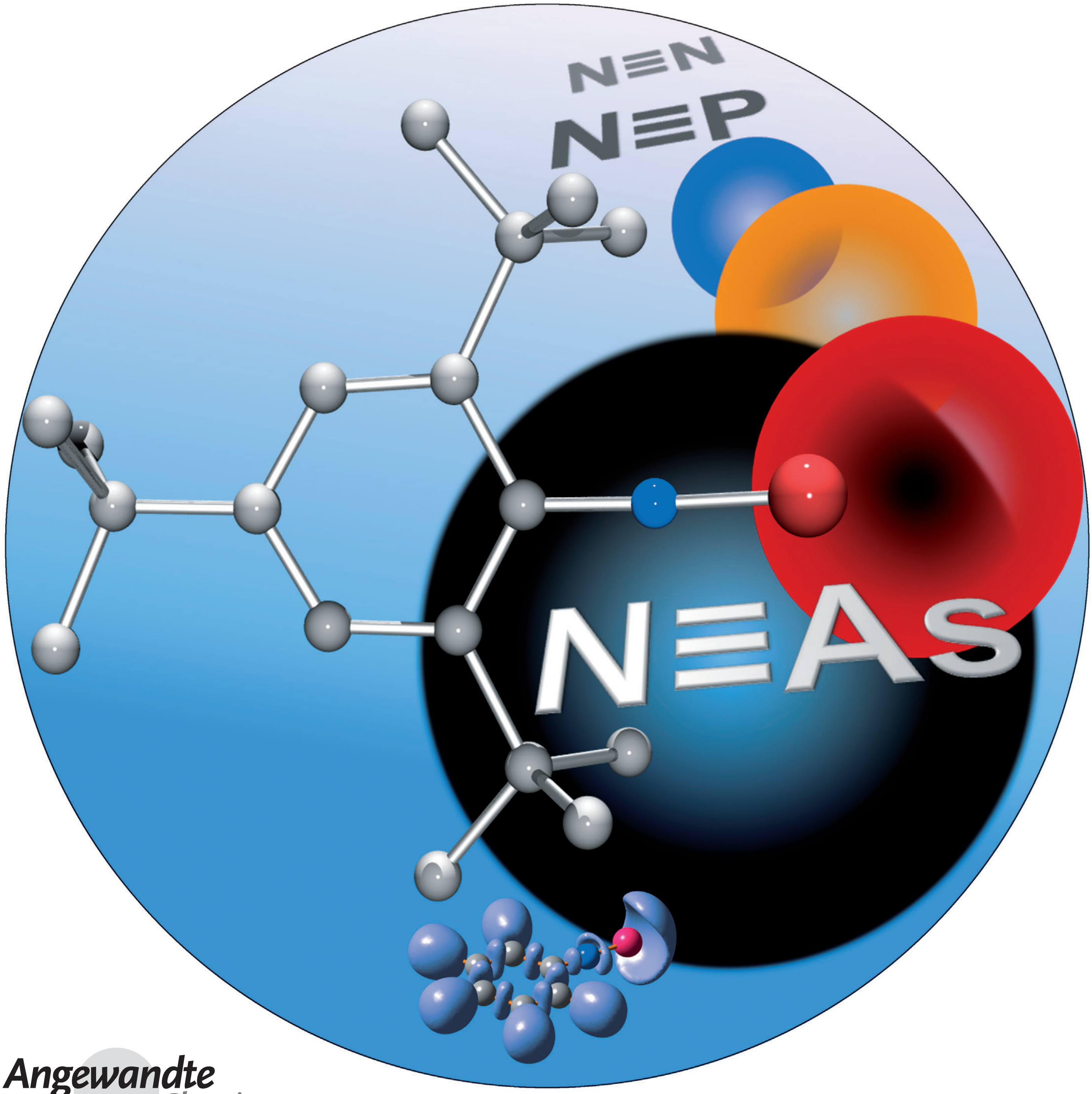
As–N Triple Bond

DOI: 10.1002/anie.201302725

Arsa-Diazonium Salts With an Arsenic–Nitrogen Triple Bond**

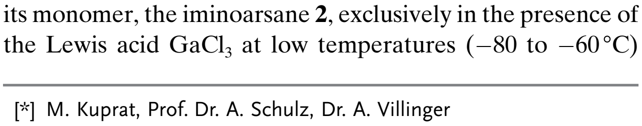
Marcus Kuprat, Axel Schulz, and Alexander Villinger*

Dedicated to Prof. Werner Uhl on the occasion of his 60th birthday

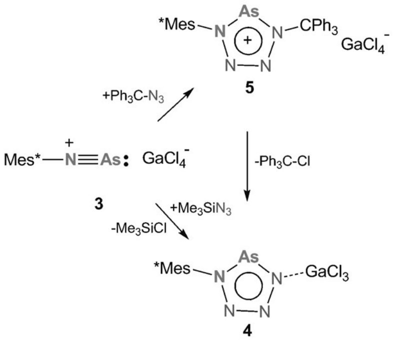


As early as 1858 Peter Griess[1] described the preparation of a salt bearing a diazonium ion, $[R\text{-}N\equiv N]^+$, which soon led to the discovery of compounds called azo dyes, compounds that contain two aromatic fragments connected by a N=N bond. Diazonium salts, the important intermediates in the diazotation/azo coupling reaction, triggered the rise of the synthetic dyestuffs industry during the nineteenth century,[2] but the impact and many-sided importance of this discovery in terms of scientific, medical, ecological, and technical relevance is still huge.[3] Besides structural simplicity, diazonium ions exhibit high electrophilicity and thermodynamic instability with respect to loss of N_2 because the presence of a nitrogen–nitrogen triple bond makes the formation of molecular dinitrogen favored. Triple bonds between nitrogen and heavier main-group elements are still scarce,[4,5] only a few examples of the type $R\text{-}E\equiv N\text{-}R$ (E = In, Ga),[6–8] $[R\text{-}N\equiv P]^+$,[9,10] and $[S\equiv N]^+$[11] could be isolated and structurally characterized. Like the discovery of diazonium salts, the first isolation of a salt containing a phospha-diazonium ion $[\text{Mes*-}N\equiv P]^+$ in 1988 by Niecke and co-workers represented a landmark in the systematic development of phosphorus chemistry.[9] In contrast to the isolobal phospha-alkynes,[12,13] it was shown that the P atom in $[\text{Mes*-}N\equiv P]^+$ has Lewis-acceptor properties,[14–17] which was illustrated, for example, by the formation of η^6-arene complexes[18,19] or tetrazaphosphole in the reaction with $Me_3Si\text{-}N_3$.[20]

First evidence for the existence of an arsa-diazonium ion (**3**) (also named arsenoazonium) was provided by high-resolution mass spectrometry in 1994[21] indicating the presence of a $[Me\text{-}N\equiv As]^+$ ion in the gas phase. The formation of the $[\text{Mes*-}N\equiv As]^+$ ion in CH_2Cl_2 solution was also assumed as a transient species in the reaction of iminoarsane $\text{Mes*-}N\equiv As\text{-}Cl$ (**2**) with $GaCl_3$ in the presence of $Me_3Si\text{-}N_3$ yielding the tetrazarsole species **4** (Schemes 1 and 2).[22] We have now studied the equilibrium between cyclic diarsadiazane **1**[23] and its monomer, the iminoarsane **2**, exclusively in the presence of the Lewis acid $GaCl_3$ at low temperatures (−80 to −60 °C) affording room-temperature stable $[\text{Mes*-}N\equiv As]^+[GaCl_4]^-$ (**3**$[GaCl_4]$, Mes* = 2,4,6-tri-*tert*-butylphenyl).



Scheme 1. Synthesis of room-temperature stable arsa-diazonium salts **3**.



Scheme 2. In the presence of an azide species, a [3+2] cycloaddition reaction occurs with **3** leading either to tetrazarsolium salt (**5**) or tetrazarsole (**4**) stabilized as $GaCl_3$ adduct.[24]

The yellowish crystalline dimer **1** is readily dissolved in CH_2Cl_2 or toluene, with the initially yellowish solution slowly turning red, the color of the monomeric species **2** at ambient temperatures (Scheme 1).[24] ^{1}H NMR spectroscopy data revealed the existence of a monomer/dimer equilibrium.[22] Addition of one equivalent of $GaCl_3$ (with respect to the concentration of the monomeric species) at −80 °C led to a red solution of arsa-diazonium ions (**3**) as demonstrated by ^{1}H, ^{13}C, and ^{14}N NMR spectroscopy studies (Figure 1). After removing the solvent under reduced pressure, $[\text{Mes*-}N\equiv As]^+[GaCl_4]^-$ (**3**$[GaCl_4]$) was obtained as an orange crystalline solid in 90 % yield, however, depending on the solvent, as the CH_2Cl_2 (**3**$[GaCl_4]\cdot CH_2Cl_2$) or toluene solvate (**3**$[GaCl_4]$·toluene, two different polymorphs, see Supporting Information Table S1). A solvate-free salt is obtained when two equivalents of $GaCl_3$ are utilized affording the digallate salt $[\text{Mes*-}N\equiv As]^+[Ga_2Cl_7]^-$ (**3**$[Ga_2Cl_7]$) in 85 % yield.[24]

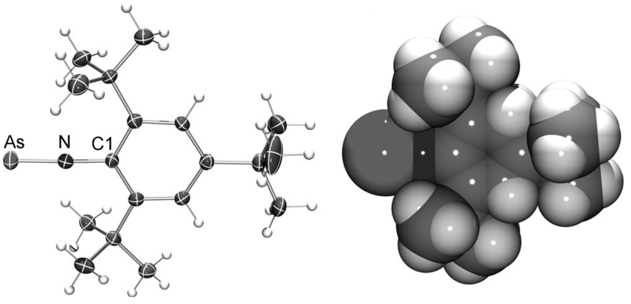


Figure 1. Left: ORTEP drawing of the molecular structure of the $[\text{Mes*-}N\equiv As]^+$ cation in **3**$[Ga_2Cl_7]$ in the crystal. Thermal ellipsoids set at 50 % probability at 173 K. Right: Space-filling model of the $[\text{Mes*-}N\equiv As]^+$ ion. As–N bond length [Å]: 1.612(2) in **3**$[Ga_2Cl_7]$, 1.591(4) and 1.613(3) in **3**$[GaCl_4]$·toluene, 1.611(3) in **3**$[GaCl_4]\cdot CH_2Cl_2$.

X-ray diffraction data could be obtained for all three species. The ^{14}N NMR spectrum shows a broad singlet at $\delta = -83$ ppm, shifted downfield in comparison with $[\text{Mes*-}N\equiv P]^+$ ($\delta = -124$ ppm) and $[Ph\text{-}N\equiv N]^+$ ($\delta = -156$ ppm, cf. $\delta = -71$ ppm for solvated N_2).[25] All the arsa-diazonium salts

---

[*] M. Kuprat, Prof. Dr. A. Schulz, Dr. A. Villinger
Universität Rostock, Institut für Chemie
Albert-Einstein-Strasse 3a, 18059 Rostock (Germany)
and
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
E-mail: axel.schulz@uni-rostock.de
Homepage: http://www.chemie.uni-rostock.de/ac/schulz

[**] Financial support by the DFG is gratefully acknowledged (SCHU 1170/8-1).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201302725.

described herein are very difficult to isolate since they are extremely air and moisture sensitive. Even at low temperatures slow decomposition cannot be avoided. The orange color of **3** vanishes rapidly when traces of H_2O are present. Fast decomposition starts at temperatures above 80 °C. Single-crystal diffraction studies reveal an almost linear arrangement of the C-N-As moiety (angles between 175.4–177.8°) with a very short N–As bond length between 1.591–1.613 Å (Figure 1) which nicely agrees with the sum of the covalent radii for an arsenic–nitrogen triple bond (Σr_{cov}(N≡As) = 1.60 Å).[26] In contrast, the As–C triple bond with 1.657(7) Å in isolobal Mes*-C≡As[27] is considerably longer which can be attributed to a smaller amount of bond polarization. In the literature, As–N bond lengths between 1.707–1.714 Å (cf. Σr_{cov}(N≡As) = 1.74 Å and Σr_{cov}(N–As) = 1.92 Å) are reported for the only three known compounds with an As–N double bond.[28–30] All these structural parameters indicate the presence of a classical As–N triple bond in **3**. In these compounds the As–N triple bond is kinetically protected by the Mes* substituent, however, not completely as can be seen from the space-filling model of [Mes*-N≡As]$^+$ in Figure 1 (right). Thus significant van der Waals interactions between **3** and the anion or solvent molecules are possible. A closer inspection of the interionic interactions as well as to the solvent molecules (**3**[$GaCl_4$]·CH_2Cl_2 and **3**[$GaCl_4$]·toluene) display a number of distances within the sum of the van der Waals radii (Σr_{vdW}(As···Cl) = 3.60 Å, Σr_{vdW}(As···C) = 3.55 Å)[31] indicating stabilizing van der Waals interactions (Figure 2). For all the species short contacts are found between the As atom of the cation and Cl atoms of the anion (d(As···Cl_{anion}) = 3.123–3.457 Å). In addition all six carbon atoms of the toluene molecule in **3**[$GaCl_4$]·toluene coordinate to the As atom (d(C···As) = 3.163–3.351 Å). Analogous η^6-toluene complexation was also reported for the isotypical phosphorus compound.[18]

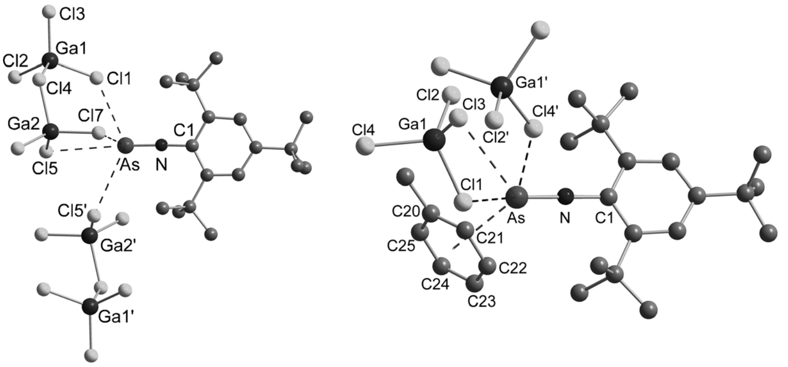


Figure 2. Left: Molecular structure of **3**[Ga_2Cl_7]; right: Molecular structure of **3**-[$GaCl_4$]·toluene (hydrogen atoms omitted for clarity). Selected interatomic separations [Å] and angles [°]: **3**[$GaCl_4$]·toluene: As-N 1.613(3), N-C1 1.389(4), As···C20 3.351(4), As···C21 3.252(4), As···C22 3.163(6), As···C23 3.151(6), As···C24 3.208(5), As···C25 3.307(4); As-N-C1 175.4(3). **3**[Ga_2Cl_7]: As-N 1.612(2), N-C1 1.372(3), As···Cl1 3.1786(8), As···Cl7 3.3437(7), As···Cl5 3.4565(6), As···Cl5′ 3.3385(7); As-N-C1 177.8(2).

Quantum chemical methods[24] were applied to study the model compound [Ph-N≡As]$^+$ (which has a phenyl group in place of the Mes* substituent). At the M06-2X/aug-cc-pvTZ level of theory, [Ph-N≡As]$^+$ is linear along the C-N-As unit with a very short N–As (1.609 Å) bond length in accord with the experimentally observed data (cf. d_{exp}(N–As) = 1.591–1.613 Å). Natural bond orbital (NBO) analysis data[32] give a large negative partial charge for the N atom (−0.86 e), whereas the arsenic atom carries a large positive charge (+1.36 e). The "Natural Resonance Theory" (NRT)[33] was used to determine the major Lewis formulae and their percentage weightings in the resonance scheme. The leading resonance structures display a triple bond between the N and As atom and a lone pair localized at the As center (Lewis representations **I** and **II** in Figure 3). Interaction between the As–N π bond and the aromatic phenyl ring is described by Lewis formulae **IV** and **V**. The NRT bond order for the As–N bond is 2.82 in accord with values expected for a triple bond (cf. 2.85 in [Ph-N≡P]$^+$ and 2.89 in [Ph-N≡N]$^+$). The strong polarization of the As–N bond towards nitrogen, which is responsible for the large positive charge at the As center, becomes clearly visible in the computed NBOs as well as in the electron localization function (ELF). In agreement with the structural and NRT/NBO data, the ELF at 0.82 exhibits a torus in the proximity of the N atom which is a good indicator for a classical (polarized) triple bond (Figure 4).[34,35]

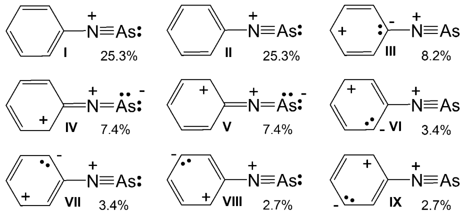


Figure 3. Lewis representations (> 1 %) of [Ph-N≡As]$^+$ along with their percentage weightings in the resonance scheme.

The reactivity of the arsa-diazonium ion was tested in [3+2] cycloadditions with Me_3Si-N_3 and Ph_3C-N_3.[24] Indeed, like diazonium[36] and phospha-diazonium salts,[20] arsa-diazonium ions form a five-membered heterocycle (Scheme 2), a tetrazarsole stabilized as $GaCl_3$ adduct (**4**), upon addition of Me_3Si-N_3 and elimination of Me_3Si-Cl,[22] while the reaction with Ph_3C-N_3 leads to the formation of a $GaCl_4^-$ salt containing the novel tetrazarsolium cation (**5**; Figure 5). Like the neutral AsN_4 heterocycle in **4**,[22] the molecular structure of the cationic AsN_4 species features a planar, formal 6π electronic, aromatic AsN_4 ring with two longer N–N bonds d(N1–N2) = 1.354(4) and d(N3–N4) = 1.353(3) (cf. **4**: 1.349(3) and 1.366(3) Å) and one very short N–N bond d(N2–N3) = 1.278(3) (cf. **4**: 1.286(2) Å). Although the release of molecular nitrogen seems to be predisposed, the AsN_4 heterocycle is stable at ambient temperatures and no significant release of N_2 is observed. Clearly, the "naked" AsN_4 ring is kinetically protected sandwiched between the large aryl groups (Figure 5). Never-

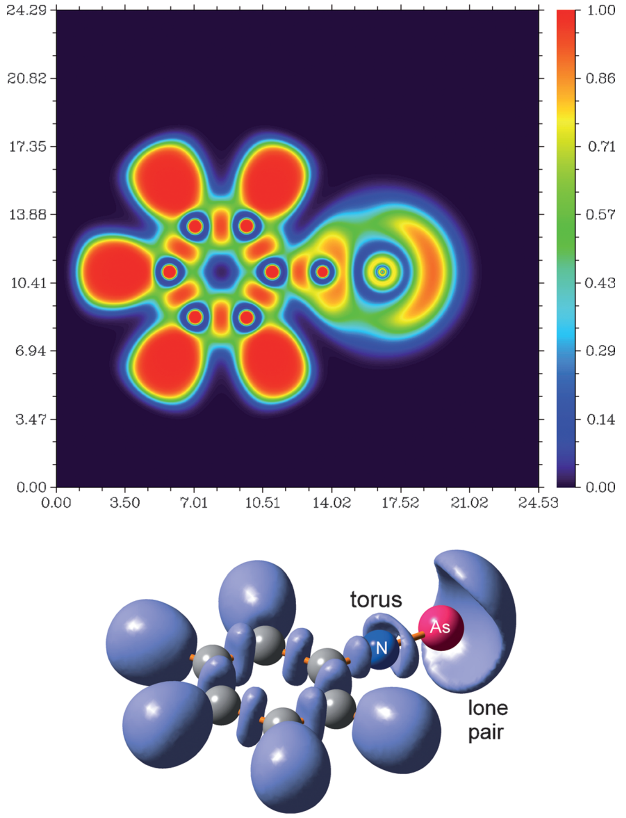


Figure 4. Top: Two-dimensional cross section through the $[Ph\text{-}N{\equiv}As]^+$ molecule plane of the electron localization function (ELF). Length unit: Bohr; the color of the ELF at each point corresponds to the values given in the color bar (right). Bottom: Three-dimensional representation of the ELF at 0.82.

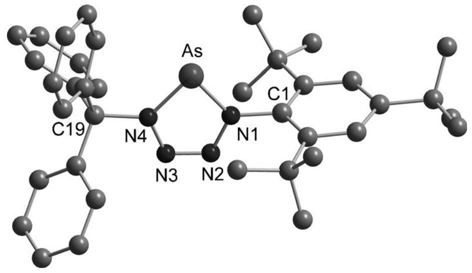


Figure 5. Molecular structure of tetrazarsolium cation **5** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: As-N1 1.803(3), As-N4 1.814(3), N1-N2 1.354(4), N2-N3 1.278(3), N3-N4 1.353(3), N1-C1 1.456(4), N4-C19 1.533(4); N1-As-N4 81.2(1), N2-N1-As 116.1(2), N3-N4-As 115.7(2).

theless, a clean transformation of **5** into **4** along with the elimination of $Ph_3C\text{-}Cl$ occurs in solution even at low temperatures within hours (Scheme 2).

In summary, more than 150 years after the discovery of a stable diazonium salt, we demonstrate that the heavier arsenic analogue, the arsa-diazonium salt, can be isolated as well. Arsa-diazonium ions feature a strongly polarized As–N triple bond and are highly reactive, strong electron-deficient species. Like diazonium salts, they can be used to act as dipolarophiles in [3+2] cycloadditions, for example, with azide to form five-membered rings, such as neutral tetrazarsoles or cationic tetrazarsolium ions.

Received: April 2, 2013
Published online: June 5, 2013

Keywords: arsenic · bond analysis · heterocycles · nitrogen · triple bond

---

[1] P. Griess, *Liebigs Ann. Chem.* **1858**, *106*, 123.
[2] R. Wizinger-Aust, *Angew. Chem.* **1958**, *70*, 199.
[3] A. Bafana, S. Devi, T. Chakrabarti, *Environ. Rev.* **2011**, *19*, 350.
[4] P. P. Power, *Chem. Rev.* **1999**, *99*, 3463.
[5] P. P. Power, *Chem. Rev.* **2010**, *110*, 3877.
[6] R. J. Wright, M. Brynda, J. C. Fettinger, A. R. Betzer, P. P. Power, *J. Am. Chem. Soc.* **2006**, *128*, 12498.
[7] N. J. Hardman, C. Cui, H. W. Roesky, W. H. Fink, P. P. Power, *Angew. Chem.* **2001**, *113*, 2230; *Angew. Chem. Int. Ed.* **2001**, *40*, 2172.
[8] R. J. Wright, A. D. Phillips, T. L. Allen, W. H. Fink, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 1694.
[9] E. Niecke, M. Nieger, F. Reichert, *Angew. Chem.* **1988**, *100*, 1781; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1715.
[10] E. Niecke, M. Nieger, F. Reichert, W. W. Schoeller, *Angew. Chem.* **1988**, *100*, 1779; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1713.
[11] W. Clegg, O. Glemser, K. Harms, G. Hartmann, R. Mews, M. Noltemeyer, G. M. Sheldrick, *Acta Crystallogr. Sect. B* **1981**, *37*, 548.
[12] C. Gaumont, J. M. Denis, *Chem. Rev.* **1994**, *94*, 1413.
[13] M. Regitz, *Chem. Rev.* **1990**, *90*, 191.
[14] N. Burford, A. D. Phillips, H. A. Spinney, K. N. Robertson, T. S. Cameron, R. McDonald, *Inorg. Chem.* **2003**, *42*, 4949.
[15] N. Burford, T. S. Cameron, K. N. Robertson, A. D. Phillips, H. A. Jenkins, *Chem. Commun.* **2000**, 2087.
[16] N. Burford, H. A. Spinney, M. J. Ferguson, R. McDonald, *Chem. Commun.* **2004**, 2696.
[17] N. Burford, A. D. Phillips, H. A. Spinney, M. Lumsden, U. Werner-Zwanziger, M. J. Ferguson, R. McDonald, *J. Am. Chem. Soc.* **2005**, *127*, 3921.
[18] N. Burford, J. A. C. Clyburne, P. Bakshi, T. S. Cameron, *J. Am. Chem. Soc.* **1993**, *115*, 8829.
[19] N. Burford, J. A. C. Clyburne, P. Bakshi, T. S. Cameron, *Organometallics* **1995**, *14*, 1578.
[20] P. Mayer, A. Schulz, A. Villinger, *Chem. Commun.* **2006**, 1236.
[21] J. M. Curtis, N. Burford, T. M. Parks, *Org. Mass Spectrom.* **1994**, *29*, 414.
[22] A. Schulz, A. Villinger, *Angew. Chem.* **2008**, *120*, 614; *Angew. Chem. Int. Ed.* **2008**, *47*, 603.
[23] M. S. Balakrishna, D. J. Eisler, T. Chivers, *Chem. Soc. Rev.* **2007**, *36*, 650 and references therein.
[24] Preparation methods and spectroscopic data for compounds **1** to **5** and computational details are available as Supporting Information.
[25] R. O. Duthaler, H. G. Förster, J. D. Roberts, *J. Am. Chem. Soc.* **1978**, *100*, 4974.
[26] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 12770.
[27] P. B. Hitchcock, C. Jones, J. f. Nixon, *J. Chem. Soc. Chem. Commun.* **1994**, 2061.
[28] P. B. Hitchcock, M. F. Lappert, A. K. Rai, H. D. Williams, *J. Chem. Soc. Chem. Commun.* **1986**, 1633.
[29] J.-T. Ahlemann, A. Künzel, H. W. Roesky, M. Noltemeyer, L. Markovskii, H.-G. Schmidt, *Inorg. Chem.* **1996**, *35*, 6644.

[30] C. Kruppa, M. Nieger, B. Ross, I. Väth, *Eur. J. Inorg. Chem.* **2000**, 165.

[31] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[32] F. Weinhold, C. Landis, *Valency and Bonding*, *A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, Cambridge, **2005**.

[33] E. D. Glendening, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 593.

[34] B. Silvi, A. Savin, *Nature* **1994**, *371*, 683.

[35] H. Grützmacher, T. F. Fässler, *Chem. Eur. J.* **2000**, *6*, 2317.

[36] R. Huisgen, I. Ugi, *Angew. Chem.* **1956**, *68*, 705.