low-pressure mercury lamp (254 nm) and an Osram HBO500 W/2 high-pressure mercury arc lamp in an Oriel housing with quartz optics and a dichroic mirror (260 – 320 nm). 1,4-Diiodotetrafluorobenzene was purchased from Aldrich and used as supplied. DFT and CASSCF calculations were performed with the Gaussian98 suite of programs.[27] CASPT2 calculations were carried out with MOLCAS.[28]

Received: December 8, 2000 [Z16242]

[1] T. P. Lockhart, P. B. Comita, R. G. Bergman, *J. Am. Chem. Soc.* **1981**, *103*, 4082 – 4090.

[2] K. C. Nicolaou, W. M. Dai, *Angew. Chem.* **1991**, *103*, 1453 – 1481; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1387 – 1416.

[3] M. F. Semmelhack, J. J. Gallagher, T. Minami, T. Date, *J. Am. Chem. Soc.* **1993**, *115*, 11618 – 11619.

[4] M. E. Maier, *Synlett* **1995**, 13 – 26.

[5] K.-I. Iida, M. Hirama, *J. Am. Chem. Soc.* **1995**, *117*, 8875 – 8876.

[6] R. Unno, H. Michishita, H. Inagaki, Y. Suzuki, Y. Baba, T. Jomori, M. Moku, T. Nishikawa, M. Isobe, *Bioorg. Med. Chem.* **1997**, *5*, 903 – 919.

[7] A. Evenzahav, N. J. Turro, *J. Am. Chem. Soc.* **1998**, *120*, 1835 – 1841.

[8] K. K. Wang, *Chem. Rev.* **1996**, *96*, 207 – 222.

[9] M. Schmittel, M. Strittmatter, W. A. Schenk, M. Hagel, *Z. Naturforsch. B* **1998**, *53*, 1015 – 1020.

[10] T. Kaneko, M. Takahashi, M. Hirama, *Angew. Chem.* **1999**, *111*, 1347 – 1349; *Angew. Chem. Int. Ed.* **1999**, *38*, 1267 – 1268.

[11] G. B. Jones, J. M. Wright, G. W. Plourde II, G. Hynd, R. S. Huber, J. E. Mathews, *J. Am. Chem. Soc.* **2000**, *122*, 1937 – 1944.

[12] P. G. Wenthold, R. R. Squires, *J. Am. Chem. Soc.* **1994**, *116*, 6401 – 6412.

[13] P. G. Wenthold, J. Hu, R. R. Squires, *J. Am. Chem. Soc.* **1996**, *118*, 11865 – 11871.

[14] P. G. Wenthold, R. R. Squires, W. C. Lineberger, *J. Am. Chem. Soc.* **1998**, *120*, 5279 – 5290.

[15] R. Marquardt, A. Balster, W. Sander, E. Kraka, D. Cremer, J. G. Radziszewski, *Angew. Chem.* **1998**, *110*, 1001 – 1005; *Angew. Chem. Int. Ed.* **1998**, *37*, 955 – 958.

[16] a) H. H. Wenk, W. Sander, *Eur. J. Org. Chem.* **1999**, 57 – 60; b) H. H. Wenk, W. Sander, *Chem. Eur. J.* **2001**, *7*, 1837 – 1844.

[17] E. Kraka, D. Cremer, *Chem. Phys. Lett.* **1993**, *216*, 333 – 340.

[18] S. G. Wierschke, J. J. Nash, R. R. Squires, *J. Am. Chem. Soc.* **1993**, *115*, 11958 – 11967.

[19] P. R. Schreiner, *J. Am. Chem. Soc.* **1998**, *120*, 4184 – 4190.

[20] C. J. Cramer, *J. Am. Chem. Soc.* **1998**, *120*, 6261 – 6269.

[21] J. Graefenstein, A. M. Hjerpe, E. Kraka, D. Cremer, *J. Phys. Chem. A* **2000**, *104*, 1748 – 1761.

[22] W. Sander, *Acc. Chem. Res.* **1999**, *32*, 669 – 676.

[23] W. R. Roth, H. Hopf, C. Horn, *Chem. Ber.* **1994**, *127*, 1765 – 1779.

[24] E. Kraka, D. Cremer, *J. Am. Chem. Soc.* **2000**, *122*, 8245 – 8264.

[25] A. Becke, *J. Chem. Phys.* **1993**, *98*, 5648 – 5652.

[26] R. Hoffmann, A. Imamura, W. J. Hehre, *J. Am. Chem. Soc.* **1968**, *90*, 1499 – 1509.

[27] Gaussian98 (Revision A.3), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

[28] K. Andersson, M. R. A. Blomberg, M. P. Fülscher, G. Karlström, R. Lindh, P.-Å. Malmqvist, P. Neogrády, J. Olsen, B. O. Roos, A. J. Sadlej, M. Schütz, L. Seijo, L. Serrano-Andrés, P. E. M. Siegbahn, P.-O. Widmark, MOLCAS, Version 4, University of Lund, **1997**.

[29] This basis set was obtained from the Extensible Computational Chemistry Environment Basis Set Database, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences laboratory which is part of the Pacific Northwest Laboratory, PO Box 999, Richland, Washington 99352 (USA).

Terminal Borylene Complexes as a Source for the Borylene $\mathrm{B{-}N(SiMe_3)_2}$: Alternative Synthesis and Structure of $\mathrm{[(OC)_5Cr{=}B{=}N(SiMe_3)_2]}$**

Holger Braunschweig,* Miriam Colling,
Carsten Kollann, Hans G. Stammler, and
Beate Neumann

The generation of hypovalent borylenes $\mathrm{B{-}R}$—the boron analogues to carbenes $\mathrm{CR_2}$—usually requires drastic conditions: the classical method involves the reduction of boron trihalides at temperatures above 2000 °C,[1] and alternatively, the silylborylene $\mathrm{B{-}SiPh_3}$ can be obtained photochemically at −196 °C from $\mathrm{RB(SiPh_3)_2}$ ($\mathrm{R = Me}$, 2,4,6-$\mathrm{Me_3C_6H_2}$ (Mes)) in hydrocarbon matrices.[2] The reductive[3] or photochemical[4] generation of species $\mathrm{B{-}R}$ in condensed phase might be assumed from the nature of the corresponding trapping products. There is, however, no direct proof for the intermediacy of borylenes—in particular, the $\mathrm{MeBBr_2/2\,C_8K}$ system as a source for $\mathrm{B{-}Me}$ appears questionable.[5]

Already in 1973 borylene complexes were recognised to be a potentially useful source for borylenes in cases where gaseous species cannot be used.[1b] Since 1995 we have reported on both bridged[6] and terminal[7] borylene complexes of the type $[\mathrm{L}_x\mathrm{M{-}B(R){-}ML}_x]$ and $[\mathrm{L}_x\mathrm{M{=}BR}]$, respectively, thus demonstrating the possibility of stabilizing borylenes $\mathrm{B{-}R}$ in the coordination sphere of a transition metal. Related species, however, showing boron in higher coordination number were also reported recently.[8] As the synthesis of borylene complexes is mainly restricted to salt elimination reactions,[6, 7, 8b] we began to investigate compounds of the type $[\mathrm{L}_x\mathrm{M{=}BR}]$ as possible sources for $\mathrm{B{-}R}$ with borylene transfer reactions between different metal centers to provide an alternative synthetic route for this novel class of compounds.

In an initial experiment the photochemically induced transfer of the aminoborylene $\mathrm{BN(SiMe_3)_2}$ from $\mathrm{[(OC)_5W{=}B{=}N(SiMe_3)_2]}$ (**1**)[7] to $\mathrm{[Cr(CO)_6]}$ was investigated, since the expected chromium–borylene complex $\mathrm{[(OC)_5Cr{=}B{=}N(SiMe_3)_2]}$ (**2**) was already obtained by a different method and known to be stable under the chosen conditions.[7] Compound **1** was irradiated at −30 °C in toluene in the presence of three equivalents of $\mathrm{[Cr(CO)_6]}$. After 12 h

---

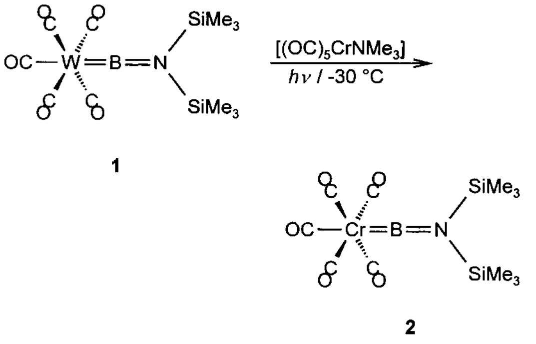
[*] Dr. H. Braunschweig
Department of Chemistry
Imperial College
London SW7 2AY (UK)
Fax: (+44) 20-7594-5900
E-mail: h.braunschweig@ic.ac.uk

M. Colling, Dr. C. Kollann
Institut für Anorganische Chemie der Technischen Hochschule
52056 Aachen (Germany)

Dr. H. G. Stammler, B. Neumann
Universität Bielefeld
Fakultät für Chemie, Anorganische Chemie III
33615 Bielefeld (Germany)

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

the ^{11}B NMR spectrum of the reaction mixture showed two signals at $\delta = 86.6$ (**1**) and 92.3 (**2**) in a 1:1 ratio, thus indicating the formation of **2** in 50% yield. Longer irradiation times gave no significant change in the ^{11}B NMR spectrum—a more complete transfer was evidently hampered by the poor solubility of $[Cr(CO)_6]$ in toluene at $-30\,^\circ C$. NMR-spectroscopic studies on corresponding reactions in THF indicated no intermetallic borylene transfer, which may be attributed to insertion of the borylene into the C–O bond of THF.[2] Photolysis of **1** with a 1.5-fold excess of the more soluble $[(OC)_5CrNMe_3]$ in toluene at $-30\,^\circ C$ for 12 h, however, afforded **2** almost quantitatively according to Equation (1) (>95% according to the ^{11}B NMR spectrum).



(1)

The structure of **2** in solution was confirmed by IR and NMR spectroscopic data, which matched those of an independently prepared sample.[7] Because there are no structural data for boryl- or borylene complexes of chromium, an X-ray structure analysis of **2** was carried out (Figure 1).[9] The compound crystallizes in the space group $P\bar{1}$, and the molecule adopts C_1 symmetry in the crystal. Similar to the W-B-N moiety of the tungsten analogue **1**, the central Cr-B-N moiety is arranged almost linearly (Cr-B-N 177.4(4)°), the Si1-Si2-B plane is twisted by 38° with respect to the C4-C5-C2 plane, and the B–N distance of 135.3(6) pm is in the expected range for a B–N double bond between a three-coordinate nitrogen and a two-coordinate boron atom.[7, 10] The Cr–B distance of 199.6(6) pm is thus 15.5 pm shorter than the corresponding W–B distance in **1**. The close resemblance of the spectroscopic and structural data of **1** and **2** corroborate the description of the Cr–B double bond in terms of a strong boron-to-metal σ-donation and weaker π-backbonding[7]—a bonding situation which was predicted on the basis of ab initio calculations of the parent complex $[(OC)_5Cr{=}B{=}NH_2]$.[11] Very recent theoretical studies on terminal borylene complexes, though, pointed out that the sum of the covalent metal–boron interactions only gives a bond order of less than one and that the nature of the M–BR bond is mainly ionic.[12]

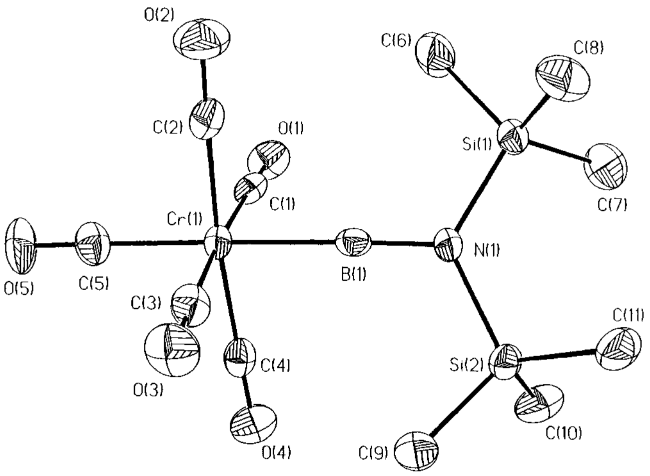
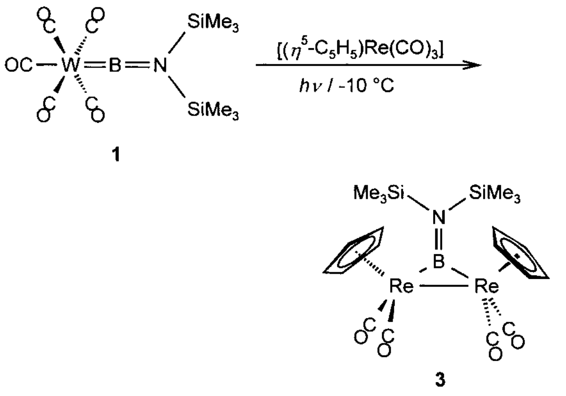


Figure 1. Structure of **2** in the crystal. Selected distances [Å] and angle [°]: Cr-B 1.996(6), B-N 1.353(6); Cr-B-N 177.4(4).

To exploit further the intermetallic borylene transfer we treated **1** with $[(\eta^5\text{-}C_5H_5)Re(CO)_3]$ under similar conditions. Although manganese complexes of the type $[(\mu\text{-}BNR_2)\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2]$ (R = Me and various other substituents) were afforded by salt elimination reactions,[6a,b,f] the corresponding rhenium complexes were not obtained.[13] After irradiation of **1** with $[(\eta^5\text{-}C_5H_5)Re(CO)_3]$ for four days at $-10\,^\circ C$ in toluene, the ^{11}B NMR spectrum showed two signals in a 3:2 ratio at $\delta = 86.6$ and 100.4, respectively, the latter indicating the formation of $[\{\mu\text{-}BN(SiMe_3)_2\}\{(\eta^5\text{-}C_5H_5)Re(CO)_2\}_2]$ (**3**) according to Equation (2). Although photolysis for another 24 h did not significantly change the ratio of **1** and **3** in the ^{11}B NMR spectrum, it was possible to isolate the new rhenium borylene complex as yellow crystals in approximately 20% yield together with some amount of the unreacted starting material **1**. The constitution of **3**, the first rhenium–borylene complex, was unambiguously deduced from multinuclear NMR spectroscopy and mass spectrometry.



(2)

So far, all investigations have shown that the photochemical activation of the borylene complex initiates the observed borylene transfer. Various compounds of the type $[(OC)_5CrL]$ (L = NMe_3, THF) underwent no reaction with **1** at ambient temperature without irradiation. Further attempts have also been made to thermally induce the borylene transfer between **1** and $[(OC)_5CrNMe_3]$ by heating both compounds in toluene to $60\,^\circ C$. ^{11}B NMR spectra of this mixture after one day indicated the formation of **2**, however, only in small amounts together with further boron-containing species.

Experimental Section

2: A solution of $[(OC)_5CrNMe_3]$[14] (0.90 g, 3.60 mmol) and **1**[7] (1.19 g, 2.40 mmol) in toluene (100 mL) was irradiated with a high-pressure Hg lamp (Hereaus TQ 150) at $-30\,^{\circ}C$ for 12 h. The reaction mixture was warmed to ambient temperature, and all volatile materials were removed under high vacuum (0.001 Torr). The brown residue was treated with hexane (50 mL) and the resulting slurry was filtered. The small amount of the remaining dark brown residue was washed with hexane (10 mL). The combined filtrates were concentrated under vacuum to 20 mL and stored at $-80\,^{\circ}C$. After 48 h, **2** (0.31 g, 0.85 mmol, 35.5 %) was obtained as light brown crystals. All NMR spectra were recorded in $[D_6]$benzene at 25 °C. ^1H NMR (500 MHz, TMS): $\delta = 0.14$ (s; $SiMe_3$); ^{11}B NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 92.3$; ^{13}C NMR (126 MHz, TMS): $\delta = 2.6$ ($SiMe_3$), 217.6 (CO_{eq}), 218.0 (CO_{ax}); IR (toluene): $\tilde{\nu} = 2064$ (w), 1981 (m), 1942 (vs) cm^{-1} (CO); elemental analysis (%) calcd for $C_{11}H_{18}CrNBO_5Si_2$: C 36.37, H 5.00, N 3.86; found: C 35.47, H 5.10, N 3.72.

3: A solution of $[(\eta^5\text{-}C_5H_5)Re(CO)_3]$ (0.68 g, 2.02 mmol) and **1** (0.50 g, 1.01 mmol) in hexane (100 mL) was irradiated at $-10\,^{\circ}C$ for five days. The reaction mixture was warmed to ambient temperature and all volatile materials were removed under high vacuum (0.001 Torr). The remaining unconverted $[(\eta^5\text{-}C_5H_5)Re(CO)_3]$ was removed by sublimation (50 °C, 0.001 Torr). The brown residue was treated with hexane (40 mL), filtered, and concentrated under vacuum to 15 mL. After storage at $-80\,^{\circ}C$ for 48 h, a mixture of **3** and the unconverted starting material **1** was obtained. This crystalline material was redissolved in hexane (10 mL) and stored at $-80\,^{\circ}C$ for another 48 h. Pure **3** (0.15 g, 0.19 mmol, 18.9 %) was obtained as light yellow crystals. All NMR spectra were recorded in $[D_6]$benzene at 25 °C. ^1H NMR (500 MHz, TMS): $\delta = 0.35$ (s, 18 H; $SiMe_3$), 4.88 (s, 10 H; C_5H_5); ^{11}B NMR (160 MHz, $Et_2O \cdot BF_3$): $\delta = 100.4$; ^{13}C NMR (126 MHz, TMS): $\delta = 3.7$ ($SiMe_3$), 86.7 (C_5H_5), 203.5 (CO); MS (eV): m/z (%): 785 (22.7) $[M^+]$, 729 (2.9) $[M^+ - 2\,CO]$, 73 (43.3) $[SiMe_3]$.

Received: February 19, 2001 [Z 16645]

---

[1] a) P. L. Timms, *J. Am. Chem. Soc.* **1967**, *89*, 1629; b) P. L. Timms, *Acc. Chem. Res.* **1973**, *6*, 118, and references therein.

[2] B. Pachaly, R. West, *Angew. Chem.* **1984**, *96*, 444; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 454.

[3] a) S. M. van der Kerk, P. H. M. Budzelaar, A. L. M. van Beijnen, G. J. M. van der Kerk, *Polyhedron* **1984**, *3*, 271, and references therein; b) A. Meller, *Pure Appl. Chem.* **1991**, *63*, 395.

[4] B. G. Ramsey, D. M. Anjo, *J. Am. Chem. Soc.* **1977**, *99*, 3182.

[5] R. Schlögl, B. Wrackmeyer, *Polyhedron* **1985**, *4*, 885.

[6] a) H. Braunschweig, T. Wagner, *Angew. Chem.* **1995**, *107*, 904–905; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 825; b) H. Braunschweig, B. Ganter, *J. Organomet. Chem.* **1997**, *545*, 163; c) H. Braunschweig, M. Müller, *Chem. Ber.* **1997**, *130*, 1295; d) H. Braunschweig, C. Kollann, U. Englert, *Eur. J. Inorg. Chem.* **1998**, 465; e) H. Braunschweig, C. Kollann, K. W. Klinkhammer, *Eur. J. Inorg. Chem.* **1999**, 1523; f) H. Braunschweig, M. Koster, *J. Organomet. Chem.* **1999**, *588*, 231.

[7] H. Braunschweig, C. Kollann, U. Englert, *Angew. Chem.* **1998**, *110*, 3355; *Angew. Chem. Int. Ed.* **1998**, *37*, 3179.

[8] a) M. Shimoi, S. Ikubo, Y. Kawano, *J. Am. Chem. Soc.* **1998**, *120*, 4222; b) A. H. Cowley, V. Lomelí, A. Voigt, *J. Am. Chem. Soc.* **1998**, *120*, 6401; c) G. J. Irvine, C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, *Angew. Chem.* **2000**, *112*, 978; *Angew. Chem. Int. Ed.* **2000**, *39*, 948.

[9] Crystal structure determination of **2**: $C_{11}H_{18}BCrNO_5Si_2$, Siemens P2(1) diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, graphite monochromator); $T = 173(2)$ K, light brown plates, $0.2 \times 0.1 \times 0.05\ mm^3$, triclinic, space group $P\bar{1}$; $a = 9.135(5)$, $b = 9.201(6)$, $c = 12.002(8)$ Å, $\alpha = 109.17(5)$, $\beta = 97.37(5)$, $\gamma = 102.18(4)^{\circ}$, $V = 909.8(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.326\ g\,cm^{-1}$, $\mu(Mo_{K\alpha}) = 7.75\ cm^{-1}$, $F(000) = 376$, 3392 measured reflections ($1.84 < \theta < 25.00^{\circ}$), $\omega - 2\theta$ scans. The empirical absorption correction provided transmission factors between 0.584 and 0.631. The structure was solved by direct methods; 3172 independent reflections, 2024 with $I > 2\sigma(I)$, $R_{int} = 0.05$, 196 variables. All non-hydrogen atoms were refined with anisotropic displacement parameters, all hydrogen atoms were included as riding (C–H = 98 pm, $U_{iso}(H) = 1.3\ U_{iso}(C)$). $R_F = 0.0590$, $wR_{F^2} = 0.0996$ for reflections with $I > 2\sigma(I)$, $w^{-1} = \sigma^2(F_o)$, GOF = 1.026. 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-158000. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] R. Boese, P. Paetzold, A. Tapper, *Chem. Ber.* **1987**, *120*, 1295–1298.

[11] A. W. Ehlers, E. J. Baerends, F. M. Bickelhaupt, U. Radius, *Chem. Eur. J.* **1998**, *4*, 210.

[12] a) J. Uddin, C. Boehme, G. Frenking, *Organometallics* **2000**, *19*, 571; b) C. Boehme, J. Uddin, G. Frenking, *Coord. Chem. Rev.* **2000**, *197*, 249.

[13] H. Braunschweig, M. Colling, unpublished results.

[14] W. Strohmeyer, J. F. Guttenberger, H. Blumenthal, G. Albert, *Chem. Ber.* **1966**, *99*, 3419.

The $[(\eta\text{-}C_6H_5Me)NbSn_6Nb(\eta\text{-}C_6H_5Me)]^{2-}$ Ion: A Complex Containing a Metal-Stabilized Sn_6^{12-} Cyclohexane-Like Zintl Ion[**]

Banu Kesanli, James Fettinger, and Bryan Eichhorn[*]

Homoatomic tin Zintl ions isolated from solution include the *nido*-Sn_9^{4-} ion,[1, 2] the *nido*/*closo*-Sn_9^{3-} ion,[3] and the *closo*-Sn_5^{2-} ion.[4] Metal-stabilized Zintl ions include the *closo*-Sn_6^{2-} ion[5] in $[Sn_6\{Cr(CO)_5\}_6]^{2-}$ and *closo*-$Li_2Sn_8^{4-}$.[6] These structures are characterized by electron-deficient boron hydride like cluster bonding described by Wades rules.[7] Related Ge and Pb Zintl ions also adopt *closo*- and *nido*-structures that are occasionally linked to form dimers or polymers.[8, 9] Although the *inter*cluster connections in the linked polyhedra are frequently two-center, two-electron bonds (2c–2e), the *intra*cluster bonding is always electron deficient.

In contrast, the Group 15 polypnictide Zintl ions are characterized by 2c–2e bonds in which structures are directly related to cyclic hydrocarbons.[10, 11] For the polypnictides, conversion of hydrocarbon-like structures into electron-deficient boron hydride like structures can be accomplished by adding verticies to the clusters that do not contribute electrons to cluster bonding. One such transformation involves the conversion of the nortricyclane-like Sb_7^{3-} cluster into the *nido*-$[Sb_7Ni_3(CO)_3]^{3-}$ complex through the addition of Ni(CO) fragments.[12] By comparison, conversion of the boron hydride like Group 14 Zintl ions into cyclic hydro-

---

[*] Prof. B. Eichhorn, B. Kesanli, Dr. J. Fettinger
Department of Chemistry and Biochemistry
University of Maryland
College Park, MD 20742 (USA)
Fax: (+1) 301-314-9121
E-mail: b._eichhorn@umail.umd.edu

[**] This work was supported by the Petroleum Research Fund of the American Chemical Society and the National Science Foundation. We thank Dr. John Watkin, Dr. David Clark, Dr. Steve Grumbine, and Donna Gardner for access and assistance with the metal vapor synthesis reactor at LANL. We also thank Dr. Yiu Fai Lam for assistance with the ^{119}Sn NMR studies.