DOI: 10.1002/anie.201000901

Charged Phosphiranes

Synthesis, Structure, and Reactivity of a Stabilized Phosphiranylium Salt**

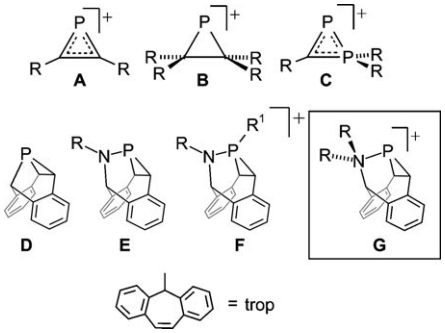
Helen Jansen, Florian B. Läng, J. Chris Slootweg, Andreas W. Ehlers, Martin Lutz, Koop Lammertsma, and Hansjörg Grützmacher**

In memory of Pascal Le Floch

Phosphiranes with a three-membered PC_2 ring have unique electronic properties.[1] Although their ring strain is smaller than that in cyclopropanes, they are highly reactive and display remarkable chemistry, such as [2+1] cycloreversions to olefins and phosphinidenes [R–P],[2] cationic ring-opening polymerization to poly(ethylenephosphine),[3] and special properties as ligands in transition-metal complexes for catalysis.[4] Positively charged species are even more reactive. Species such as **A** (phosphirenylium ion) or **B** (phosphiranylium ion), which may be viewed as π-complexes of P^+ to alkynes or alkenes,[5] respectively (Scheme 1), have never been isolated.[6] A notable exception is the crystalline diphosphirenium ion **C**.[7]

The dibenzo[*a*,*d*]cycloheptatrienyl (trop) platform was used for the synthesis of the highly strained dibenzophosphasemibullvalene **D**,[8] very robust aminophosphiranes (BABAR-Phos) **E**,[9] and the phosphiranium ion **F** (R = *i*Pr, R^1 = *t*Bu; Scheme 1).[10] Isolated examples of the latter are likewise rare.[11]

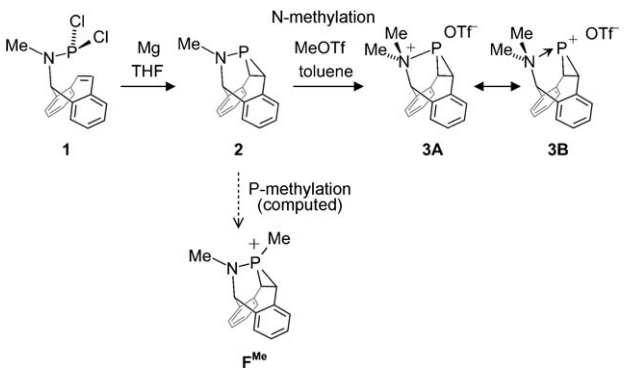
Because the lone pair at phosphorus has a very high s-orbital character,[10] phosphiranes are generally reluctant to be alkylated, oxygenated, or sulfurated, and with bulky substituents R in **E** these reactions are suppressed. However, transition-metal ions (Pt^{II}, Rh^{I}) bind to the phosphorus center, albeit very weakly.[4b]



Scheme 1. Cationic three-membered phosphorus heterocycles (**A**–**C**) and BABAR-Phos derivatives **D**–**G**.

We now report on the synthesis of a sterically unshielded BABAR-Phos derivative that reacts with methyl triflate, a "hard" alkylation reagent, at the "hard" nitrogen center, to give the cation **G**, which can be described as an intramolecular amine complex of the elusive phosphiranylium ion **B**.

The synthesis of the ^{Me}BABAR-Phos **2** is straightforward, as is shown in Scheme 2 (see the Supporting Information for details). As previously reported,[4a] the reduction of the amino(dichloro)trop phosphane **1** with magnesium turnings (room temperature, 3 h) results in the rather clean formation of ^{Me}BABAR-Phos **2** (73%; $\delta_{^{31}P} = -149.0$ ppm) as a result of the spatial proximity of the PCl_2 unit and the olefin. The characteristic low-frequency shifts of the ^{1}H and ^{13}C resonances of the $HCCH_{trop}$ unit and the *J*(H,P) and *J*(C,P) couplings in **2** ($\delta_{^1H} = 2.55$ ppm (^2J(H,P) = 18.3 Hz); $\delta_{^{13}C} =$



Scheme 2. Synthesis of **2** and **3**.

[*] H. Jansen, Dr. J. C. Slootweg, Dr. A. W. Ehlers, Prof. Dr. K. Lammertsma
Department of Chemistry and Pharmaceutical Sciences, VU University Amsterdam
De Boelelaan 1083, 1081 HV, Amsterdam (The Netherlands)
Fax: (+31) 20-598-7488
E-mail: k.lammertsma@few.vu.nl
Dr. F. B. Läng, Prof. Dr. H. Grützmacher
Department of Chemistry and Applied Biosciences, ETH-Hönggerberg
Wolfgang-Pauli-Strasse, 8093 Zurich (Switzerland)
E-mail: gruetz@inorg.chem.ethz.ch
Dr. M. Lutz
Bijvoet Center for Biomolecular Research
Crystal and Structural Chemistry, Utrecht University (The Netherlands)

[**] This work was supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (NWO/CW), the ETH Zürich, and the Swiss National Science Foundation. We acknowledge the National Center for Computing Facilities (SARA) and NWO/NCF for computer time and the VU University Amsterdam for a travel grant (H.J.). We thank Dr. M. Smoluch for the exact mass determination.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201000901.

24.1 ppm (^1J(C,P) = 41.7 Hz)) clearly indicate its formation (vs. $\delta_{^1H}$ = 6.83 ppm and $\delta_{^{13}C}$ = 130.9 ppm in **1**).

Reaction of ^{Me}BABAR-Phos **2** with methyl triflate in toluene (room temperature, 2 h) resulted exclusively in N-alkylation (91%; $\delta_{^{31}P}$ = −83.6 ppm; Scheme 2). The structure of the novel salt **3** was established by X-ray crystal structure determination (Figure 1)[12] and displays a remarkable long P–N bond (1.845(1) Å) compared with that in the neutral analogues **E** (1.73–1.74 Å)[4a,13] and phosphiranium ion **F** (1.628(4) Å).[10]

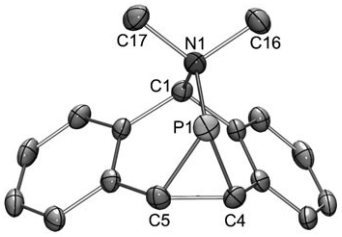


Figure 1. Displacement ellipsoid plot (50% probability) of **3**. The OTf^- anion is omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–N1 1.8449(14), P1–C4 1.8532(18), P1–C5 1.8593(17), N1–C1 1.541(2), N1–C16 1.509(2), N1–C17 1.510(2), C4–C5 1.523(2); N1-P1-C4 97.68(7), N1-P1-C5 97.95(7), C5-P1-C4 48.44(7); Σ(P): 244.1°.

DFT calculations at the B3PW91/6-311 + G(d,p) level of theory were performed to understand and compare the electronic structure and reactivity of **2**, **3**, and the non-observed P-methylated product $\mathbf{F^{Me}}$.[14] The HOMO of **2** (−5.81 eV) is mainly located on the nitrogen atom, while the HOMO−1 (−6.35 eV; Figure 2) can be attributed to the "lone pair" located on the phosphorus atom. This finding is in accord with the preferred alkylation at nitrogen. Further, the N-alkylated cation **3** is 9.5 kcal mol^{-1} more stable than the computed P-alkylated derivative $\mathbf{F^{Me}}$.

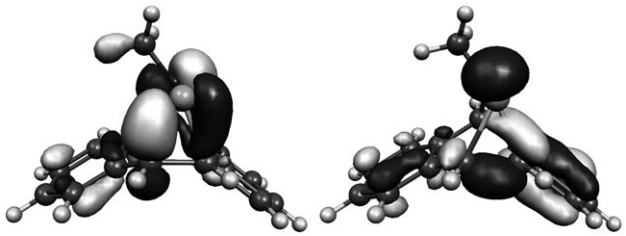


Figure 2. HOMO (left) and HOMO−1 (right) of ^{Me}BABAR-Phos **2**.

The nature of the P–N bond was studied by analyzing the electron density by using the theory of atoms in molecules (AIM)[15] to investigate the relative weight of the resonance structures **3A** (ammonium salt with the positive charge on N) and **3B** (intramolecular amino-stabilized phosphiranylium cation with the positive charge localized on the PC_2 ring; Scheme 2).[5e] The atomic charges of the basins for nitrogen Q(N) and phosphorus Q(P) of **2**, **3**, and $\mathbf{F^{Me}}$ are given in Table 1. As expected, the positive charge at the P atom in phosphonium-type ion $\mathbf{F^{Me}}$ is the highest (+2.47 *e*). With respect to **2**, N-methylation diminishes both the negative charge at N and the positive charge on P. That is, **3** contains the longest, weakest, and least-polar P–N bond (ΔQ(N,P) = 2.20 *e* [vs. 2.67 *e* (**2**) and 3.88 *e* ($\mathbf{F^{Me}}$)].

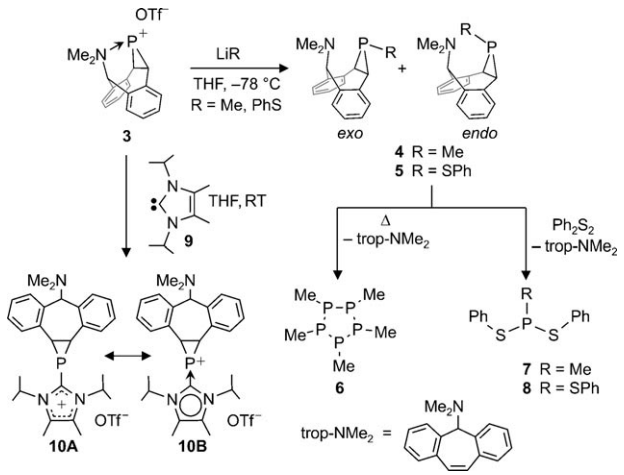
Table 1: Characterization of the P–N bond with AIM.[a]

	P–N Bond Length	$H(r_c)$[b]	Q(P)	Q(N)
2	1.727 Å	−0.912	1.34	−1.33
3	1.885 Å	−0.670	1.09	−1.11
$\mathbf{F^{Me}}$	1.660 Å	−1.102	2.47	−1.41

[a] The B3PW91/6-311 + G(d,p) calculated structures were used; [b] the bond critical point r_c corresponds to a saddle point of the electron density in the bonding region.

From the obtained energy densities ($H(r_c)$; Table 1), it can be derived that the P–N bond in **2** and $\mathbf{F^{Me}}$ has a strong covalent character.[16] However, the decreased energy density ($H(r_c)$ = −0.670 hartree Å^{-3}) of the P–N bond in **3** indicates a significant contribution of resonance structure **3B** to the electronic ground state of **3**, which may be viewed as an intramolecular donor–acceptor N→P complex[17] of an amino-stabilized phosphiranylium ion (**B**).

The reactivity of the amino phosphiranylium salt **3** was investigated as well. Addition of methyl lithium at −78 °C resulted in *P*-alkylation under breaking of the P–N bond yielding the *P*-methyl phosphiranes *endo*-**4** ($\delta^{31}P$ = −173.3 ppm) and *exo*-**4** ($\delta^{31}P$ = −205.7 ppm; 4:1 ratio; Scheme 3) quantitatively.[18] The reaction of **3** with thiolate [Li(SPh)] gives exclusively the sterically less encumbered isomer *exo*-**5** ($\delta_{^{31}P}$ = −132.8 ppm), which is stable in solution and in the solid state.



Scheme 3. Reactivity of the amino phosphiranylium salt **3**.

Solutions of **4** can be stored at −18 °C for days, but within 24 h at room temperature clean fragmentation to the cyclic phosphinidene oligomer $(PMe)_5$ (**6**; Scheme 3)[19] and (5-*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-dimethylamine (trop-NMe_2) occurs. Addition of diphenyldisulfide to a freshly prepared solution of the phosphiranes **4** or **5** resulted in the quantitative formation of the phosphonodithious acids **7** ($\delta_{^{31}P}$ = 85.2 ppm)[20] and **8** ($\delta_{^{31}P}$ = 130.8 ppm),[21] respectively

(Scheme 3). Formally, these reactions correspond to the expulsion of a phosphinidene [R–P],[22] but at this stage of our investigations, we assume a [R–P] transfer process without the intermediacy of free phosphinidenes as our calculations predict that this process costs approximately 50 kcal mol^{-1}.

Interestingly, **3** also reacts with neutral nucleophiles such as N-heterocyclic carbenes (NHCs; Scheme 3). Namely, addition of I*i*Pr_2Me_2 **9** resulted in the NHC-stabilized phosphiranylium cation **10** ($\delta_{^{31}P} = -214.3$ ppm).[23,24]

The molecular structure of **10**, established by X-ray crystal structure analysis (Figure 3),[12] may be viewed as an olefin carbene P^I cation. The sum of bond angles at the phosphorus

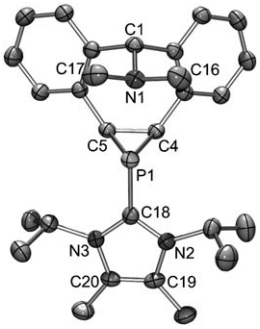


Figure 3. Displacement ellipsoid plot (50% probability) of **10**. Only one of two independent molecules is shown. The OTf^- anion and ordered/disordered THF solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–N1 2.581(2), P1–C4 1.908(3), P1–C5 1.896(2), P1–C18 1.881(3), N1–C1 1.478(3), N1–C16 1.467(3), N1–C17 1.466(3), N2–C18 1.350(3), N2–C19 1.384(3), N3–C18 1.351(3), N3–C20 1.391(3), C4–C5 1.500(3), C19–C20 1.354(4); C4-P1-C5 46.43(11), C4-P1-C18 95.32(11), C5-P1-C18 96.22(11), C5-C4-P1 66.36(13), C4-C5-P1 67.21(13), N2-C18-N3 106.8(2); Σ(P): 238.0°.

center (Σ(P): 238.0°) is small (cf. 244.1° for **3**) despite the sterically demanding substituents. The strength of the P–$C_{carbene}$ interaction in **10** (P1–C18 1.881(3) Å) was investigated with a bond decomposition scheme (ADF on model system **10′** with H for all NHC substituents).[25] Strong σ-donation of the lone pair of the C center of the carbene to the empty p orbital at the phosphorus atom makes up for 91% (-130 kcal mol^{-1}) of the orbital interaction energy (E^{oi}) to which a small contribution from π-back-donation of the phosphorus lone pair into the empty π* orbital of the carbene is added (-13 kcal mol^{-1}, 9% of E^{oi}). In contrast, in Macdonald's bis(carbene) P^I cation $[P(I\mathit{i}Pr_2Me_2)_2]^+$,[26] the contribution of the π-back-donation to the interaction energy is significantly higher (-27 kcal mol^{-1}; 13%).[24] This is reflected in the P–C bond dissociation energies (BDEs), which are much smaller in **10′** (-54.9 kcal mol^{-1}) than in $[P(NHC)_2]^+$ (-105.6 kcal mol^{-1}). Interestingly, the low energy density at the bond critical point of the P–$C_{carbene}$ bond in **10** ($H(r_c) = -0.763$ hartree $Å^{-3}$) is comparable to that of the P–N bond in **3**, which underlines the contribution of resonance structure **10B** (Scheme 3) to the electronic ground state of **10**.

In conclusion, our computational and experimental results indicate that [*N*,*N*-dimethyl-BABAR-Phos]OTf **3** and [(Me_2N-trop)P(I*i*Pr_2Me_2)]OTf **10** may be regarded as the first isolated examples of intra- and intermolecular amino- or carbene-stabilized phosphiranylium salts, respectively.

Received: February 12, 2010
Revised: April 26, 2010
Published online: July 2, 2010

Keywords: carbenes · cations · heterocycles · phosphiranes · phosphorus

[1] a) F. Mathey, *Pure Appl. Chem.* **1987**, *59*, 993–998; b) F. Mathey, *Chem. Rev.* **1990**, *90*, 997–1025; c) F. Mathey, M. Regitz in *Comprehensive Heterocyclic Chemistry II*, *Vol. 1A* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Amsterdam, **1997**, pp. 277–304; d) F. Mathey, M. Regitz in *Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain* (Ed.: F. Mathey), Pergamon, Amsterdam, **2001**, pp. 17–55.

[2] a) K. Lammertsma, *Top. Curr. Chem.* **2003**, *229*, 95–119; b) K. Lammertsma, M. J. M. Vlaar, *Eur. J. Org. Chem.* **2002**, 1127–1138; c) F. Mathey, N. H. Tran Huy, A. Marinetti, *Helv. Chim. Acta* **2001**, *84*, 2938–2957; d) X. Li, S. I. Weismann, T.-S. Lin, P. P. Gasper, A. H. Cowley, A. I. Smirnov, *J. Am. Chem. Soc.* **1994**, *116*, 7899–7900; e) G. Bucher, M. L. G. Borst, A. W. Ehlers, K. Lammertsma, S. Ceola, M. Huber, D. Grote, W. Sander, *Angew. Chem.* **2005**, *117*, 3353–3357; *Angew. Chem. Int. Ed.* **2005**, *44*, 3289–3293.

[3] S. Kobayashi, J.-I. Kadokawa, *Macromol. Rapid Commun.* **1994**, *15*, 567–571.

[4] a) J. Liedtke, H. Rüegger, S. Loss, H. Grützmacher, *Angew. Chem.* **2000**, *112*, 2596–2599; *Angew. Chem. Int. Ed.* **2000**, *39*, 2478–2481; b) C. Laporte, G. Frison, H. Grützmacher, A. C. Hillier, W. Sommer, S. P. Nolan, *Organometallics* **2003**, *22*, 2202–2208, and references therein.

[5] a) R. Chen, Y.-H. Cheng, L. Liu, X.-S. Li, Q.-X. Guo, *Res. Chem. Intermed.* **2002**, *28*, 41–48; b) X. Liu, D. M. Ivanova, D. Giblin, M. L. Gross, P. P. Gaspar, *Organometallics* **2005**, *24*, 3125–3135; c) W. W. Schoeller, U. Tubbesing, *J. Mol. Struct.* **1995**, *343*, 49–55; d) A. Largo, C. Barrientos, X. Lopez, F. P. Cossío, J. M. Ugalde, *J. Phys. Chem.* **1995**, *99*, 6432–6440; e) W. W. Schoeller, *Top. Curr. Chem.* **2003**, *229*, 75–94.

[6] a) **A** in solution at low temperature: K. K. Laali, B. Geissler, O. Wagner, J. Hoffmann, R. Armbrust, W. Eisfeld, M. Regitz, *J. Am. Chem. Soc.* **1994**, *116*, 9407–9408. For stable transition-metal complexes of **A**, see: b) J. Simon, U. Bergsträsser, M. Regitz, K. K. Laali, *Organometallics* **1999**, *18*, 817–819; c) F. G. N. Cloke, P. B. Hitchcock, J. F. Nixon, D. M. Vickers, *C. R. Chim.* **2004**, *7*, 931–940; d) Gas phase reactivity of **A**: A. A. Sabino, M. N. Eberlin, L. A. B. Moraes, K. K. Laali, *Org. Biomol. Chem.* **2003**, *1*, 395–400. Phosphiranylium ions were postulated as intermediates, see: e) E. Niecke, M. Leuer, M. Nieger, *Chem. Ber.* **1989**, *122*, 453–461; f) W. W. Schoeller, W. Haug, J. Strutwolf, T. Bush, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 1751–1755.

[7] a) M. Soleilhavoup, Y. Canac, A. M. Polozov, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1994**, *116*, 6149–6152; b) D. Bourissou, G. Bertrand, *Top. Curr. Chem.* **2002**, *220*, 1–25.

[8] J. Geier, G. Frison, H. Grützmacher, *Angew. Chem.* **2003**, *115*, 4085–4087; *Angew. Chem. Int. Ed.* **2003**, *42*, 3955–3957.

[9] J. Liedtke, S. Loss, G. Alcaraz, V. Gramlich, H. Grützmacher, *Angew. Chem.* **1999**, *111*, 1724–1727; *Angew. Chem. Int. Ed.* **1999**, *38*, 1623–1626.

[10] The phosphiranium ion **F** was obtained by a halide abstraction reaction from trop-P(*t*Bu)Cl with $AlCl_3$; see: J. Liedtke, S. Loss, Ch. Widauer, H. Grützmacher, *Tetrahedron* **2000**, *56*, 143 – 156.
[11] The only other example is reported in: D. C. R. Hockless, M. A. McDonald, M. Pabel, S. B. Wild, *J. Chem. Soc. Chem. Commun.* **1995**, 257 – 258, and was obtained by alkylation at the P atom of $PhP(CH_2)_2$.
[12] CCDC 765756 (**3**) and 765757 (**10**) 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. For the experimental details of the X-ray crystal structure determinations, see the Supporting Information.
[13] a) F. B. Läng, H. Grützmacher, *Chimia* **2003**, *57*, 187 – 190; b) J. Liedtke, Dissertation, ETH Zürich, *Synthese und Koordinationschemie neuer polycyclischer Phosphirane*, Nr. 13688, **2000**.
[14] Gaussian 03 (Revision C.02): M. J. Frisch et al., see the Supporting Information.
[15] a) R. F. W. Bader in *Atoms in Molecules: a quantum theory* (Ed.: R. F. W. Bader) Clarendon, Oxford, **1990**; b) P. L. Popelier in *Atoms in Molecules: An Introduction* (Ed.: P. L. Popelier), Prentice Hall, UK, **2000**.
[16] The energy density ($H(r) = G(r) + V(r)$) is the sum of the kinetic and potential energy density. For covalent bonds, the energy density at the bond critical point is negative (stabilization), whereas ionic and closed shell interactions are characterized by $H(r_c) \approx 0$; see: D. Cremer, E. Kraka, *Angew. Chem.* **1984**, *96*, 612 – 614; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 627 – 628.
[17] a) C. Chuit, C. Reyé, *Eur. J. Inorg. Chem.* **1998**, 1847 – 1857; b) M. Yoshifuji, S. Sangu, K. Kamijo, K. Toyota, *Chem. Ber.* **1996**, *129*, 1049 – 1055.
[18] It is unclear whether *exo*-**4** and *endo*-**4** are in a very slow equilibrium (not detectable on the NMR time scale) through an inversion of the central ring or are formed through an attack of MeLi form either side on the P center.
[19] L. R. Smith, J. L. Mills, *J. Am. Chem. Soc.* **1976**, *98*, 3852 – 3857.
[20] a) S. C. Peake, R. Schmutzler, *J. Chem. Soc. A* **1970**, 1049 – 1054; b) A. I. Razumov, N. I. Sinitsyn, R. A. Salakhyt, N. N. Bankovsk, E. A. Krasilni, *J. Gen. Chem. USSR* **1972**, *42*, 1245 – 1248.
[21] a) K. A. Petrov, G. I. Abramtseva, V. P. Evdakov, A. K. Strautman, *J. Gen. Chem. USSR* **1962**, *32*, 3019 – 3023; b) T. König, W. D. Habicher, U. Hähner, J. Pionteck, C. Rüger, K. Schwetlick, *J. Prakt. Chem.* **1992**, *334*, 333 – 349.
[22] Diphenyldisulfide is well known trapping agent for triplet phosphinidenes; see: a) U. Schmidt, C. Osterroht, *Angew. Chem.* **1965**, *77*, 455; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 437; b) J. C. Slootweg, K. Lammertsma in *Science of Synthesis*, *Vol. 42* (Eds.: B. M. Trost, F. Mathey), Georg Thieme, Stuttgart, **2009**, pp. 15 – 36.
[23] For NHC-stabilized phosphinidenes, see: a) A. J. Arduengo III, H. V. Rasika Dias, J. C. Calabrese, *Chem. Lett.* **1997**, 143 – 144; b) A. J. Arduengo III, J. C. Calabrese, A. H. Cowley, H. V. Rasika Dias, J. R. Goerlich, W. J. Marshall, B. Riegel, *Inorg. Chem.* **1997**, *36*, 2151 – 2158.
[24] For the related diphenylphosphenium ion $[IiPr_2Me_2 \rightarrow PPh_2]^+$, see: a) N. Kuhn, J. Fahl, D. Bläser, R. Boese, *Z. Anorg. Allg. Chem.* **1999**, *625*, 729 – 734; b) B. D. Ellis, P. J. Ragogna, C. L. B. Macdonald, *Inorg. Chem.* **2004**, *43*, 7857 – 7867.
[25] Energy decomposition analyses were performed on B3PW91/6-311 + G(d,p) optimized structures[14] using ADF2007.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com. See the Supporting Information for details.
[26] a) B. D. Ellis, C. A. Dyker, A. Decken, C. L. B. Macdonald, *Chem. Commun.* **2005**, 1965 – 1967; see also: b) B. D. Ellis, C. L. B. Macdonald, *Coord. Chem. Rev.* **2007**, *251*, 936 – 973; c) O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2009**, *121*, 5638 – 5641; *Angew. Chem. Int. Ed.* **2009**, *48*, 5530 – 5533.

