Phosphorus Mononitride

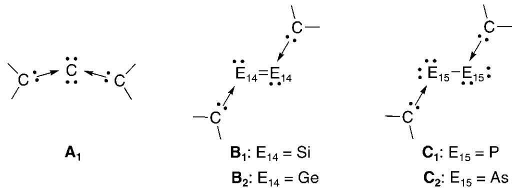
DOI: 10.1002/anie.201002889

Isolation of a Carbene-Stabilized Phosphorus Mononitride and Its Radical Cation ($PN^{+\bullet}$)**

*Rei Kinjo, Bruno Donnadieu, and Guy Bertrand**

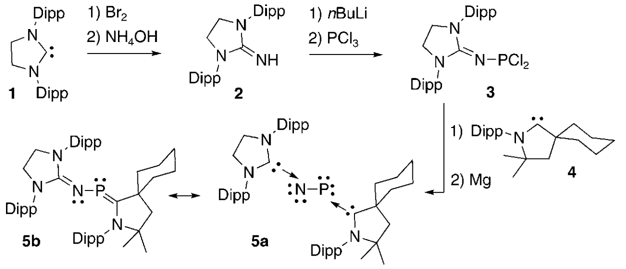
In contrast to the inert nature of N_2, diphosphorus (P_2)[1] and diarsenic (As_2)[2] are only persistent in the gas phase at high temperatures; otherwise, they dimerize to form the stable tetrahedral white phosphorus (P_4) and yellow arsenic (As_4). Phosphorus mononitride (PN) has attracted a lot of interest,[3] mostly because it is an important component of the interstellar medium and the atmospheres of Jupiter and Saturn.[4] In the laboratory, gaseous PN has been synthesized by pyrolysis of different precursors, and the phosphorus–nitrogen bond length (1.49 Å) determined by microwave spectroscopy.[5] In the condensed phase, PN is even more prone to association than P_2 and As_2. Its dimer, P_2N_2, has not yet been detected experimentally, and its trimer has only been observed spectroscopically in a krypton matrix at 40 K.[6] Although the combination of two Group 15 elements does not preclude the isolation of small clusters, as shown by the recent discovery of AsP_3,[7] the smallest discrete binary PN molecule that has been structurally characterized is P_3N_{21}.[8,9] However, P_4N_4,[10a] PN_9,[10b] and PN_{15}[10c] have been observed. Even more surprisingly, in contrast to the large number of N_2,[11a,b] P_2,[11c–e] and As_2[11e,f] transition-metal complexes that have been isolated,[11g] only a single report describes the reaction of PN with metal atoms of Group 11 at 10 K.[12] The corresponding complexes have only been characterized by IR spectroscopy, and the description as monomeric PN complexes has been debated.[3d]

Recently, it was shown that, just like transition metals, stable singlet carbenes can activate small molecules.[13] They also coordinate main group elements in their zero oxidation state,[14] leading to stable species such as carbodicarbenes (bent allenes) **A**[15,16] and diatomic silicon **B$_1$**,[17a] germanium **B$_2$**,[17b] phosphorous **C$_1$**,[13e,18] and arsenic **C$_2$**[19] (Scheme 1). Herein we report the isolation of phosphorus mononitride stabilized by two carbenes. We also describe the one-electron oxidation of PN, which allows the complete characterization of the first isolable PN radical cation.



Scheme 1. Carbene-stabilized main-group elements in their zero oxidation state.

The nitrogen atom was installed by treatment of NHC **1**[20] with bromine, followed by addition of aqueous ammonia. Deprotonation of **2** with *n*BuLi and addition of phosphorus trichloride afforded compound **3** in 68% yield. The desired product **5** was then obtained in 88% yield by reacting **3** with cyclic alkyl amino carbene (CAAC) **4**[21] and subsequent reduction with excess magnesium (Scheme 2).



Scheme 2. Synthesis of bis(carbene)–PN adduct **5**. Dipp = 2,6-diisopropylphenyl.

Compound **5** is indefinitely stable, even in air at room temperature, both in the solid state and in solution. The ^{31}P NMR signal ($\delta = +134.0$ ppm) appears at lower field than those of **C$_1$** ($\delta = +59.4$–-73.6 ppm),[18] which is expected because of the difference of electronegativity between nitrogen and phosphorus. Single crystals of **5** melt at 215 °C, and no decomposition was observed by heating a toluene solution under reflux for 24 h. According to the X-ray diffraction study[22] (Figure 1a), compound **5** has a planar *trans*-bent geometry (N1-P1-C4 102.78°, C1-N1-P1 122.12°, C1-N1-P1-C4 torsion angle 179.38°). Both the P1–C4 (1.719 Å) and C1–N1 (1.282 Å) bonds are rather short, and the central P–N bond (1.7085 Å) is in the normal range for a P–N single bond. The molecular structure of **5** is thus very similar to that reported by Robinson et al. for NHC-stabilized diphosphorus **C$_1$**[18a] and diarsenic **C$_2$**.[19] All these carbene adducts do not feature an EE triple bond, as is found in free P_2, As_2, and

---

[*] Dr. R. Kinjo, B. Donnadieu, Prof. G. Bertrand
UCR-CNRS Joint Research Chemistry Laboratory (UMI 2957)
Department of Chemistry, University of California Riverside
Riverside, CA 92521-0403 (USA)
Fax: (+1) 951-827-2725
E-mail: guy.bertrand@ucr.edu
Homepage: http://research.chem.ucr.edu/groups/bertrand/guybertrandwebpage/

[**] We are grateful to the NSF (CHE-0924410) and RHODIA Inc. for financial support of this work, and to the Japan Society for the Promotion of Science for a Fellowship (R.K.).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201002889.

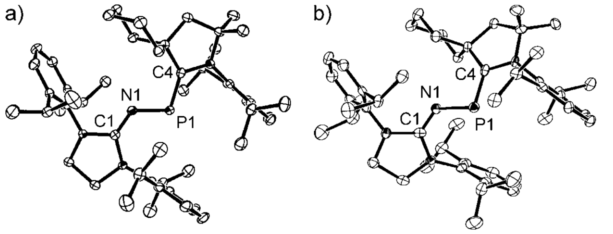


Figure 1. ORTEP for **5** (a) and **5**$^{+\bullet}$ (b). Ellipsoids set at 50% probability; hydrogen atoms, solvent molecules, and the counteranion are omitted for clarity. Selected bond lengths [Å] and angles [°]: **5**: P1–N1 1.7085(16), C1–N1 1.282(3), P1–C4 1.719(2); C1-N1-P1 122.12(14), N1-P1-C4 102.78(9). **5**$^{+\bullet}$: P1–N1 1.645(4), C1–N1 1.313(5), P1–C4 1.788(5); C1-N1-P1 119.3(3), N1-P1-C4 102.1(2).

PN,[5] but rather an EE single bond. Similarly to $\mathbf{C_1}$ and $\mathbf{C_2}$, **5** can be regarded as containing either a phosphinidene–nitrene fragment or a phosphazabutadiene skeleton, as shown by canonical structures **5a** and **5b**, respectively. Note that form **5b** is reminiscent of the end-on dinuclear N_2 transition-metal complexes, the historically most common bonding motif of nitrogen, and a form that is considered as corresponding to a strong activation of N_2.[11a,b]

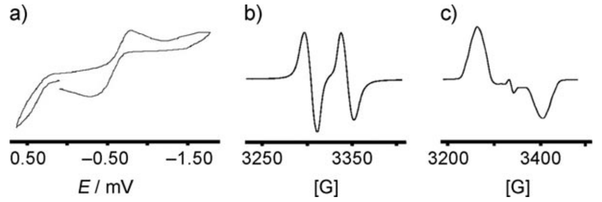


Figure 2. a) Cyclic voltammogram of a THF solution of **5** (0.1 M *n*BuNPF$_6$ as electrolyte, scan rate 100 mV s^{-1}, potential versus Fc$^+$/Fc); b) EPR spectrum (9.3305 GHz) of **5**$^{+\bullet}$ in a fluorobenzene solution at 298 K; c) EPR spectrum of **5**$^{+\bullet}$ in a fluorobenzene frozen solution at 100 K.

We have recently shown that $\mathbf{C_1}$ can be reversibly oxidized,[23] and therefore to further demonstrate the analogy between this compound and **5**, we carried out an electrochemical study. The cyclic voltammogram of a THF solution of **5**, containing 0.1 M *n*BuNPF$_6$ as electrolyte, shows a reversible one-electron oxidation at $E_{1/2} = -0.51$ V versus Fc$^+$/Fc, and a second oxidation at about +0.60 V, which is irreversible (Figure 2a). These data prompted us to carry out the chemical synthesis of radical cation **5**$^{+\bullet}$. When toluene was added at room temperature to an equimolar mixture of **5** and $[Ph_3C][B(C_6F_5)_4]$ in an argon atmosphere, the color immediately changed to dark brown. After 2 h of stirring, the ^{31}P NMR spectrum was silent, indicating the paramagnetic character of the resulting product. After work up, radical cation **5**$^{+\bullet}$ was quantitatively obtained as an air-sensitive microcrystalline powder (m.p. 216 °C). Not surprisingly, treatment of a toluene solution of **5**$^{+\bullet}$ with KC$_8$ rapidly gave back **5**, demonstrating a fully reversible redox system. The room-temperature ESR spectrum of a fluorobenzene solution of **5**$^{+\bullet}$ displays a doublet owing to a large coupling with phosphorous ($g = 2.0048$; $a(^{31}P) = 44$ G; Figure 2b), which is comparable to the coupling constant found in radical cations $\mathbf{C_1}^{+\bullet}$ ($a(^{31}P) = 42$–44 G).[23] However, coupling with the nitrogen atom was not observed, indicating a relatively small distribution of spin density on the central nitrogen atom. To determine the anisotropic coupling constant, the frozen fluorobenzene solution EPR spectrum was recorded at 100 K (Figure 2c). The simulation of the spectrum shows that the tensors are aligned, which is consistent with the π* geometry of the SOMO: $A_z(^{31}P) = 143$ G, $A_x(^{31}P) = -10$ G, and $A_y(^{31}P) \approx 0$; $g_z = 2.0028$, $g_x = 2.0052$, $g_y = 2.0087$. These features are also very comparable to those observed for radical cations $\mathbf{C_1}^{+\bullet}$.[23]

Single crystals suitable for an X-ray diffraction study were obtained by layering hexane on a fluorobenzene solution of **5**$^{+\bullet}$ at 0 °C.[22] Similar to **5**, radical cation **5**$^{+\bullet}$ has an almost planar *trans*-bent structure (Figure 1b). The P–N bond (1.645 Å) is 3.7% shorter, whereas P1–C4 (1.788 Å) and C1–N1 (1.313 Å) bonds are significantly longer than in **5**.

All these experimental findings are readily rationalized by ab initio calculations performed on the simplified model compounds **6** and **6**$^{+\bullet}$ that feature the parent NHC and CAAC. The optimized geometries of both molecules at the (U)B3LYP/6-31G(d) level of theory agree well with experiment. The frontier orbitals ((U)HF/6-311G(d)) are depicted in Figure 3. The HOMO of **6** is the π*(PN) orbital, which mixes in a bonding fashion with p(π) AO of the carbene carbon atoms. This indicates that the electronic reference state of PN in the carbene complex is the doubly excited $^1\Gamma(\pi \rightarrow \pi'^*)$ state, where the doubly occupied π′* MO backdonates electronic charge into the formally empty p(π) AO of the carbene. The carbene→PN donation takes place from the σ lone pairs of carbene donors into the empty in-plane $\pi(PN)_{\parallel}$ MO, which yields two low-lying orbitals (not shown). The $\pi^*(PN)_{\perp}$ orbital in **6** is doubly occupied (HOMO), and is of course singly occupied in **6**$^{+\bullet}$ (SOMO). The change in the occupation of the $\pi^*(PN)_{\perp}$ orbital yields a shortening of the central P–N bond and weakening of both C1–N1 and P1–C4 bonds.

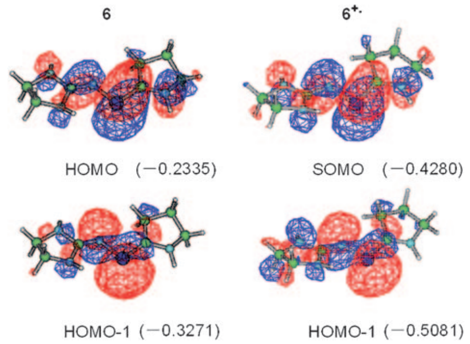


Figure 3. Selected molecular orbitals for **6** (left) and **6**$^{+\bullet}$ (right) calculated at the (U)HF/6-311G(d)//(U)B3LYP/6-31G(d) level of theory.

The atomic partial charges and spin distribution, calculated by NBO method at (U)B3LYP/6-311G(d) level of theory,[24] provide an interesting information about the bonding situation in these molecules. The PN fragments in neutral **6** and radical cation $\mathbf{6}^{+\bullet}$ carry a negative charge of $-0.37e$ and $-0.12e$, respectively. The spin density in $\mathbf{6}^{+\bullet}$ is mainly distributed on the phosphorous atom ($0.40e$). Interestingly, the spin distribution on a central nitrogen atom ($0.18e$) is comparable to the nitrogen atom of CAAC ligand ($0.19e$), which is attributed to the higher acceptor strength of CAAC compared with NHC.

In summary, these results demonstrate the powerful ability of bulky singlet carbenes to stabilize very reactive species, including those for which transition metals have so far failed. Moreover, as singlet carbenes, and especially NHCs,[25] are known to be good leaving groups, the next challenge is to use carbene adducts as PN delivery molecules.

Experimental Section

All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques.

5: Hexanes (20 mL) was added at −78 °C to a mixture of **3** (1270 mg, 2.50 mmol) and CAAC **4** (814 mg, 2.5 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The white precipitate was filtered, washed with hexanes, and dried under vacuum. Magnesium (91 mg, 3.75 mmol) and THF (40 mL) were added to the solid, and the solution was stirred at room temperature for 14 h. After the solvent was removed under vacuum, the residue was extracted with toluene (40 mL) and dried under vacuum to afford **5** as light orange powder (88 % yield). Single crystals of **5** were obtained by recrystallization from a mixture of THF/hexane (1:1) solution at room temperature. M.p.: 216 °C; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 7.04$–7.00 (m, 4H, C*H*), 6.96–6.91 (m, 5H, C*H*), 3.22 (br, 4H, $CH_2 \times 2$), 3.13 (sept, $J = 7.0$ Hz, 2H, $CH(CH_3)_2$), 2.79 (sept, $J = 7.0$ Hz, 2H, $CH(CH_3)_2$), 2.49 (sept, $J = 7.0$ Hz, 2H, $CH(CH_3)_2$), 1.70 (s, 2H, CH_2), 1.27–1.13 (m, 10H, CH_2), 1.10 (d, $J = 7.0$ Hz, 12H, $CH(CH_3)_2 \times 2$), 1.07 (d, $J = 7.0$ Hz, 12H, $CH(CH_3)_2 \times 2$), 1.02 (d, $J = 7.0$ Hz, 12H, $CH(CH_3)_2 \times 2$), 0.85 ppm (s, 6H, CH_3); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 199.2$ (d, $^1J_{\text{P-C}} = 50.0$ Hz, NP*C*), 152.4 (d, $^2J_{\text{P-C}} = 21.3$ Hz, *C*NP), 149.3 (*o*), 148.5 ($o \times 2$), 138.9 (br, *ipso*), 135.3 (*ipso*), 128.5 ($p \times 2$), 128.3 (*p*), 125.2 (*m*), 124.7 ($m \times 2$), 66.4 (C^q), 53.5 (d, $^2J_{\text{P-C}} = 9.1$ Hz, PCC^q), 51.2 (CH_2), 49.0 (br, $CH_2 \times 2$), 36.8 (CH_2), 30.1 (CH_3), 29.1 ($CH \times 2$), 28.9 (CH), 28.4 (CH_3), 28.3 (CH_3), 25.7 ($CH_3 \times 2$), 25.2 (CH_3 and CH_2), 24.3 (CH_3), 24.0 ppm (CH_2); ^{31}P NMR (121.4 MHz, C_6D_6): $\delta = 134.0$ ppm.

Radical cation $\mathbf{5}^{+\bullet}$: Toluene (15 mL) was added at room temperature to a mixture of **5** (400 mg, 0.53 mmol) and $Ph_3C^+B(C_6F_5)_4^-$ (485 mg, 0.53 mmol), and the solution was stirred at room temperature for 2 h. After the solvent was removed under vacuum, the dark brown residue was washed with hexanes (50 mL) and dried under vacuum to give radical cation $\mathbf{5}^{+\bullet}$ (623 mg; 82 % yield) as a highly air-sensitive dark brown powder. Single crystals of $\mathbf{5}^{+\bullet}$ were grown by layering hexanes on top of a fluorobenzene solution at 0 °C. M.p.: 215 °C (dec).

Received: May 13, 2010

Keywords: carbenes · phosphorus mononitride · radical cations

---

[1] a) O. J. Scherer, *Angew. Chem.* **2000**, *112*, 1069–1071; *Angew. Chem. Int. Ed.* **2000**, *39*, 1029–1030; b) A. Kornath, A. Kaufmann, M. Torheyden, *J. Chem. Phys.* **2002**, *116*, 3323–3326; c) N. A. Piro, J. S. Figueroa, J. T. McKellar, C. C. Cummins, *Science* **2006**, *313*, 1276–1279; d) N. A. Piro, C. C. Cummins, *J. Am. Chem. Soc.* **2008**, *130*, 9524–9535.

[2] a) *Gmelin Handbuch der Anorganischen Chemie, Arsen, Vol. 17*, Verlag Chemie, Weinheim, **1952**; b) K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, Van Nostrand, Reinhold, New York, **1979**; c) A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, Chapman Hak, London, **1968**; d) G. Huttner, B. Sigwarth, O. Scheidsteger, L. Zsolnai, O. Orama, *Organometallics* **1985**, *4*, 326–332.

[3] a) R. B. Viana, P. S. S. Pereira, L. G. M. Macedo, A. S. Pimentel, *Chem. Phys.* **2009**, *363*, 49–58; b) L. M. Ziurys, S. N. Milam, A. J. Apponi, N. J. Woolf, *Nature* **2007**, *447*, 1094–1097; c) A. E. Kemeny, J. S. Francisco, D. A. Dixon, D. Feller, *J. Chem. Phys.* **2003**, *118*, 8290–8295; d) O. J. Scherer, *Angew. Chem.* **1992**, *104*, 177–178; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 170–171.

[4] a) W. W. Dulley, D. A. A. Williams, *Interstellar Chemistry*, Academic Press, New York, **1984**; b) Y. L. Yung, W. B. DeMore, *Photochemistry of Planetary Atmospheres*, Oxford University Press, Oxford, **1998**.

[5] a) R. Ahlrichs, S. Schunck, H. Schnöckel, *Angew. Chem.* **1988**, *100*, 418–420; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 421–423; b) R. Ahlrichs, M. Bär, H. S. Plitt, H. Schnöckel, *Chem. Phys. Lett.* **1989**, *161*, 179–184.

[6] R. M. Atkins, P. L. Timms, *Spectrochim. Acta Part A* **1977**, *33*, 853–857.

[7] a) B. M. Cossairt, M. C. Diawara, C. C. Cummins, *Science* **2009**, *323*, 602–602; b) B. M. Cossairt, C. C. Cummins, *J. Am. Chem. Soc.* **2009**, *131*, 15501–15511.

[8] M. Göbel, K. Karaghiosoff, T. M. Klapötke, *Angew. Chem.* **2006**, *118*, 6183–6186; *Angew. Chem. Int. Ed.* **2006**, *45*, 6037–6040.

[9] The solid-state structure of three-dimensional polymeric P_3N_5 has also been reported; see: a) S. Horstmann, E. Irran, W. Schnick, *Angew. Chem.* **1997**, *109*, 1938–1940; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1873–1875; b) K. Landskron, H. Huppertz, J. Senker, W. Schnick, *Angew. Chem.* **2001**, *113*, 2713–2716; *Angew. Chem. Int. Ed.* **2001**, *40*, 2643–2645.

[10] a) E. H. Kober, H. F. Lederle, G. F. Ottmann, USA Patent US 32918645, **1966**; b) X. Zeng, W. Wang, F. Liu, M. Ge, Z. Sun, D. Wang, *Eur. J. Inorg. Chem.* **2006**, 416–421; c) P. Volgnandt, A. Schmidt, *Z. Anorg. Allg. Chem.* **1976**, *425*, 189–192.

[11] For Reviews, see: a) E. A. MacLachlan, M. D. Fryzuk, *Organometallics* **2006**, *25*, 1530–1543; b) B. A. MacKay, M. D. Fryzuk, *Chem. Rev.* **2004**, *104*, 385–401; c) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* **2010**, DOI: 10.1021/cr900349u; d) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, DOI: 10.1021/cr9003709; e) O. J. Scherer, *Acc. Chem. Res.* **1999**, *32*, 751–762; f) A. J. Dimaio, A. L. Rheingold, *Chem. Rev.* **1990**, *90*, 169–190; g) O. J. Scherer, *Angew. Chem.* **1985**, *97*, 905–924; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 924–943.

[12] R. M. Atkins, P. L. Timms, *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 113–115.

[13] a) V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Angew. Chem.* **2006**, *118*, 3568–3571; *Angew. Chem. Int. Ed.* **2006**, *45*, 3488–3491; b) G. D. Frey, V. Lavallo, B. Donnadieu, G. Bertrand, *Science* **2007**, *316*, 439–441; c) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2007**, *129*, 14180–14181; d) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2007**, *119*, 7182–7185; *Angew. Chem. Int. Ed.* **2007**, *46*, 7052–7055; e) O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2009**, *121*, 5638–5641; *Angew. Chem. Int. Ed.* **2009**, *48*, 5530–5533.

[14] a) Y. Wang, G. H. Robinson, *Chem. Commun.* **2009**, 5201–5213; b) C. A. Dyker, G. Bertrand, *Nat. Chem.* **2009**, *1*, 265–266; c) C. A. Dyker, G. Bertrand, *Science* **2008**, *321*, 1050–1051.

[15] a) C. A. Dyker, V. Lavallo, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2008**, *120*, 3250 – 3253; *Angew. Chem. Int. Ed.* **2008**, *47*, 3206 – 3209; b) A. Fürstner, M. Alcarazo, R. Goddard, C. W. Lehmann, *Angew. Chem.* **2008**, *120*, 3254 – 3258; *Angew. Chem. Int. Ed.* **2008**, *47*, 3210 – 3214; c) M. Alcarazo, C. W. Lehmann, A. Anoop, W. Thiel, A. Fürstner, *Nat. Chem.* **2009**, *1*, 295 – 301.

[16] The carbo(dicarbene) concept was devised by Frenking et al.; see for example: a) R. Tonner, G. Frenking, *Angew. Chem.* **2007**, *119*, 8850 – 8853; *Angew. Chem. Int. Ed.* **2007**, *46*, 8695 – 8698; b) N. Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.* **2009**, *15*, 8593 – 8604; c) G. Frenking, R. Tonner, *Pure Appl. Chem.* **2009**, *81*, 597 – 614; d) N. Takagi, T. Shimizu, G. Frenking, *Chem. Eur. J.* **2009**, *15*, 3448 – 3456; e) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3260 – 3272; f) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3273 – 3289; g) M. M. Deshmukh, S. R. Gadre, R. Tonner, G. Frenking, *Phys. Chem. Chem. Phys.* **2008**, *10*, 2298 – 2301.

[17] a) Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069 – 1071; b) A. Sidiropoulos, C. Jones, A. Stasch, S. Klein, G. Frenking, *Angew. Chem.* **2009**, *121*, 9881 – 9884; *Angew. Chem. Int. Ed.* **2009**, *48*, 9701 – 9704.

[18] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 14970 – 14971.

[19] M. Y. Abraham, Y. Wang, Y. Xie, P. Wei, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *Chem. Eur. J.* **2010**, *16*, 432 – 435.

[20] a) A. J. Arduengo III, R. Krafczyk, R. Schmutzler, *Tetrahedron* **1999**, *55*, 14523 – 14534; b) K. M. Kuhn, R. H. Grubbs, *Org. Lett.* **2008**, *10*, 2075 – 2077.

[21] a) V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 5851 – 5855; *Angew. Chem. Int. Ed.* **2005**, *44*, 5705 – 5709; b) R. Jazzar, R. D. Dewhurst, J. B. Bourg, B. Donnadieu, Y. Canac, G. Bertrand, *Angew. Chem.* **2007**, *119*, 2957 – 2960; *Angew. Chem. Int. Ed.* **2007**, *46*, 2899 – 2902.

[22] CCDC 776656 (**5**), and 776657 ($\mathbf{5}^{+\bullet}$) 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.

[23] O. Back, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Nat. Chem.* **2010**, *2*, 369 – 373.

[24] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899 – 926.

[25] a) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606 – 5655; b) N. Marion, S. Diez-Gonzalez, S. P. Nolan, *Angew. Chem.* **2007**, *119*, 3046 – 3058; *Angew. Chem. Int. Ed.* **2007**, *46*, 2988 – 3000.