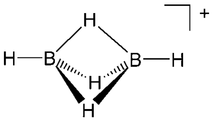
B–B Bond Protonation

DOI: 10.1002/anie.200901842

Synthesis of a Stable $B_2H_5^+$ Analogue by Protonation of a Double Base-Stabilized Diborane(4)**

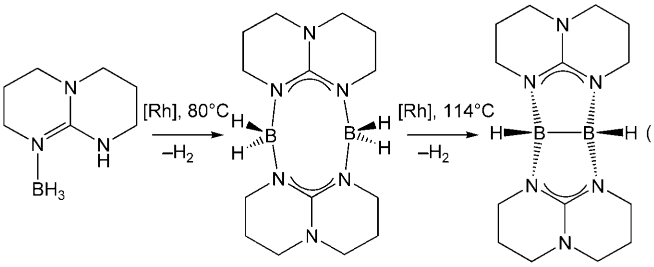
*Oxana Ciobanu, Elisabeth Kaifer, Markus Enders, and Hans-Jörg Himmel**

On the basis of an analysis of the products formed in the course of reaction between B_2H_6 and the deuterated magic acid ($FSO_3D{\cdot}SbF_5$), Olah et al. postulated the $B_2H_5^+$ cation in 1988 as a short-lived intermediate formed by protonation of B_2H_6 and subsequent H_2 elimination.[1] The cation had previously been observed in the gas phase after photoionization of B_2H_6.[2] However, a salt of this cationic boron hydride has not been synthesized on a preparative scale to date. Because of the scarceness of experimental information, the cation was the subject of several quantum-chemical calculations.[3–5] These calculations found a global energy minimum structure with three bridging hydrogen atoms (Scheme 1). The distance between the two boron atoms is 149.5 pm according to HF/6-31G*,[3] and 151.8 pm according to more recent QCISD(T)/6-311G** calculations.[4] These values might argue for B–B bonding, although it has been shown in many cases that a short distance does not automatically imply the presence of a significant chemical bond. To obtain more information, the cation was subjected to an NBO charge and Wiberg bond analysis.[4] The NBO analysis suggested a charge of 0.20e on each boron atom, and the Wiberg bond analysis returned an index of 1.0 for the B–B bond, which is clearly different to the situation in, for example, B_2H_6. The detailed description of the bonding situation in species such as this with multicenter bonds is still the subject of debate.[6]



Scheme 1. Calculated energy minimum structure for $B_2H_5^+$.

Herein we report the synthesis of the first cationic binuclear borohydride $[B_2H_3L_2]^+$, where L is the anionic guanidinate ligand 1,3,4,6,7,8-hexahydro-2*H*-pyrimido-[1,2-*a*]pyrimidinate (hpp)). The geometry is similar to that of $B_2H_5^+$, with two bridging hydrogen atoms being replaced by two hpp units. The synthesis commences with the complex $hppH{\cdot}BH_3$ (**1**), which can be dehydrogenated, via $[BH_2(hpp)]_2$ (**2**), to give the doubly base-stabilized diborane(4) $[BH(hpp)]_2$ (**3**). Although we have previously reported the structure of **3**,[7] we have only now found a route to **3** in high yield and purity. The initial thermal dehydrogenation of **1** proved not to be the ideal route to **3**; however, we recently showed that **1** can be catalytically dehydrogenated with $[\{Rh(1,5\text{-cod})Cl\}_2]$ in toluene at 80 °C to give **2** (with a B···B separation of 306.5 pm).[8] This species, dissolved in toluene, can be further dehydrogenated at 114 °C in the presence of catalytic amounts of $[\{Rh(1,5\text{-cod})Cl\}_2]$ to yield **3** [Eq. (1)], with a B–B bond distance of 177.2 pm, in a clean reaction. The IR spectrum in the ν(B-H) stretching region for pure **3** is shown in Figure 2a. It features two overlapping bands, which can be assigned to the in-phase (2272 cm^{-1}) and out-of-phase (2249 cm^{-1}) combination of the two B-H oscillators. By applying a simple formula,[9] the angle between the two B-H oscillators can be estimated from the relative intensity (obtained by a fit with two Lorentz curves) of these two modes to be 84°, resulting in an average value of 132° for the two B-B-H angles. This value is in good agreement with the estimates from B3LYP/6-31++G* quantum-chemical calculations (128.8° and 128.0°) and from the X-ray diffraction data (B1-B2-H 127°, B2-B1-H 132°). Compound **3** adopts a "roof-type" conformation, which has consequences for the ^{1}H NMR spectra. Thus the *endo* protons (pointing into the roof) have different chemical shifts than the *exo* protons. The hydrogen atoms attached to boron give rise to a sharp singlet at $\delta = 3.37$ ppm in the $^1H\{^{11}B\}$ NMR spectra. The molecular structures of the three boron hydrides **1**, **2**, and **3** are shown in Figure 1.



1 **2** **3**

(1)

Having established the new route to **3**, we started to inspect its chemical properties.[10] In the course of these studies, we reacted **3** with I_2 in toluene solutions. A product **4a** was formed (in addition to traces of $[hppH_2]I$; see the Supporting Information). The IR spectrum of **4a** (Figure 2a) has strong bands with absorption maxima at 2425 and 1872 cm^{-1}. These bands can be unambiguously assigned to B-H stretching modes of terminal and bridging hydrogen atoms, respectively. For comparison, in B_2H_6 the IR active

---

[*] O. Ciobanu, Dr. E. Kaifer, Prof. Dr. M. Enders, Prof. Dr. H.-J. Himmel
Anorganisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
Fax: (+49) 6221-545-707
E-mail: hans-jorg.himmel@aci.uni-heidelberg.de

[**] Continuous financial support from the DFG is gratefully acknowledged. The authors thank Prof. Dr. W. Siebert for valuable discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200901842.

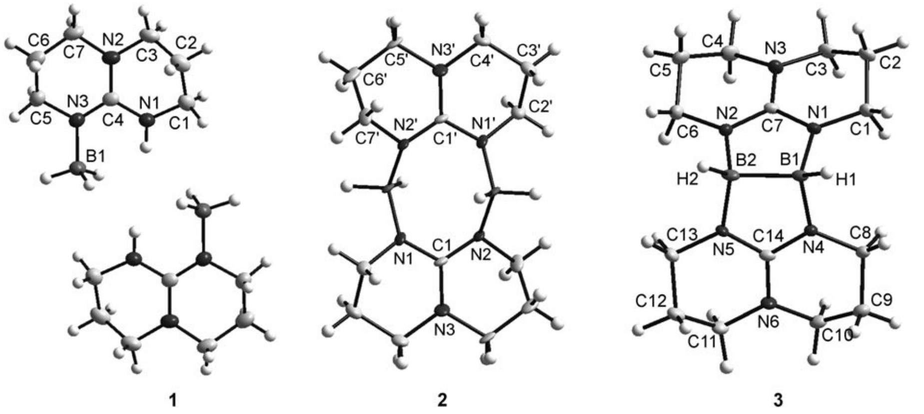


Figure 1. The molecular structures of **1**, **2**, and **3** from X-ray diffraction results.[7,8]

stretching modes $\nu(\text{B-H}_t)$ appear at 2613/2518 cm^{-1} and the stretching modes $\nu(\text{B-H}_b)$ at 1924/1615 cm^{-1}.[11] The difference between the wavenumbers of $\nu(\text{B-H}_t)$ and $\nu(\text{B-H}_b)$ is thus as expected; however, much larger shifts have also been reported. Thus, in the IR spectrum of $[R'B(\mu\text{-CCR}_3)(\mu\text{-H})BR']$ (R = $SiMe_3$, R′ = CMe_3), which can be described as a 1,3-diboraalkyl system with a B-H-B bridge, a broad band at 1580 cm^{-1} was assigned to ν(B-H).[12]

The number of hpp signals in the ^{1}H NMR spectrum of **4a** indicates a roof-type conformation of the $\{B_2(hpp)_2\}$ group (*endo* and *exo* hydrogen atoms). The $^1H\{^{11}B\}$ NMR spectrum exhibits a triplet and a doublet for the boron-bonded hydrogen atoms at $\delta = 1.97$ and 3.44 ppm, respectively. These positions are characteristic for terminal and bridging B−H bonds (Table 1). In the ^{11}B NMR spectrum (Figure 2b), a broad doublet is found at $\delta = -2.20$ ppm ($J = 125$ Hz). For comparison, in the case of the μ-bis(diisopropylamino)diborane **5**, a broad doublet at $\delta = -10.3$ ppm was observed.[13] ^{11}B NMR spectra with selective decoupling of the bridging hydrogen atom (^{1}H resonance at $\delta = 1.97$ ppm) were also recorded (Figure 2b), and coupling constants $^1J(^1H_t,^{11}B) = 125$ Hz and $^1J(^1H_b,^{11}B) = 40$ Hz were obtained from a spectrum simulation. The spectroscopic measurements thus leave no doubt of the formation of a new binuclear boron hydride featuring terminal and bridging hydrogen atoms.

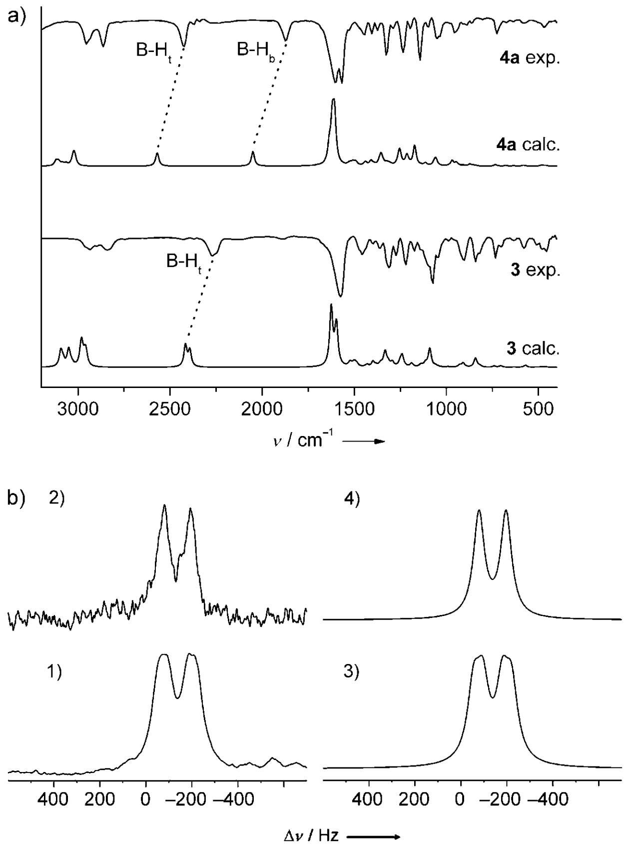
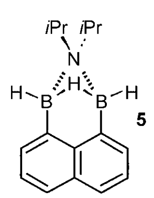


Figure 2. a) Comparison of experimental and calculated IR spectra (CsI disks) of solids **3** and **4a**. For the simulation of the calculated spectra, Lorentz band profiles were assumed. b) Experimental and simulated ^{11}B NMR spectra (64.1 MHz) of **4a** in [D$_8$]toluene at 80 °C. 1) ^{11}B NMR spectrum without ^{1}H decoupling, 2) ^{11}B NMR with selective decoupling of the bridging H atom (^{1}H resonance at 1.97 ppm), 3) simulation with the following parameters: $^1J(^1H_t{}^{11}B) = 125$, $^1J(^1H_b{}^{11}B) = 40$, lineshape = 65 Hz, 4) simulation with coupling to terminal H atoms only.

Table 1: Comparison of selected properties of $[B_2H_3(hpp)_2]^+$, $B_2H_5^+$, and B_2H_6.

	$[B_2H_3(hpp)_2]^+$		$B_2H_5^+$	B_2H_6
	expt.	calcd[a]	calcd[a]	calcd[a]
B···B [pm]	222.9(4)	221.9	150.2	176.6
B-H$_t$ [pm]	108.2/113.4[b]	120.0	117.1	119.0
B-H$_b$ [pm]	134.9/127.4[b]	132.1/131.7	133.5	131.6
$\nu(\text{B-H}_t)$ [cm^{-1}]	2425	2572[c]	2844[c]	2720/ 2616[c]
$\nu(\text{B-H}_b)$ [cm^{-1}]	1872	2050[c]	2220/ 1420[c]	2008/ 1718[c]
$\delta(H_t)$ [ppm]	3.44	3.89	4.48	4.55
$\delta(H_b)$ [ppm]	1.97	1.45	1.77	−0.49
$\delta(^{11}B)$ [ppm]	−2.2	−3.45	−11.26	16.01

[a] The energy-minimum structures were calculated at the B3LYP/6-31++G** level. The $\delta(^{11}B)$ and $\delta(^1H)$ chemical shifts were calculated at the DFT-GIAO//B3LYP/6-311+G* level. The $\delta(^{11}B)$ and $\delta(^1H)$ chemical shifts were referenced to $F_3B{\cdot}OEt_2$ and TMS, respectively. [b] Estimates from X-ray diffraction. [c] Unscaled values. For comparison, the experimentally observed wavenumbers for B_2H_6 are 2613/2518 cm^{-1} ($\nu(\text{B-H}_t)$) and 1924/1615 cm^{-1} ($\nu(\text{B-H}_b)$).



5

Crystals of **4a** suitable for X-ray diffraction measurements were obtained from a toluene/hexane solution. From the X-ray diffraction analysis, **4a** can be identified unambiguously as the binuclear B^{III} compound $[B_2H_3(hpp)_2]^+I^-$ that is formally the product of an oxidative addition of the B^{II}B^{II} unit. The molecular structure is shown in Figure 3. As already suggested on the basis of the NMR data (the number of *endo* and *exo* signals of the hpp group), the molecule again adopts a "roof-type" conformation. The B···B separation is 222.9 pm, and is thus considerably larger than in **3** (177.2 pm). It also is significantly larger than the value of 150.2 pm calculated for $B_2H_5^+$ (Table 1). The B–N bond lengths fall in the region 150.2–152.3 pm, and are somewhat shorter that for **2** (156.18–156.42 pm) and for **3** (156.3–158.17 pm). The N-B-N bond angles (116.6(2)° and 117.4(2)°) are slightly larger than in **3** (111.0(2)° and 110.8(2)). The separated iodide counterion is positioned below the cationic roof.

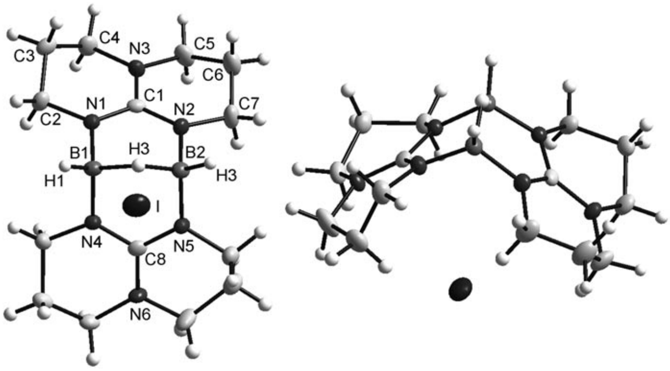
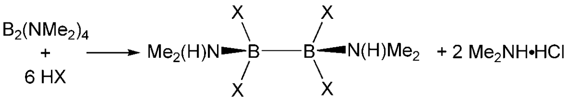


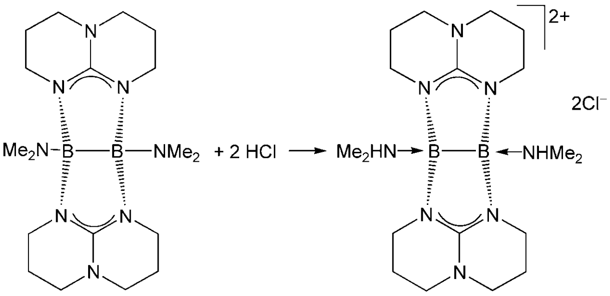
Figure 3. Molecular structure of **4a**. Thermal ellipsoids are set at 50% probability.

A possible reaction pathway leading to **4a** is shown in Scheme 2. The HI formed in the first step can react in the second step with **3** to give the product. Normally protonation of a diborane(4) proceeds very differently. For example, tetrakis(dimethylamino) diborane reacts with HX (X = Cl or Br) according to Equation (2) to form $[B_2X_4(HNMe_2)_2]$.[14] Another example is provided by protonation of the doubly

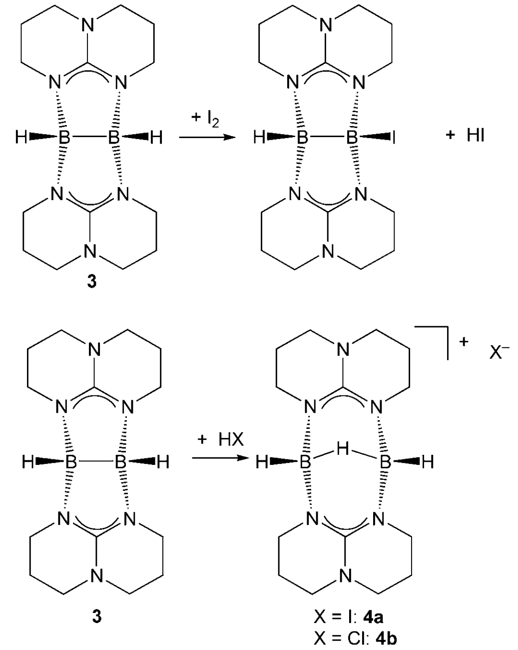


$$B_2(NMe_2)_4 + 6\,HX \longrightarrow Me_2(H)N\rightarrow BX_2{-}BX_2\leftarrow N(H)Me_2 + 2\,Me_2NH{\cdot}HCl \qquad (2)$$

base-stabilized diborane(4) $[(hpp)_2B_2(NMe_2)_2]$ with HCl, producing $[(hpp)_2B_2(NMe_2H)_2]^{2+}(Cl^-)_2$, again without B(II) oxidation [Eq. (3)].[15,16] To find out if direct protonation of **3** is possible, and to find further support for the proposed reaction pathway, we reacted **3** with $HCl{\cdot}Et_2O$. Spectroscopic data (IR, NMR) indeed confirmed that $[B_2H_3(hpp)_2]^+Cl^-$ (**4b**) is formed (Scheme 2). However, in addition to **4b**, we obtained the salt $[hppH_2]Cl$ as a side product in considerable quantities, which arises from protonation and elimination of the hpp ligand in a reaction similar to that in Equation (2). Indeed, solutions of **4a** or **4b** in toluene are not stable for prolonged periods of time (several days); slow protonation of the hpp ligand was observed. In the solid state, however, both $B_2H_5^+$ analogues are stable compounds.



(3)



Scheme 2. Possible reaction pathway to compound **4**.

We were able to crystallize an intermediate of this decomposition route, namely $[BH_2(hppH)_2]Cl$ (**6**), which can be described as a boronium cation with extended hydrogen bonding to the chloride ion (Figure 4). The remaining two B–N bond distances in **6** (156.8(4) and

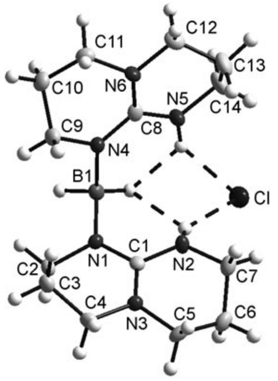
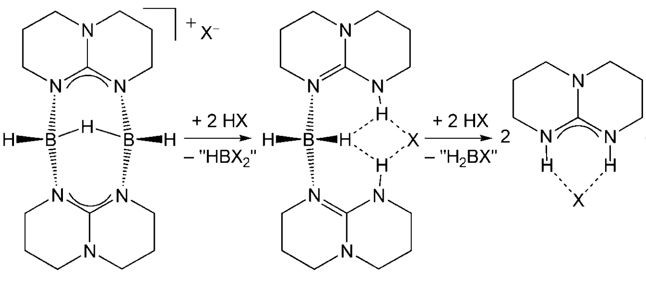


Figure 4. Molecular structure of **5**. Thermal ellipsoids are set at 50% probability.

155.6(4) pm) are considerably elongated with respect to **4a**. Thus decomposition is likely to occur according to Equation (4). Both decomposition end-products, [hppH$_2$]Cl[17] and [hppH$_2$]I (see the Supporting Information), were also structurally characterized. The hydrogen bonding network between the [hppH$_2$]$^+$ cations and the anions differs depending on the halide counterion (see Supporting Information).



(4)

4a: X = I, **4b**: X = Cl

6: X = Cl

As already mentioned, the B···B separation in **4a** (222.9(4) pm) is significantly larger than the value of 151.8 pm calculated with QCISD(T)/6-311G**,[4] or 150.2 pm calculated herein for $B_2H_5^+$. The isolation of compound **3** with a short B–B bond shows that the large distance is not necessarily caused by the presence of the hpp ligands. To obtain further information about the bond properties, we calculated the electron density distribution in **4a** and compared the results with the parent compound $B_2H_5^+$. An analysis of the topology of the electron distribution has previously been applied successfully for the analysis of other boron hydrides with multicenter bonds, such as B_2H_6.[18] Figure 5 shows the topology of the electron density for **4a**, $B_2H_5^+$, and B_2H_6. The bond critical points are also shown. The agreement between the electron densities determined for B_2H_6 at the bond critical points (see Figure 5 caption) with those obtained previously experimentally[18] is very good, and shows that the applied level of theory yields reasonable results. It can be seen that the B-H-B bonding in B_2H_6 and the $[B_2H_3(hpp)_2]^+$ cation can be described as three-center two-electron bonds, whereas the bonding in $B_2H_5^+$ involves the five centers (both boron atoms and all three bridging hydrogen atoms). Apart from their bonding properties, compounds **4a** and **4b** could be attractive protonation reagents, and **3** might be an interesting complex ligand. The protonated forms **4a** and **4b** serve as smallest possible model systems for the bonding situation in such complexes.

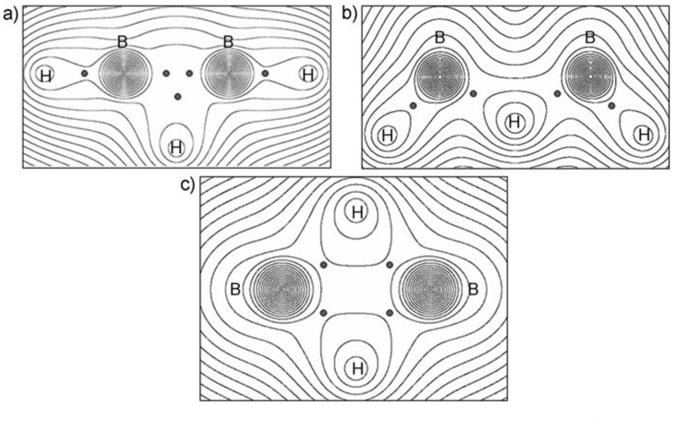


Figure 5. Topology of the electron density distribution of a) $B_2H_5^+$, b) $[B_2H_3(hpp)_2]^+$, and c) B_2H_6. Electron density (in e Å^{-3}) at the bond critical points: $B_2H_5^+$: B-H$_b$ 1.07, B-H$_t$ 1.36. $[B_2H_3(hpp)_2]^+$: B-H$_b$ 0.77, B-H$_t$ 1.23. B_2H_6: B-H$_b$ 0.84, B-H$_t$ 1.24.

Received: April 6, 2009

Keywords: boron · diborane(4) · hydrides · main-group elements · protonation

---

[1] G. A. Olah, R. Aniszfeld, G. K. S. Prakash, R. E. Williams, K. Lammertsma, O. F. Guner, *J. Am. Chem. Soc.* **1988**, *110*, 7885 – 7886.

[2] B. Ruščić, C. A. Mayhew, J. Berkowitz, *J. Chem. Phys.* **1988**, *88*, 5580 – 5593.

[3] a) L. A. Curtiss, J. A. Pople, *J. Chem. Phys.* **1988**, *89*, 4875 – 4879; b) L. A. Curtiss, J. A. Pople, *J. Chem. Phys.* **1989**, *91*, 4189 – 4192.

[4] J. F. Dias, G. Rasul, P. R. Seidl, G. K. S. Prakash, G. A. Olah, *J. Phys. Chem. A* **2003**, *107*, 7981 – 7984.

[5] L. D. Betowski, M. Enlow, *J. Mol. Struct.* **2003**, *638*, 189 – 195.

[6] a) A. B. Sannigrahi, T. Kar, *J. Mol. Struct. (Theochem)* **2000**, *496*, 1 – 17; b) A. J. Bridgeman, C. J. Empson, *New J. Chem.* **2008**, *32*, 1359 – 1367.

[7] O. Ciobanu, P. Roquette, S. Leingang, H. Wadepohl, J. Mautz, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2007**, 4530 – 4534. In the light of the new results we had to reassign the NMR spectra of **3**.

[8] O. Ciobanu, F. Allouti, P. Roquette, S. Leingang, M. Enders, H. Wadepohl, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2008**, 5482 – 5493.

[9] See, for example: a) W. M. A. Smit, *J. Mol. Struct.* **1973**, *19*, 789 – 798; b) I. R. Beattie, J. S. Ogden, D. D. Price, *J. Chem. Soc. Dalton Trans.* **1982**, 505 – 510; c) H.-J. Himmel, A. J. Downs, T. M. Greene, *J. Am. Chem. Soc.* **2000**, *122*, 922 – 930.

[10] One aim of our research is to use compound **3** for oxidative addition reactions.

[11] a) C. Liang, R. D. Davy, H. F. Schaefer III, *Chem. Phys. Lett.* **1989**, *159*, 393 – 398; b) J. L. Duncan, D. C. McKean, I. Torto, *J. Mol. Spectrosc.* **1981**, *85*, 16 – 39.

[12] R. Wehrmann, H. Meyer, A. Berndt, *Angew. Chem.* **1985**, *97*, 779 – 781; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 788 – 790.

[13] A. Hergel, H. Pritzkow, W. Siebert, *Angew. Chem.* **1994**, *106*, 1342 – 1343; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1247 – 1248.

[14] S. C. Malhotra, *Inorg. Chem.* **1964**, *3*, 862 – 865.

[15] R. Dinda, O. Ciobanu, H. Wadepohl, O. Hübner, R. Acharraya, H.-J. Himmel, *Angew. Chem.* **2007**, *119*, 9270 – 9273; *Angew. Chem. Int. Ed.* **2007**, *46*, 9110 – 9113.

[16] O. Ciobanu, D. Emeljanenko, E. Kaifer, H.-J. Himmel, *Inorg. Chem.* **2008**, *47*, 4774 – 4778.

[17] U. Wild, P. Roquette, E. Kaifer, J. Mautz, O. Hübner, H. Wadepohl, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2008**, 1248 – 1257.

[18] C. B. Hübschle, M. Messerschmidt, D. Lentz, P. Luger, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1313 – 1316.