{-1}, 5919 independent reflexes ($2\theta_{max} = 55°$), 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).

[16] A. Simon, H. Borrmann, J. Horakh, *Chem. Ber./Recueil* **1997**, *130*, 1235–1240.

[17] M. Scheer, K. Schuster, A. Krug, H. Hartung, *Chem. Ber.* **1997**, *130*, 1299–1304.

[18] The increase of the bond length is a result of the backbonding from the metal to the antibonding π^* orbital of the P=P double bond.

[19] J. E. Huheey, *Inorganic Chemistry*, 2nd ed., Harper International, New York, **1978**; J. E. Huheey, E. A. Keiter, R. L. Keiter, *Anorganische Chemie*, de Gruyter, Berlin, **1995**, p. 1165.

[20] The molecular geometry of **3** was calculated for the point group C_2: selected bond lengths [Å] and angles [°]: P-P 2.175, P-Cl 2.119, P-W$_{bridge}$ 2.697, P-W$_{terminal}$ 2.534; P-W$_{bridge}$-P 47.6, P-P-W$_{bridge}$ 66.2, Cl-P-P 99.6, W$_{terminal}$-P-P 134.6, Cl-P-W$_{terminal}$ 112.1.

[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}.

[22] a) G. M. Sheldrick, SHELXS-86, University of Göttingen, **1986**; b) G. M. Sheldrick, SHELXL-93, University of Göttingen, **1993**.

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$_3$B$_4$) or double chains (M$_2$B$_3$) 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$_3$B$_4$, Nb$_3$B$_4$, 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$_2$BC, 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$_4$C$_3$ dominates. The same is true in attempts to prepare boridecarbides as carbon again reacts to give Al$_4$C$_3$.[5] With copper, which forms neither borides (exception CuB$_{\sim 24}$) nor carbides,[11] as an auxiliary metal single crystals of boron

---

[*] Prof. Dr. H. Hillebrecht, Dr. K. Gebhardt
Laboratorium für Anorganische Chemie, NW I
95447 Bayreuth (Germany)
Fax: (+49) 921-55-2788
E-mail: harald.hillebrecht@uni-bayreuth.de

[**] This work was supported by the DFG and the Fonds der Chemischen Industrie.