Main-Group Chemistry

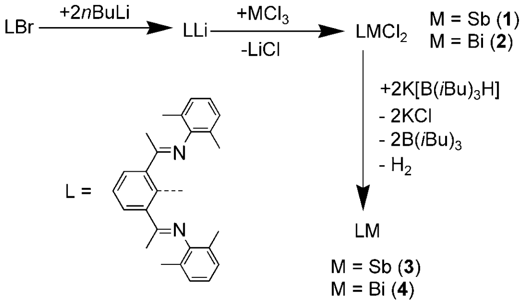
DOI: 10.1002/ange.201002209

Monomeric Organoantimony(I) and Organobismuth(I) Compounds Stabilized by an NCN Chelating Ligand: Syntheses and Structures[**]

Petr Šimon, Frank de Proft, Roman Jambor, Aleš Růžička, and Libor Dostál[*]

Dedicated to Professor Herbert W. Roesky on the occasion of his 75th birthday

The synthesis and structure of compounds containing multiple bonds between heavier Group 15 (Sb, Bi) elements, or analogous low-valent compounds with the central atom in the formal oxidation state +1, have been among the most exciting targets in the chemistry of main-group elements.[1] However, these compounds are often very unstable under normal conditions. The introduction of sufficiently large substituents is necessary for kinetic stabilization of such reactive species. Utilizing very effective and bulky ligands, such as 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, 2,6-bis-[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]-phenyl,[2] or various *m*-terphenyl ligands,[3] allowed isolation of stable heavier-element dipnictenes RMMR (M = Sb, Bi). Related ligands are able to stabilize unsymmetric compounds, where two different heavier Group 15 elements are connected.[4] Using less stericaly crowded ligands, such as bis(trimethylsilyl)methyl[5] resulted in formation of various cluster compounds, and coordination of a transition metal was necessary for stabilization of the RMMR fragment.[5] Nevertheless, monomeric compounds of the type RM (stibinidenes or bismuthinidenes) have not been isolated in the condensed phase to date, although the existence of such compounds with two lone pairs for bismuth has been predicted based on relativistic effects.[6] We and others have recently demonstrated that using of so-called NCN pincer-type ligand, [2,6-bis(dimethylamino)methyl]phenyl (denoted as Ar hereafter), is an alternative to sterically overcrowded ligands for stabilization of low-valent antimony and bismuth compounds[7] and the terminal $ArSb{=}E$ ($E = S$, Se, Te) bonds.[8] In view of this fact, it was believed that using of even more rigid and more sterically demanding NCN pincer ligand may lead to a stabilization of monomeric RM species (stibinidenes or bismuthinidenes) by combination of thermodynamical and kinetic influence of the ligand. Herein, we present the syntheses and structures of unprecedented monomeric stibinidene and bismuthinidene by taking advantage of using of 2,6-bis[*N*-(2′,6′-dimethylphenyl)ketimino]phenyl (denoted as L hereafter; Scheme 1).[9]



Scheme 1. Preparation of the compounds studied.

The starting chlorides $LMCl_2$ (M = Sb (**1**) and Bi (**2**)) were prepared by standard metathesis of the lithium compound LLi and MCl_3 in Et_2O and were isolated as slightly yellow powders that are soluble in chlorinated solvents. The key step of the syntheses is using of two equivalents of *n*BuLi (Et_2O, −60 °C) for successful lithiation of the ligand. Compounds **1** and **2** were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis (Supporting Information).

The reactions of **1** and **2** with two equivalents of $K[B(iBu)_3H]$ proceeded smoothly in THF. The reaction mixture turned deep blue in color upon addition of $K[B(iBu)_3H]$, and evolution of a gas was clearly visible, thus indicating formation of unstable hydrides LMH_2 that immediately lose hydrogen. Similar dehydrocoupling reactions have been recently used for other element–element bond formations.[7b,10] Compounds **3** and **4** were isolated by crystallization from saturated hexane solution as deep blue microcrystalline materials in lower, but still reasonable, yields (25 % for **3** and 35 % for **4**). Both compounds have been characterized by the help of satisfactory elemental analysis. The ^1H and ^{13}C NMR spectra of **3** and **4** revealed one set of sharp signals corresponding to the ligand L, showing the presence of only one species in [D$_6$]benzene solution.

The molecular structures of **3** and **4** were unambiguously determined by the single-crystal X-ray diffraction analysis (Figure 1). Both compounds crystallize in the *C*2/*c* space group and are closely related in structure.

---

[*] Ing. P. Šimon, Prof. R. Jambor, Prof. A. Růžička, Dr. L. Dostál
Department of General and Inorganic Chemistry
Faculty of Chemical Technology, University of Pardubice
Studentská 573, Pardubice 53210 (Czech Republic)
Fax: (+42) 40-6603-7068
E-mail: libor.dostal@upce.cz
Prof. F. de Proft
Eenheid Algemene Chemie (ALGC), Vrije Universiteit Brussel (VUB)
Pleinlaan 2, 1050 Brussels (Belgium)

[**] The authors thank the GAČR (P207/10/0130) and the Ministry of Education of the Czech Republic (MSM0021627501) for financial support. F.D.P. wishes to acknowledge the Fund for Scientific Research Flanders (Belgium) FWO and the Vrije Universiteit Brussel for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201002209.

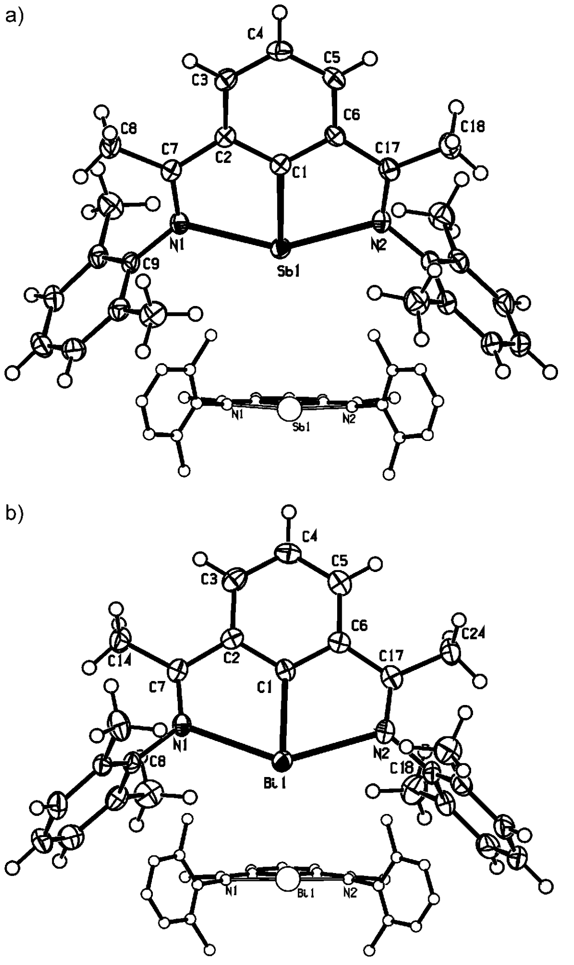


Figure 1. Molecular structures of **3** (a) and **4** (b), with ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°] (computed values given in parentheses): **3**: Sb1–C1 2.052(3) (2.058), Sb1–N1 2.352(3) (2.371), Sb1–N2 2.346(3) (2.372), C7–N1 1.302(4) (1.304), C17–N2 1.300(4) (1.304); C1-Sb1-N1 73.60(11) (73.3), C1-Sb1-N2 73.26(11) (73.3), N1-Sb1-N2 146.66(9) (146.6). **4**: Bi1–C1 2.150(5) (2.165), Bi1–N1 2.461(5) (2.484), Bi1–N2 2.464(4) (2.484), C7–N1 1.289(7) (1.300), C17–N2 1.296(7) (1.300); C1-Bi1-N1 71.43(16) (71.1), C1-Bi1-N2 70.83(16) (71.1), N1-Bi1-N2 142.07(14) (142.2).

There is no close intermolecular contact between the central atom Sb1 in **3** or Bi1 in **4** and other atoms in the crystal structures confirming an exclusively monomeric nature of both compounds. The metal atoms are encapsulated well in the ligand cavity. The central part of the structure remains essentially planar, as the antimony (**3**) and bismuth atom (**4**) is only slightly bent out of the plane defined by C1-N1-N2 atoms (0.108 Å for **3** and 0.125 Å for **4**). The flanking aromatic rings are nearly perpendicular to the central ring of the ligand. The metal atoms are three-coordinate, and form a M–C1 covalent bond (2.052(3) Å for **3** and 2.150(5) Å for **4**) and two strong intramolecular M···N interactions (Sb1–N1 2.352(3) and Sb1–N2 2.346(3) Å for **3**, and Bi1–N1 2.461(5), Bi1–N2 2.464(4) Å for **4**). The molecular structures of **3** and **4** substantially differ in comparison to organoantimony(I) compound substituted with the ligand Ar. This compound forms tetrameric structure Ar_4Sb_4 with central four-membered ring. The Sb–N intramolecular interactions are significantly weaker in this case (the distances are in the range 3.016(4)–4.950(5) Å). The central antimony atom is thus marginaly influenced by the nitrogen donor atoms in comparison with compounds **3** and **4**.

The monomeric stibinidenes of the type RSb (R = organic substituent, Br) have been stabilized by donating two antimony electron lone pairs to two transition-metal fragments, such as $\{W(CO)_5\}$, $\{CpMo(CO)_2\}$.[11] These compounds are believed to feature an sp^2 σ-bonding framework and π delocalization of the lone pairs of the antimony atom between both transition-metal centers. The antimony center, with trigonal planar geometry, posses significant Lewis acidity because of the presence of an empty p orbital.[12] These Lewis acidic properties have been were later reflected by the isolation of compounds $[RM\{W(CO)_5\}_2]$ (M = Sb, Bi), where R = NC chelating ligand, 2-(dimethylaminomethyl)phenyl, and the pendant ligand arm is strongly coordinated to the central atom.[13] On the contrary, in the case of **3** and **4**, the central atom is stabilized by two nitrogen donor atoms rather than by donation of the lone pairs to the transition metal acceptors. The bonding angle between both nitrogen donor atoms and the central metal N1-M-N2 is 146.66(9)° for **3** and 142.07(14) for **4**. These values may suggest that in the case of **3** and **4** the monomeric structures are stabilized by blocking of the empty p orbital by partial donation of electron density from the nitrogen atoms N1 and N2.

To gain more insight into the structure and bonding of **3** and **4**, a theoretical survey focused on both compounds has been performed. Starting from the crystal structures, the geometries of compounds **3** and **4** were optimized at the B3LYP[14]/cc-pVTZ[15] level of theory; on Sb and Bi, the cc-pVTZ-PP[16] basis set was used. The equilibrium geometries were confirmed to be minima on the potential energy surface, and subsequent NBO analysis[17] was performed. All computations were performed using the Gaussian03 program.[18] The Wiberg bond orders[19] and atomic charges are given in the Supporting Information. The resulting theoretical geometries are in very good agreement with the experimental values (Figure 1, caption). This analysis reveals a single σ bond between C1 and Sb or Bi mediated by one of the p orbitals of the central atom (Figure 2a). The two lone pairs at Sb and Bi atoms remain as an s-type (inert) (Figure 2b) and p-type lone pair that is orientated perpendicularly to the central aryl ring of the ligand. It seems that this p-type lone pair is also sufficiently shielded by flanking aryl rings and their *ortho* methyl substituents (Figure 2c).

The empty p orbital on the Sb and Bi atoms is located in the plane of the central aryl of the ligand and importantly shows considerable overlap with the N1 and N2 lone pairs (Figure 2d). This fact supports our previous presumption that the empty p-type orbital might be stabilized by effective interaction with the nitrogen donor atoms of the ligand. Furthermore, the partial atomic charges on the nitrogen atoms (−0.546 a.u. for **3** and −0.533 a.u. for **4**) and those on the central atoms Sb (0.696 a.u.) and Bi (0.646 a.u.) are very close to each other and opposite in magnitude.

As mentioned, using of the same ligand Ar did not led to the stabilization of stibinidene ArSb, which is most probably due to the non-rigidity of the Sb–N interaction (caused in part

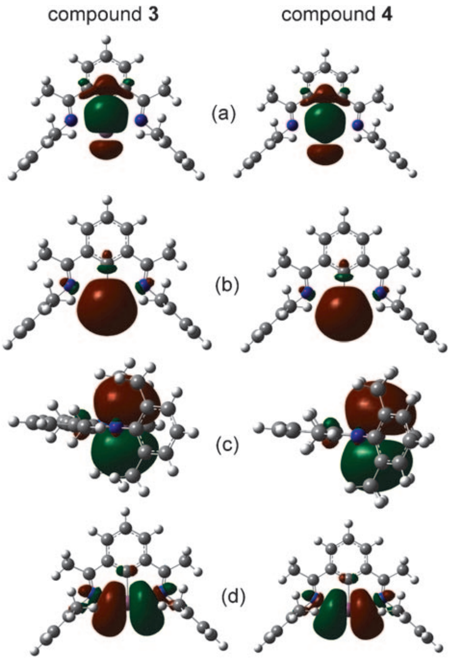


Figure 2. Relevant NBOs (isosurface value: 0.02 a.u.) involving antimony in **3** (left) and bismuth in **4** (right). NBO populations are given in parentheses. a) σ bond between Sb/Bi and C (**3**: 1.956, **4**: 1.952), b) s-type lone pair on Sb/Bi (**3**: 1.985, **4**: 1.989), c) p-type lone pair on Sb/Bi (**3**: 1.391, **4**: 1.456), and d) empty p orbital on Sb/Bi (**3**: 0.339, **4**: 0.311).

by low Lewis acidity of the central atom and also by high fluxionality of the ligands donor groups (arms) in Ar in comparison with the ligand L used herein), and only a tetrameric molecule could be isolated.[7b] These facts further support the conclusion that the monomeric structures of **3** and **4** are mainly stabilized by virtue of donating of donor atoms electron density to the empty p-type orbital of the central atoms. Similar Sn−N interactions have been detected in an intramolecularly coordinated diorganostannyne ArSnSnAr recently.[20] In this distannyne, the Lewis basic nitrogen atoms also stabilize the emtpy p-type orbitals.

In conclusion, it was shown that combination of steric shielding and intramolecular Sb/Bi⋯N interactions causing protection of both empty p-type and lone p-type orbitals of the central atoms (Sb or Bi) using a 2,6-bis(ketimine)phenyl ligand allowed the isolation of the first monomeric stibinidene and bismuthinidene. We are currently investigating reactivity of these compounds as we are extensively working on utilization of the ligand L in other low-valent organometallic compounds.

Experimental Section

All operations on air-sensitive compounds were performed under an argon atmosphere using Schlenk techniques. All solvents were dried by standard procedures and degassed prior to use.

3: A THF solution of K[B(*i*Bu)$_3$H] (4.1 mL, 1 M solution, 4.1 mmol) was added to a stirred suspension of **1** (1.19 g, 2.1 mmol) in THF (50 mL) at room temperature. Immediately after addition, elimination of hydrogen was observed and the reaction mixture turned to deep blue color. The resulting mixture was stirred for additional 1 h at room temperature and evaporated in vacuo. The residue was extracted with hexane (60 mL, 50 °C) and the insoluble material was filtered off. The deep blue filtrate was concentrated to about 10 mL. On standing overnight at −30 °C the solution afforded blue microcrystals of **3** (0.25 g, 24 %). Single crystals of **3** were obtained by re-crystallization from saturated hexane solution at 5 °C. M.p. 208–210 °C (dark oil). ^{1}H NMR (500 MHz, [D$_6$]benzene, 25°): $\delta = 7.96$ (d, ^3J(H,H) = 8 Hz, 2 H, *meta*-Ph), 7.29 (t, ^3J(H,H) = 8 Hz, 1 H, *para*-Ph), 6.98 (d, ^3J(H,H) = 8 Hz, 4 H, *meta*-(2,6-Me$_2$)Ph), 6.94 (t, ^3J(H,H) = 8 Hz, 2 H, *para*-(2,6-Me$_2$)Ph), 2.06 (s, 6 H, CH$_3$CN), 2.03 ppm (s, 12 H, CH$_3$); ^{13}C NMR (125.8 MHz, [D$_6$]benzene, 25°): $\delta = 172.6$ (CN), 162.8, 146.9, 137.7, 131.3, 130.4, 128.8, 125.8, 120.5 ((2,6-Me$_2$)C$_6$H$_3$ and Ph), 19.0 (CH$_3$CN), 16.3 ppm (CH$_3$). Elemental analysis (%) calcd for $C_{26}H_{27}N_2Sb$ (489.25): C 63.8, H 5.6; found: C 63.5, H 5.8.

4: A THF solution of K[B(*i*Bu)$_3$H] (1.3 mL, 1 M solution, 1.3 mmol) was added to a stirred suspension of **2** (0.42 g, 0.65 mmol) in THF (50 mL) at room temperature. Immediately after addition, elimination of hydrogen was observed and the reaction mixture turned to deep blue color. The resulting mixture was stirred for additional 1 h at room temperature and evaporated under reduced pressure. The residue was extracted with hexane (30 mL) and the insoluble material was filtered off. The deep blue filtrate was concentrated to about 10 mL. On standing overnight at −30 °C, the solution afforded blue microcrystals (directly suitable for X-ray crystallography) of **4** (0.13 g, 35 %). M.p. 252–255 °C (dark oil). ^{1}H NMR (500 MHz, [D$_6$]benzene, 25°): $\delta = 8.10$ (d, ^3J(H,H) = 8 Hz, 2 H, *meta*-Ph), 7.11 (t, ^3J(H,H) = 8 Hz, 1 H, *para*-Ph), 7.01 (d, ^3J(H,H) = 8 Hz, 4 H, *meta*-(2,6-Me$_2$)Ph), 6.90 (t, ^3J(H,H) = 8 Hz, 2 H, *para*-(2,6-Me$_2$)Ph), 2.48 (s, 6 H, CH$_3$CN), 2.02 ppm (s, 12 H, CH$_3$); ^{13}C NMR (125.8 MHz, [D$_6$]benzene, 25°): $\delta = 204.6$ (C-ipso), 172.4 (CN), 148.5, 146.8, 133.9, 129.7, 128.8, 125.8, 122.4 ((2,6-Me$_2$)Ph and Ph), 19.9 (CH$_3$CN), 18.5 ppm (CH$_3$). Elemental analysis (%) calcd for $C_{26}H_{27}N_2Bi$ (576.50): C 54.2, H 4.7; found: C 54.5, H 4.8.

The suitable single crystals of **3** and **4** were measured on four-circle diffractometer KappaCCD with CCD area detector by monochromatized MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). The numerical[21] absorption correction from crystal shape was applied for both crystals. The structures were solved by direct methods (SIR92[22]) and refined by a full-matrix least-squares procedure based on F^2 (SHELXL97[23]). Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{\mathrm{iso}}(\mathrm{H}) = 1.2\,U_{\mathrm{eq}}$ (pivot atom); for the methyl groups, a multiplication factor of 1.5 was chosen. The final difference maps displayed no peaks of chemical significance as the highest peaks and holes are in close vicinity (< 1 Å) of heavy atoms. CCDC 771563 (**3**) and 771564 (**4**) contain 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. **3**: $C_{26}H_{27}N_2Sb$, $M_r = 489.25$, monoclinic, *C2/c*, $T = 150(2)$ K, $a = 28.4712(9)$, $b = 8.3513(10)$, $c = 21.9987(8)$ Å, $\beta = 122.87(2)°$, $V = 4393.1(2)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.479\ \mathrm{g\,cm^{-3}}$, $\mu = 1.270\ \mathrm{mm^{-1}}$, $0.75 \times 0.4 \times 0.04\ \mathrm{mm^3}$, $2\Theta_{\max} = 27.5°$; 4953 reflections collected, 3867 independent and used in the structure refinement of 262 parameters. $R_{\mathrm{int}} = 0.067$, $R1 = 0.030$ ($I > 2\sigma(I)$), w$R = 0.068$ (all data), min./max. residual electron density: 0.772/−0.646 e Å^{-3}. **4**: $C_{26}H_{27}N_2Bi$, $M_r = 576.48$, monoclinic, *C2/c*, $T = 150(1)$ K, $a = 28.6974(9)$, $b = 8.2791(8)$, $c = 22.0978(10)$ Å, $\beta = 122.19(2)°$, $V = 4442.9(1)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.724\ \mathrm{g\,cm^{-3}}$, $\mu = 7.951\ \mathrm{mm^{-1}}$, $0.30 \times 0.25 \times 0.03\ \mathrm{mm^3}$, $2\Theta_{\max} = 27.5°$; 5093 reflections collected, 4097 independent and used in the structure refinement of 262 parameters. $R_{\mathrm{int}} = 0.060$, $R1 = 0.036$ ($I > 2\sigma(I)$), w$R = 0.062$ (all data), min./max. residual electron density: 1.461/−1.096 e Å^{-3}.

Received: April 14, 2010

Keywords: antimony · bismuth · chelates · ligand effects · main-group elements

---

[1] For reviews see: a) T. Sasamori, N. Tokitoh, *Dalton Trans.* **2008**, 1395–1408; b) L. Balázs, H. J. Breunig, *Coord. Chem. Rev.* **2004**, *248*, 603–621; c) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463–3503.

[2] a) N. Tokitoh, Y. Arai, T. Sasamori, R. Okazaki, S. Nagase, H. Uekusa, Y. Ohashi, *J. Am. Chem. Soc.* **1998**, *120*, 433–434; b) N. Tokitoh, Y. Arai, R. Okazaki, S. Nagase, *Science* **1997**, *277*, 78–80.

[3] B. Twamley, C. D. Sofield, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1999**, *121*, 3357–3367.

[4] a) B. Twamley, P. P. Power, *Chem. Commun.* **1998**, 1979–1980; b) T. Sasamori, N. Takeda, N. Tokitoh, *Chem. Commun.* **2000**, 1353–1354; c) T. Sasamori, N. Takeda, M. Fujio, M. Kimura, S. Nagase, N. Tokitoh, *Angew. Chem.* **2002**, *114*, 147–149; *Angew. Chem. Int. Ed.* **2002**, *41*, 139–141.

[5] a) H. J. Breunig, L. Balázs, *Organometallics* **2004**, *23*, 304–310; b) H. J. Breunig, R. Rösler, *Chem. Soc. Rev.* **2000**, *29*, 403–410; c) H. J. Breunig, R. Rösler, E. Lork, *Angew. Chem.* **1998**, *110*, 3361–3363; *Angew. Chem. Int. Ed.* **1998**, *37*, 3175–3177; d) H. J. Breunig, R. Rösler, E. Lork, *Angew. Chem.* **1997**, *109*, 2333–2334; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2237–2238.

[6] P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563–594.

[7] a) L. Balázs, H. J. Breunig, E. Lork, A. Soran, C. Silvestru, *Inorg. Chem.* **2006**, *45*, 2341–2346; b) L. Dostál, R. Jambor, A. Růžička, J. Holeček, *Organometallics* **2008**, *27*, 2169–2171.

[8] a) L. Dostál, R. Jambor, A. Růžička, A. Lyčka, J. Brus, F. de Proft, *Organometallics* **2008**, *27*, 6059–6062; b) L. Dostál, R. Jambor, A. Růžička, R. Jirásko, V. Lochař, L. Beneš, F. de Proft, *Inorg. Chem.* **2009**, *48*, 10495–10497.

[9] This ligand has been recently utilized by G. van Koten for stabilization of nickel compounds, and the ligand has been synthesized according to the published procedure: M. S. Stol, D. J. M. Snelders, M. D. Godbole, R. W. A. Havenith, D. Haddleton, G. Clarkson, M. Lutz, A. L. Spek, G. P. M. van Klink, G. van Koten, *Organometallics* **2007**, *26*, 3985–3994, and references therein.

[10] For example see: a) R. Waterman, T. D. Tilley, *Angew. Chem.* **2006**, *118*, 2992–2995; *Angew. Chem. Int. Ed.* **2006**, *45*, 2926–2929; b) E. Rivard, J. Steiner, J. C. Fettinger, J. R. Guiliani, M. P. Augustine, P. P. Power, *Chem. Commun.* **2007**, 4919–4921.

[11] a) A. M. Arif, A. H. Cowley, N. C. Norman, M. Pakulski, *Inorg. Chem.* **1986**, *25*, 4836–4840; b) G. Balázs, H. J. Breunig, E. Lork, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1937–1942; c) J. von Seyerl, G. Huttner, *Angew. Chem.* **1978**, *90*, 911–912; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 843–844; d) J. von Seyerl, G. Huttner, *J. Organomet. Chem.* **1980**, *195*, 207–212; e) U. Weber, L. Zsolnai, G. Huttner, *J. Organomet. Chem.* **1984**, *260*, 281–291; f) B. Sigwarth, U. Weber, L. Zsolnai, G. Hutter, *Chem. Ber.* **1985**, *118*, 3114–3126.

[12] A. H. Cowley, N. C. Norman, M. Pakulski, *Inorg. Chem.* **1984**, *106*, 6844–6845.

[13] a) L. Balázs, H. J. Breunig, E. Lork, C. Silvestru, *Eur. J. Inorg. Chem.* **2003**, 1361–1365; b) L. M. Opris, A. Silvestru, C. Silvestru, H. J. Breunig, E. Lork, *Dalton Trans.* **2004**, 3575–3585.

[14] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.

[15] T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007–1023.

[16] K. A. Peterson, *J. Chem. Phys.* **2003**, *119*, 11099–11112.

[17] a) J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211–7281; b) A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1983**, *78*, 4066–4073; c) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746; d) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926; e) F. Weinhold in *Encyclopedia of Computational Chemistry*, *Vol. 3* (Eds.: P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, P. R. Schreiner), Wiley, Chichester, UK, **1998**, pp. 1792–1811.

[18] Gaussian 03, Revision E.01, M. J. Frisch, et al. Gaussian, Inc., Wallingford CT, **2004**.

[19] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083–1096.

[20] R. Jambor, B. Kašná, K. N. Kirschner, M. Schürmann, K. Jurkschat, *Angew. Chem.* **2008**, *120*, 1674–1677; *Angew. Chem. Int. Ed.* **2008**, *47*, 1650–1653.

[21] P. Coppens in *Crystallographic Computing* (Eds.: F. R. Ahmed, S. R. Hall, C. P. Huber), Munksgaard, Copenhagen, **1970**, pp. 255–270.

[22] A. Altomare, G. Cascarone, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 1045–1050.

[23] G. M. Sheldrick, SHELXL-97, A Program for Crystal Structure Refinement. University of Göttingen, Germany **1997**.