Boron Triangle

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Synthesis and Characterization of a Doubly Base-Stabilized $B_3H_6^+$ Analogue**

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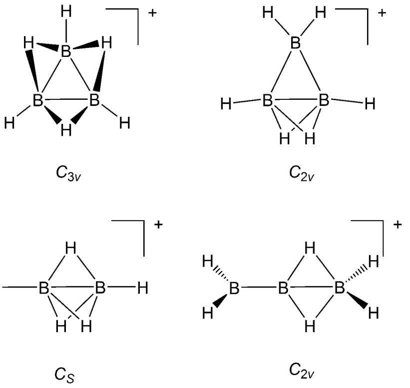
There is long-standing interest in the electronic structure of small-ring compounds containing boron.[1] However, the simple boron hydride $B_3H_6^+$, being isoelectronic to the smallest aromatic organic compound, namely the 2π system $C_3H_3^+$, has not yet been prepared. The possible structure of $B_3H_6^+$ was assessed in a number of quantum-chemical calculations using various levels of theory.[2,3] These calculations predicted a C_{3v}-symmetric, nonplanar global minimum structure with three bridging hydrogen atoms (see Scheme 1). The D_{3h}-symmetric planar form does not represent an energy minimum, is approximately 175 kJ mol^{-1} higher in energy than the C_{3v}-symmetric global energy minimum. $B_3H_6^+$ was therefore declared to be the "first three-membered nonplanar 2π aromatic" species.[2a]

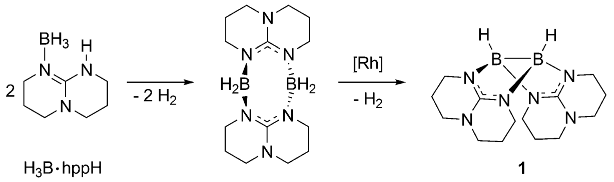
Korkin, Schleyer, and McKee also considered other isomers in their calculations.[3] They found in total four energy minimum structures, which are displayed in Scheme 1. According to their ab initio (MP2) calculations, a C_{2v}-symmetric isomer featuring a B_3 triangle with one short (150.1 pm) and two longer B–B bonds (184.9 pm) as well as two bridging hydrogen atoms (see Scheme 1) lies 49 kJ mol^{-1} higher in energy than the C_{3v}-symmetric global energy minimum. In two further C_S- and C_{2v}-symmetric isomers a B-B-B chain is established. The energies of these two isomers are already 60 and 77 kJ mol^{-1} higher than the C_{3v} global energy minimum structure. Up to date, none of these isomers or even a derivative of $B_3H_6^+$ have been structurally characterized. Herein we report the synthesis and complete characterization of a doubly base-stabilized $B_3H_6^+$ analogue.



Scheme 1. The energy-minimum structures calculated for $B_3H_6^+$.

In our studies we used the doubly base-stabilized diborane(4) $[HB(\mu\text{-hpp})]_2$ (**1**), which was synthesized as described previously by catalytic dehydrogenation of the adduct $H_3B{\cdot}hppH$ (Scheme 2).[4] We recently reported on different aspects of the reactivity of **1**. For example, sulfuration was shown to give $[HB(\mu\text{-hpp})]_2(\mu\text{-S})$,[5] and protonation leads to the cation and doubly base-stabilized $B_2H_5^+$ analogue $[B_2H_3(\mu\text{-hpp})_2]^+$.[6] Moreover, the complexes $[\{HB(\mu\text{-hpp})\}_2ZnX_2]$ and $[\{HB(\mu\text{-hpp})\}_2ZnMe_2]$ were obtained as the products of reaction with zinc halides ZnX_2 (X = Cl, Br) or dimethylzinc, respectively.[7] These reactions demonstrated the high nucleophilicity of **1**. In the light of this chemical behavior, we tested the reaction of **1** with BR_2^+ (R = H or alkyl) cationic species.

In the course of our research, we treated **1** with *N*-borabicyclo[3.3.1]nonan-9-yl (9-BBN) bis-(trifluoromethanesulfonyl)imide (**2a**) and trifluoromethanesulfonate (**2b**) (see Scheme 3), which are known as easily accessible sources of a highly electrophilic boronium ion.[8] We indeed observed the formation of a single reaction product.



Scheme 2. Synthesis of the doubly base-stabilized diborane(4) $[HB(\mu\text{-hpp})]_2$. hppH = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine.

Both salts **3a** and **3b** could be crystallized from toluene or toluene/petroleum ether (40/60) solutions. However, only for the crystals of **3b** was a good-quality structure derived on the basis of the X-ray diffraction data. The unit cell contains two slightly different cationic units, both featuring B_3 triangles. Figure 1a depicts the structure, and Figure 1b shows in detail the central boron triangle in both molecules together with the atom numbering. The B–B bond between the two boron atoms which are bridged by the two hpp substituents increases

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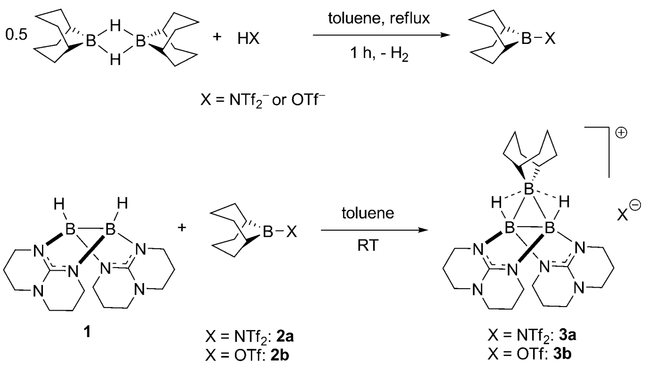

Scheme 3. Synthesis of **3a** and **3b**.

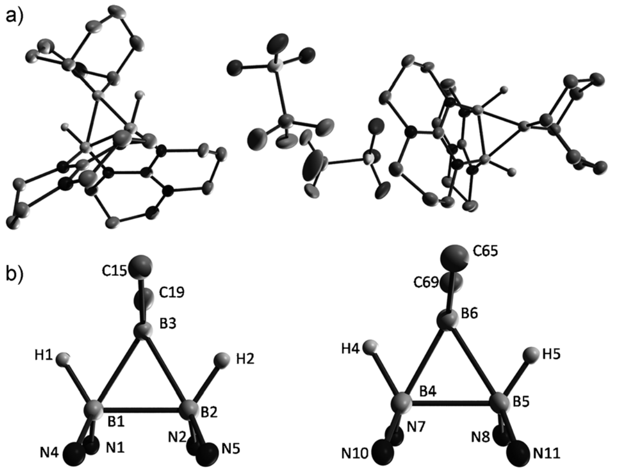

Figure 1. a) Molecular structure of **3b**. Vibrational ellipsoids drawn at the 50% probability level. The hydrogen atoms of the hpp- and 9-BBN groups were omitted for sake of clarity. b) Boron triangles of both molecules in detail, only atoms bound to boron are shown. Selected distances [pm]: B1–B2 184.9(5), B1–B3 181.9(5), B2–B3 178.4(5), B4–B5 184.2(5), B4–B6 178.0(5), B5–B6 184.1(5), B1–H1 115(3), B2–H2 116(4), B4–H4 119(4), B5–H5 108(4).

considerably from 177.2(3) pm in **1** to 184.9(5)/184.2(5) pm in **3b**. The B−B bond lengths involving the 9-BBN group are 181.9(5) and 178.4(5) pm in the first and 178.0(5) and 184.1(5) pm in the second molecule. The hydrogen atoms attached to boron were fully refined, and asymmetric B−H···B bridges are present. The B-B-H angles (122(2)/124(2)° and 124(2)/119(2)°) are significantly smaller than those in **1** (XRD and IR estimates of 127°/132° and 132°).[6] Together with the short distances to the boron atom of the 9-BBN group, this suggests an additional stabilization by the hydrogen atoms.

In contrast to the IR spectrum of **1**, the spectra of **3a** and **3b** are free of bands assignable to terminal B−H valence vibrations (Figure 2). Instead an additional strong absorption around 1614 (for **3a**)/1610 (for **3b**) cm^{-1} appears, indicating the presence of B-H-B bridges. These vibrations are close to the ν(CN) wavenumbers at 1571 cm^{-1} (for **1**), 1565 cm^{-1} (for **3a**), and 1574 cm^{-1} (for **3b**).

A signal at *m/z* 421.2 due to the $[M-NTf_2]^+$ and $[M-OTf]^+$ cation was detected in the ESI^+ mass spectrum. The ^1H and ^{11}B NMR spectra of **3a** and **3b** are similar; Figure 3 shows those of **3a** exemplarily. The $^{11}B\{^1H\}$ NMR spectrum contains a sharp singlet at $\delta = -1.87$ ppm, which splits into a doublet ($^1J(B,H) = 79.9$ Hz) when proton coupling is allowed. The chemical shift is typical for tetracoordinate boron, and the signal can be assigned to the boron atoms attached to the hpp substituents. In addition, a broad feature was detected around $\delta = 39$ ppm (half line width ca. 5.4 ppm), arising from the boron atom of the 9-BBN unit. In ^{11}B decoupled ^1H NMR spectra one signal for the boron-bounded hydrogen atoms can be found at $\delta = 2.31$ ppm (for **3a**) and at $\delta = 2.38$ ppm (for **3b**).

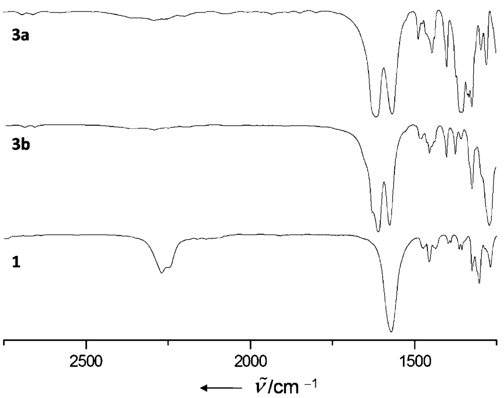

Figure 2. IR spectra (KBr disks, transmittance) of **3a**, **3b**, and **1**.

To obtain further information about the bonding properties, quantum-chemical calculations were carried out on the model compound $[\{HB(\mu\text{-hpp})\}_2BH_2]^+$. With RI-MP2/def2-TZVPP[9] an almost symmetrical structure was achieved, while with B3LYP/6-311++G(d,p)[10] an unsymmetrical B_3 triangle resulted. In the case of B3LYP a frequency calculation was performed, to ensure that it is a real minimum without imaginary frequencies. If the structure is optimized in C_2, one imaginary frequency resulted, corresponding to the vibration of the BH_2 group between H1 and H2. This indicates a transition state. Selected experimentally determined structural parameters are compared with calculated ones in Table 1.

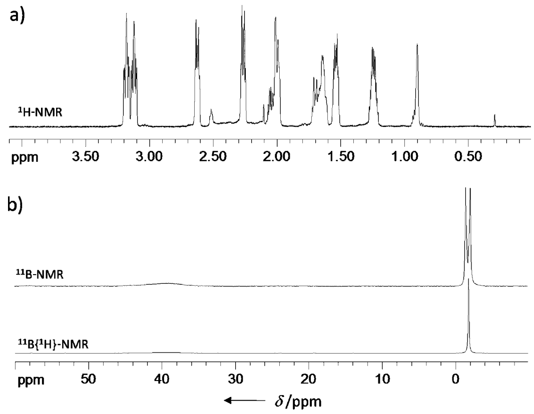

Figure 3. a) ^1H NMR (600 MHz, C_6D_6) and b) ^{11}B and $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6) spectra of **3a**.

Table 1: Comparison between selected parameters (bond lengths in pm, bond angles in degrees) for **3b** with calculated parameters for $[\{HB(\mu\text{-}hpp)]_2BH_2]^+$.

	exp.	RI-MP2/ def2-TZVPP	B3LYP/ 6-311 ++G(d,p)
B1-B2/B4-B5	184.9(5)/184.2(5)	181.8	183.3
B1-B3/B4-B6	181.9(5)/178.0(5)	178.1	175.9
B2-B3/B5-B6	178.4(5)/184.1(5)	178.0	182.6
B3-C15/B6-C65	158.4(5)/159.1(5)	–	–
B3-C19/B6-C69	158.8(5)/158.4(5)	–	–
B–N (av)	151.4	151.5/151.7	152.8
B1-H1/B4-H4	115(3)/119(4)	124.2	122.5
B2-H2/B5-H5	116(4)/108(4)	124.3	125.9
B3⋯H1/B6⋯H4	166(4)/153(4)	156.4	172.1
B3⋯H2/B6⋯H5	164(4)/171(4)	156.0	148.0
B1-B2-B3/B4-B5-B6	60.08(19)/57.8(2)	59.3	57.5
B2-B3-B1/B5-B6-B4	61.74(19)/61.1(2)	61.4	61.5
B3-B1-B2/B6-B4-B5	58.18(18)/61.1(2)	59.3	61.1
B1-B2-H2/B4-B5-H5	124.3(18)/124(2)	118.3	116.9
B2-B1-H1/B5-B4-H4	121.6(18)/119.3(17)	118.4	122.7

The topology of the electron-density distribution in $[\{HB(\mu\text{-}hpp)\}_2BH_2]^+$ is shown in Figure 4. The bond critical points are highlighted. Four bond critical points are located in the B_3 plane, two along the B1/B2–H bonds, one between B1 and B2, and another one in the center of the B_3 ring. The B1–B2 bonding path is significantly bent towards B3, indicating 3-center-2-electron bonding. The presence of closed B-B-B three-center bonding is in accordance with σ-aromatic character. The bonding is therefore comparable to that in the $B_3H_8^-$ ion.[11,12]

Finally, we calculated the electron affinity of the model cation $[\{HB(\mu\text{-}hpp)\}_2BH_2]^+$. Using B3LYP/6-311++G(d,p) a ΔH^0 value of −2.3 eV was obtained for the addition of one electron to give the neutral radical. The ΔH^0 value for addition of a second electron to yield the monoanion was close to zero.

These results are indicative of interesting chemical reactivity of the synthesized $B_3H_6^+$ analogue, which will be the subject of future work.

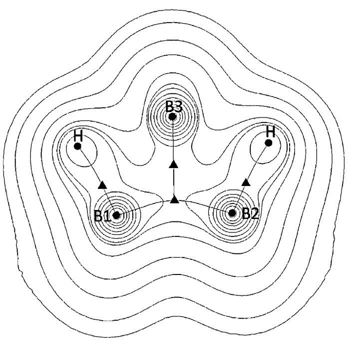

Figure 4. Topology of the electron-density distribution of $[\{HB(\mu\text{-}hpp)\}_2BH_2]^+$ (RI-MP2/def2-TZVPP) and bond paths in the plane defined by the three B atoms. Electron density (av, in $e\,Å^{-3}$) at the (3,−1) bond critical points (triangles): 0.152 (B–H), 0.128 (B1–B2), 0.118 (B1-B2-B3). Lines were drawn at 0.004, 0.008, 0.02, 0.04, 0.08, 0.11, 0.13, 0.2, 0.4, 0.8, 2, 4, 8, 20, 40, 80, 200, 400, 800 $e\,Å^{-3}$.

Experimental Section

The reactions were carried out under an Ar atmosphere using standard Schlenk techniques. All solvents were rigorously dried by applying standard procedures prior to their use. The synthesis of $[HB(\mu\text{-}hpp)]_2$ (**1**) was accomplished as reported previously in reference [5].

2a: 9-BBN dimer (67 mg, 0.55 mmol of the monomer) and bis(trifluoromethanesulfonyl)imide (140 mg, 0.50 mmol) were dissolved in toluene (1 mL) and refluxed for 1 h. The solution was used without further purification.

2b: 9-BBN dimer (134 mg, 1.10 mmol of the monomer) and trifluoromethanesulfonic acid (89 μL, 1.00 mmol) were dissolved in toluene (1.5 mL) and refluxed for 1 h. The solution was used without further purification.

3a: The solution of **2a** was slowly added to a suspension of **1** (150 mg, 0.50 mmol) in toluene (10 mL). After the mixture had been stirred at room temperature for 2 h, it was filtered, concentrated, and stored at 3 °C. After a few days pure **3a** crystallized in 31 % yield (107 mg, 0.15 mmol). C,H,N analysis (%) for $C_{24}H_{40}B_3F_6N_7O_4S_2$ (701.17 $g\,mol^{-1}$): calcd: C 41.11, H 5.75, N 13.98; found: C 39.93, H 5.59, N 13.25; ^1H NMR (C_6D_6, 600 MHz): $\delta = 3.20$–3.10 (m, 8 H, CH_2-N), 2.64–2.60 (m, 4 H, CH_2-N), 2.31 (bs, 2 H, B-H), 2.28–2.24 (m, 4 H, CH_2-N), 2.07–1.98 (m, 6 H, $CH_{2\,9\text{-}BBN}$), 1.72–1.60 (m, 6 H, $CH_{2\,9\text{-}BBN}$), 1.55–1.52 (m, 4 H, $CH_{2\,hpp}$), 1.27–1.20 (m, 4 H, $CH_{2\,hpp}$), 0.90 ppm (bs, 2 H, CH-B); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): $\delta = 156.5$ (C_{quart}), 121.2 (q, $^1J(C,F) = 322$ Hz, CF_3), 54.8 (CH_2-N), 43.3 (CH_2-N), 35.7 ($CH_{2\,9\text{-}BBN}$), 24.9 ($CH_{2\,9\text{-}BBN}$), 22.5 (bs, CH-B), 21.5 ppm ($CH_{2\,hpp}$); ^{11}B NMR (128 MHz, C_6D_6): $\delta = 38.98$ (bs, half line width ca. 5.4 ppm, $B_{9\text{-}BBN}$), −1.87 ppm (d, $^1J(B,H) = 79.9$ Hz, B_{hpp}); ^{19}F NMR (375 MHz, C_6D_6): $\delta = -80.34$ ppm (CF_3); IR (KBr): $\tilde{\nu} = 2979$ (m; C-H val.), 2947 (s; C-H val.), 2915 (s; C-H val.), 2886 (s; C-H val.), 2689 (w), 2655 (w), 2290 (w), 1614 (s) (B-H-B), 1565 (s; C=N val.), 1486 (w), 1444 (m), 1400 (m), 1359 (s), 1352 (s), 1323 (s), 1296 (w), 1280 (m), 1225 (s), 1198 (s), 1140 (s), 1054 (s) cm^{-1}; MS (ESI^+): *m*/*z* (%): 421.2 (67) $[M-NTf_2]^+$, 299.4 (100) $[\mathbf{1}-H]^+$.

3b: The solution of **2b** was slowly added to a suspension of **1** (300 mg, 1.00 mmol) in toluene (12 mL). After the mixture had been stirred at room temperature for 2 h, it was filtered and concentrated. The product was precipitated by addition of petroleum ether (40/60). After filtration and drying in vacuo, colorless solid **3b** was obtained in 30 % yield (170 mg, 0.30 mmol). Crystals suitable for X-ray crystallography were grown by overlayering a toluene solution with petroleum ether (40/60) at 3 °C. C,H,N analysis (%) for $C_{23}H_{40}B_3F_3N_6O_3S$ (570.10 $g\,mol^{-1}$): calcd: C 48.46, H 7.07, N 14.74; found: C 47.24, H 6.88, N 14.44; ^1H NMR (600 MHz, C_6D_6): $\delta = 3.42$–3.37 (m, 8 H, CH_2-N), 2.65–2.62 (m, 4 H, CH_2-N), 2.38 (bs, 2 H, B-H), 2.30–2.26 (m, 4 H, CH_2-N), 2.09–2.01 (m, 6 H, $CH_{2\,9\text{-}BBN}$), 1.75–1.68 (m, 6 H, $CH_{2\,9\text{-}BBN}$), 1.58–1.53 (m, 4 H, $CH_{2\,hpp}$), 1.33–1.26 (m, 4 H, $CH_{2\,hpp}$), 1.04 ppm (bs, 2 H, CH-B); $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): $\delta = 157.7$ (C_{quart}), 45.9 (CH_2-N), 43.3 (CH_2-N), 35.7 ($CH_{2\,9\text{-}BBN}$), 25.1 ($CH_{2\,9\text{-}BBN}$), 22.5 (bs, CH-B), 21.7 ($CH_{2\,hpp}$); ^{11}B NMR (128 MHz, C_6D_6): $\delta = 39.05$ (bs, half line width ca. 5.4 ppm, $B_{9\text{-}BBN}$), −1.73 (d, $^1J(B,H) = 80.6$ Hz, B_{hpp}); ^{19}F NMR: $\delta = -77.80$ ppm (s, CF_3); IR (KBr): $\tilde{\nu} = 2940$ (m) (C-H val.), 2918 (m) (C-H val.), 2880 (s) (C-H val.), 2840 (s) (C-H val.), 2686 (w), 2657 (w), 2293 (w) (B-H val.), 1626 (s), 1610 (s) (B-H-B), 1574 (s) (C=N val.), 1476 (w), 1453 (w), 1401 (m), 1374 (m), 1356 (w), 1323 (s), 1270 (s), 1222 (m), 1236 (m), 1222 (s), 1146 (6), 1109 (w), 1068 (m), 1051 (m), 1031 (s) cm^{-1}; MS (ESI^+): *m*/*z* (%): 421.2 (54) $[M-OTf]^+$, 301.4 (100) $[\mathbf{1}+H]^+$.

Crystal data for **3b**: $C_{23}H_{40}B_3F_3N_6O_3S$, $M_r = 570.10$, $0.40 \times 0.25 \times 0.10\ mm^3$, monoclinic, space group $P2_{1/n}$, $a = 13.206(9)$, $b = 28.39(2)$, $c = 14.501(10)$ Å, $\beta = 91.84(1)°$, $V = 5434(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.394\ Mg\,m^{-3}$, $Mo_{K\alpha}$ radiation (graphite-monochromated, $\lambda = 0.71073$ Å), $T = 100$ K, θ range 2.0 to 27.9°. Reflections measured 110786, independent 22952, $R_{int} = 0.0571$. Final *R* indices $[I > 2\sigma(I)]$: $R_1 = 0.0610$, $wR_2 = 0.1624$. H-atoms on B refined.

CCDC 833477 (**3b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Details of the quantum-chemical calculations: see the Supporting Information. The AIM 2000[13] guise of program was used to calculate the topology of the electron density distribution for $[\{HB(\mu\text{-}hpp)\}_2BH_2]^+$.

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Keywords: boron · guanidine · hydride · small rings

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[1] See, for example: a) H. Grützmacher, *Angew. Chem.* **1992**, *104*, 1358 – 1360; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1329 – 1331; and references therein; b) A. Neu, K. Radacki, P. Paetzold, *Angew. Chem.* **1999**, *111*, 1358 – 1360; *Angew. Chem. Int. Ed.* **1999**, *38*, 1281 – 1283; c) C. Präsang, A. Mlodzianowska, Y. Sahin, M. Hofmann, G. Geiseler, W. Massa, A. Berndt, *Angew. Chem.* **2002**, *114*, 3529 – 3531; *Angew. Chem. Int. Ed.* **2002**, *41*, 3380 – 3382; d) Y. Sahin, A. Ziegler, T. Happel, H. Meyer, M. J. Bayer, H. Pritzkow, W. Massa, M. Hofmann, P. von R. Schleyer, W. Siebert, A. Berndt, *J. Organomet. Chem.* **2003**, *680*, 244 – 256, and references therein, e) M. Hofmann, A. Berndt, *Heteroat. Chem.* **2006**, *17*, 224 – 237.

[2] a) E. D. Jemmis, G. Subramanian, G. N. Srinivas, *J. Am. Chem. Soc.* **1992**, *114*, 7939 – 7941; b) E. D. Jemmis, G. Subramanian, *Inorg. Chem.* **1995**, *34*, 6559 – 6561.

[3] A. A. Korkin, P. von R. Schleyer, M. L. McKee, *Inorg. Chem.* **1995**, *34*, 961 – 977.

[4] O. Ciobanu, P. Roquette, S. Leingang, H. Wadepohl, J. Mautz, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2007**, 4530 – 4534.

[5] N. Schulenberg, O. Ciobanu, E. Kaifer, H. Wadepohl, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2010**, 5201 – 5210.

[6] O. Ciobanu, E. Kaifer, M. Enders, H.-J. Himmel, *Angew. Chem.* **2009**, *121*, 5646 – 5649; *Angew. Chem. Int. Ed.* **2009**, *48*, 5538 – 5541.

[7] N. Schulenberg, S. Litters, E. Kaifer, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2011**, 2657 – 2661.

[8] A. Prokofjevs, J. W. Kampf, E. Vedejs, *Angew. Chem.* **2011**, *123*, 2146 – 2149; *Angew. Chem. Int. Ed.* **2011**, *50*, 2098 – 2101.

[9] a) F. Weigend, M. Häser, *Theor. Chem. Acc.* **1997**, *97*, 331 – 340; b) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143 – 152.

[10] a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785 – 789; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648 – 5653.

[11] C. R. Peters, C. E. Nordman, *J. Am. Chem. Soc.* **1960**, *82*, 5758 – 5758.

[12] M. Sironi, M. Raimondi, D. L. Cooper, J. Gerratt, *J. Phys. Chem.* **1991**, *95*, 10617 – 10623.

[13] *AIM 2000*, Version 2.0, Copyright **2002** Build: 2.04, Program designed by Friedrich Biegler-König and Jens Schönbohm, Chemical advice by R. F. W. Bader, McMaster University, Hamilton, Canada.