

1,3-Dipole Behavior of Phosphagermaallene $\text{Tip}(\text{tBu})\text{Ge}=\text{C}=\text{PMes}^*$ Leading to a Phosphagermaheterocyclic Carbene**

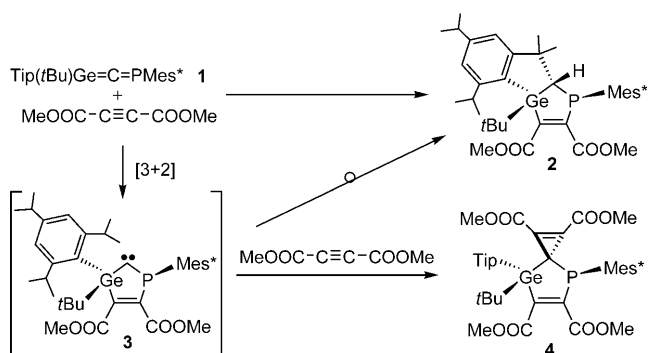
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The study of low-coordinate species of heavier Group 14 (Si, Ge, Sn) and of Group 15 (N, P, As, Sb) elements, and particularly that of heavy heteroalkenes $\text{E}=\text{E}'$ and heavy heteroallenes $\text{E}=\text{C}=\text{E}'$ ($\text{E}, \text{E}' = \text{Group 14 and 15 elements}$) has attracted much attention during the last decades. Such compounds are powerful building blocks in organometallic and heterocyclic chemistry. Heteroallenes $\text{E}=\text{C}=\text{E}'^{[1-4]}$ behave as 1,2-dipoles, leading to addition or cycloaddition onto the $\text{E}=\text{C}$ or $\text{C}=\text{E}'$ double bonds.^[5,6]

Herein we present the 1,3-dipole behavior of a heteroallene, a new type of behavior for such a family of compounds, in the reaction of phosphagermaallene $\text{Tip}(\text{tBu})\text{Ge}=\text{C}=\text{PMes}^*$ **1** towards dimethyl acetylenedicarboxylate. This reaction led to a transient cyclic phosphagermaheterocyclic carbene (PGeHC). DFT calculations allowed this unprecedented type of reaction to be understood. By taking into account the important role of N-heterocyclic carbenes (NHCs) in modern coordination chemistry, the access to higher homologues of such ligands is highly interesting. The only example of a higher homologue of NHCs is the diphosphinocarbene of Bertrand and co-workers.^[7] To our

knowledge, no other example of a system containing two heteroatoms, even a transient one, has been reported.

Addition of a solution of dimethyl acetylenedicarboxylate in Et_2O to a molar equivalent of phosphagermaallene **1** resulted in the formation of the sole derivative **2** in a nearly quantitative yield (Scheme 1). All of the NMR spectroscopic



Scheme 1. Reactivity of **1** with dimethyl acetylenedicarboxylate. Tip = 2,4,6-triisopropylphenyl, Mes* = 2,4,6-tri-*tert*-butylphenyl.

data are in agreement with a tricyclic structure that includes a 1-phospha-3-germacyclopent-4-ene, which was unambiguously confirmed by an X-ray determination (Figure 1 and Table 1).

The formation of this tricyclic derivative can only be understood by the intermediate formation of the PGeHC **3**, followed by insertion of the carbenic carbon atom into the C–H bond of an ortho isopropyl group of the Tip (2,4,6-*i*Pr₃C₆H₃) group on the germanium atom. Such inser-

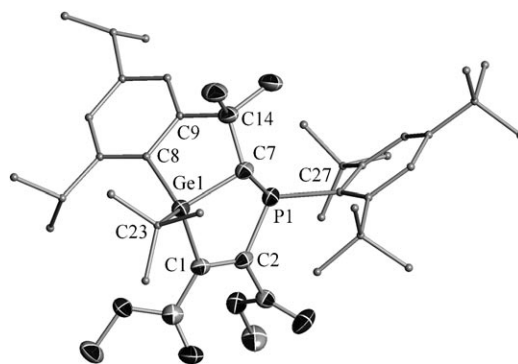


Figure 1. Crystal structure of **2**. Ellipsoids are set at 50% probability; hydrogen atoms are omitted and Tip, tBu, and Mes* groups have been simplified for clarity.

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[**] We are grateful to the Agence Nationale pour la Recherche (contract ANR-08-BLAN-0105-01) and PhoSciNet (CM0802) for financial support. For the theoretical work, we were granted access to the HPC resources of IDRIS under allocation 2010 (i2010080045) made by GENCI (Grand Equipement National de Calcul Intensif). Tip = 2,4,6-triisopropylphenyl, Mes* = 2,4,6-tri-*tert*-butylphenyl.

Supporting information for this article, including full experimental details for compounds **2**, **4**, **5**, and **6** and details of calculations, is available on the WWW under <http://dx.doi.org/10.1002/anie.201003044>.

Table 1: Comparison of pertinent geometrical parameters in **2**, **3**, **3H**, and **TS**.

	2 ^[a]	2 ^[b]	3 ^[b]	3H ^[b]	TS ^[b]
Ge1–C7	1.976(4)	1.97	1.95	1.96	1.82
C7–P1	1.849(3)	1.85	1.63	1.65	1.64
P1–C2	1.822(4)	1.86	1.85	1.83	2.70
C2–C1	1.341(5)	1.36	1.35	1.34	1.24
C1–Ge1	1.966(4)	1.96	2.05	1.98	2.85
Ge1–C7–P1	103.3(2)	102.0	103.1	97.4	126.6

[a] X-ray data. [b] B3LYP/6-31G(d,p). Bond lengths in Å, angles in °.

tions into C–H bonds are well known and characteristic for carbenes.^[8]

Carbene **3** would be formed by an unexpected [3+2] cycloaddition between the Ge=C=P moiety of the phosphagermaallene **1**, which behaves as a 1,3-dipole, and the C≡C triple bond. Such a 1,3-dipole behavior of a heteroallene of type E=C=E' is observed for the first time herein. To gain more insight into this unprecedented behavior, DFT calculations^[9] were carried out at the B3LYP/6-31G(d,p) level of theory.^[10]

Carbene **3** is a minimum on the potential energy surface and has a singlet ground state.^[11] The [3+2] cycloaddition between the Ge=C=P moiety and the C≡C triple bond is predicted to be exothermic (ΔG : $-13 \text{ kcal mol}^{-1}$) and the carbene **3** is less stable than **2** by about 50 kcal mol^{-1} , in agreement with the formation of the insertion derivative as the only product.

Concerning the geometrical parameters of the carbene **3**, the Ge1–C7 bond is calculated to be about 1.95 Å in length (Table 1), which is in the range of a single bond. A short P1–C7 bond (1.63 Å) was calculated, which corresponds to a P=C double bond with a planar geometry around the phosphorus lone pair (ΣP : 360°), thus allowing a strong donation of the phosphorus lone pair into the $2p_\pi$ vacant orbital of the carbene. Thus, this compound can be described as a λ^4 -phosphavinylidene, as found in the noncyclic silyl(phosphino)carbene of Bertrand and co-workers.^[12] A very long C1–Ge1 bond (2.05 Å) was determined (standard Ge–C bond lengths: $1.95\text{--}1.98 \text{ Å}$ ^[13]). This lengthening is due to stabilizing interactions between the $\sigma_{\text{Ge1C8}}/\sigma_{\text{Ge1C23}}$ and the σ^*_{Ge1C1} orbitals, as confirmed by NBO analysis^[14] (sum of stabilizing interactions: about 5 kcal mol^{-1}).

NBO analysis also shows other interactions that allow an electronic stabilization of the carbene. Indeed, interaction between the σ_{Ge1C7} orbital and the antiperiplanar σ^*_{P1C27} orbital is large in magnitude (ca. 18 kcal mol^{-1}), probably owing to ring constraint.^[15] Moreover, the carbon lone pair n^{C7} interacts with the vicinal σ^*_{P1C2} orbital (ca. 15 kcal mol^{-1}), the $\pi_{\text{C1=C2}}$ orbital with the $\pi^*_{\text{C7=P1}}$ orbital, and the $\pi_{\text{C7=P1}}$ orbital with the $\pi^*_{\text{C1=C2}}$ orbital (ca. 8 kcal mol^{-1}).

The energy profile for the cycloaddition reaction was calculated on model compounds (**1H** + dimethyl acetylenedicarboxylate) to lower calculation times.^[16] As previously observed for the real molecules, the formation of carbene **3H** is exothermic ($\Delta G = -20 \text{ kcal mol}^{-1}$; Figure 2) and non-reversible. Moreover, the geometrical parameters of **3H** are close to those of **3**.^[17] A transition state (TS) involving a syn

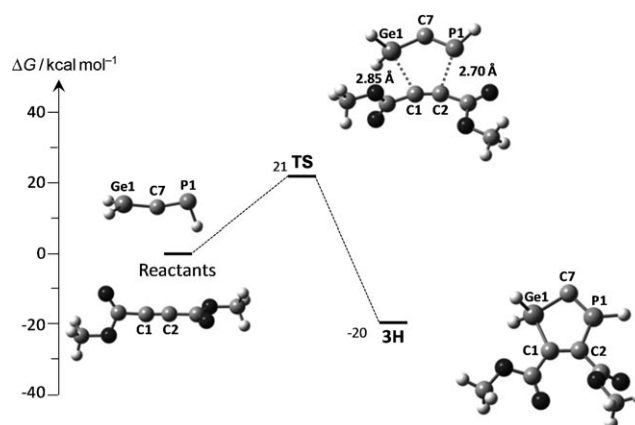


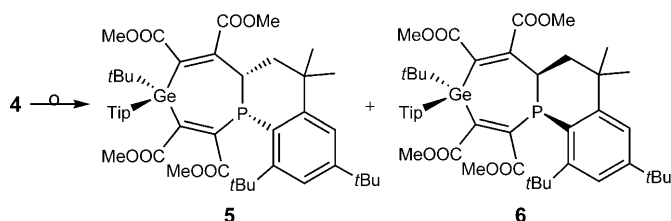
Figure 2. Energy profile for the [3+2] cycloaddition reaction involved in the formation of the carbene **3H** via the transition state **TS** from the parent compounds **1H** and MeOOC–C≡C–COOMe. H denotes the simplified forms of the molecules used in the calculations.

approach of the reactants has been found. Calculations predict that this five-center transition state is located 21 kcal mol^{-1} higher than the reactants. This TS has a planar structure with a large synchronous character: the forming Ge1–C1 and P1–C2 bond lengths are 2.85 and 2.70 Å , respectively (compared to 1.98 and 1.83 Å in **3H**) (see the Supporting Information for all molecular orbitals involved in this study, their shapes, and their energies). It is interesting to note the importance of the acetylene derivative involved. Indeed, with the bis(trifluoromethyl)acetylene, the reaction is exothermic ($-21 \text{ kcal mol}^{-1}$), as previously observed with the dicarboxylate compound, and the barrier has the same magnitude (ca. 20 kcal mol^{-1}). In contrast, the use of dimethylacetylene gives a weakly stabilized carbene (-9 kcal mol^{-1} ; see the Supporting Information). Consequently, electron-deficient alkynes seem necessary to stabilize the carbene.

Despite the theoretical results (electronic stabilization of the carbene, exothermic reaction), monitoring the reaction by ^{31}P NMR between -80°C and room temperature did not allow the transient carbene **3** to be characterized. The reason is that the insertion product **2** is more stable than the carbene **3**; this insertion reaction is certainly facilitated by the proximity between the carbenic carbon atom and the C–H bond of the *i*Pr group (3.18 Å between the two carbon atoms and 2.35 Å between carbon C7 and the H atom of the *i*Pr group).

To characterize the carbene **3**, a trapping experiment was performed. Due to its short lifetime, the trapping agent must be added to the phosphagermaallene solution before addition of dimethyl acetylenedicarboxylate, but the high reactivity of the Ge=C double bond of **1** complicates and limits the choice; the best trapping agent appeared to be the acetylenic derivative itself used in excess. Considering the frontier molecular orbital of the dimethyl acetylenedicarboxylate ($-1.50 \text{ eV}/\pi^*_{\text{C=C}} + \pi^*_{\text{C=O}}$ and $-7.87 \text{ eV}/\pi_{\text{C=C}} - \pi_{\text{C=O}}$ for the LUMO and HOMO respectively), and those of the carbene (LUMO: $-1.99 \text{ eV}/\pi^*_{\text{P=C}} + \pi^*_{\text{C=C}}$, HOMO: $-5.65 \text{ eV}/n^{\text{C7}}$), the latter could behave as a nucleophile, leading to a cyclopropanation adduct.

Thus, slow addition of phosphagermaallene **1** to two equivalents of dimethyl acetylenedicarboxylate at low temperature, led, along with about 10% of the derivative **2**, to the spiro compound **4** (Scheme 1). Compound **4** is stable in the solid state, but slowly decomposes in solution (Et_2O or pentane) to give two diastereoisomeric compounds **5** and **6** ($\delta^{31}\text{P}$: -36.2 and -18.5 ppm; Scheme 2), probably via a



Scheme 2. Decomposition reaction of **4**.

transient seven-membered ring phosphinocarbene (see the Supporting Information). Single crystals suitable for an X-ray determination have not been obtained; however, the structure of **4** was unambiguously shown by its physicochemical data: mass spectrometry ($m/z = 906$) and elemental analyses showed the presence of two molecules of acetylenic reagent for one of **1**, ^{13}C NMR spectra showed a quaternary carbon atom bonded to phosphorus ($\delta = 104.17$ ppm, $^1J_{\text{PC}} = 146.0$ Hz), two $\text{C}=\text{C}$ double bonds, and four different COOMe groups, and ^1H NMR spectra showed three isopropyl groups for the Tip group, thus excluding a similar cyclization observed in **2**. Although not yet observed with a $\text{C}\equiv\text{C}$ triple bond, rather similar trapping of silyl(phosphino)-carbene with $\text{C}=\text{C}$ double bonds of various electron-poor alkenes has already been reported.^[18]

In conclusion, this first example of a 1,3-dipole behavior of a heteroallene $\text{E}=\text{C}=\text{E}'$ is an important milestone in the chemistry of these cumulative doubly-bonded species and opens new perspectives in their use as building blocks in heterocyclic chemistry. Furthermore, a highly interesting access to heavy heteroatom containing cyclic carbenes has been opened. DFT calculations points out that this PGeHC is more stable than the starting compounds. Our research is now focused on the goal to find the right combination between heteroallenes and unsaturated systems for the isolation of stable heterocyclic carbenes of this type.

Experimental Section

2: Dimethyl acetylenedicarboxylate (1 mmol) dissolved in Et_2O (10 mL) was slowly added to a solution of phosphagermaallene (**1**, 1 mmol)^[4c] in Et_2O (20 mL) cooled to -80°C . A brown coloration appeared after warming to room temperature. The solvents were removed under reduced pressure and replaced by pentane (30 mL), and LiF was removed by filtration. After concentration of the filtrate, white crystals of **2** (0.55 g, 72%, m.p. 153°C) were obtained by cooling the pentane solution to -20°C . ^1H NMR (300.13 MHz, CDCl_3): $\delta = 2.63$ (d, $^2J_{\text{PH}} = 6.0$ Hz, 1H, $\text{CH}-\text{P}$), 3.61 and 3.75 ppm (2s, $2 \times 3\text{H}$, COOCH_3); ^{13}C NMR (75.47 MHz, CDCl_3): $\delta = 49.96$ (d, $^1J_{\text{CP}} = 33.2$ Hz, $\text{CH}-\text{P}$), 51.68 and 51.91 (COOCH_3), 134.66 (d, $^2J_{\text{CP}} = 31.5$ Hz, $\text{GeC}=\text{C}$), 166.61 (d, $^1J_{\text{CP}} = 44.8$ Hz, $\text{PC}=\text{C}$); 168.65 (d,

$^2J_{\text{CP}} = 2.7$ Hz, PCCOOCH_3), 168.88 ppm (GeCCOOCH_3); ^{31}P NMR (121.51 MHz, CDCl_3): $\delta = 15.35$ ppm.

4: A solution of phosphagermaallene **1** (1 mmol) in Et_2O (20 mL) was added to a solution of two equivalents of dimethyl acetylenedicarboxylate dissolved in Et_2O (10 mL) cooled to -80°C . The reaction mixture was slowly warmed to room temperature and turned brown in color. The solvents were removed under reduced pressure and replaced by 30 mL of pentane, and LiF was removed by filtration. After concentration to 5 mL, light brown crystals of **4** (0.73 g, 81%, mp 147°C) were obtained by cooling the pentane solution to -20°C . ^1H NMR (300.13 MHz, CDCl_3): $\delta = 2.90, 3.68, 3.78, 3.84$ ppm (4 s, $4 \times 3\text{H}$, COOCH_3); ^{13}C NMR (75.47 MHz, CDCl_3): $\delta = 51.40, 51.66, 51.75$, and 52.18 (COOCH_3), 104.17 (d, $^1J_{\text{CP}} = 146.0$ Hz, GeCP), 114.95 (d, $J_{\text{CP}} = 9.9$ Hz), 124.29 (d, $J_{\text{CP}} = 45.8$ Hz), 145.57 (d, $J_{\text{CP}} = 20.1$ Hz) and 152.20 (d, $J_{\text{CP}} = 34.9$ Hz) ($\text{C}=\text{C}$), 160.15 (d, $J_{\text{CP}} = 7.6$ Hz), 165.41 (d, $J_{\text{CP}} = 10.0$ Hz), 170.87 (d, $J_{\text{CP}} = 15.6$ Hz), 173.02 ppm (d, $J_{\text{CP}} = 3.2$ Hz) (COOCH_3); ^{31}P NMR (121.51 MHz, CDCl_3): $\delta = -34.71$ ppm (d, $^4J_{\text{PH}} = 6.2$ Hz).

For crystal data for **2**, **5**, and **6**, see the Supporting Information. CCDC 777357 (**2**), 777358 (**5**), and 777359 (**6**) 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.

Received: May 19, 2010

Revised: July 2, 2010

Published online: September 10, 2010

Keywords: carbenes · 1,3-dipoles · germanium · heteroallenes · phosphorus

- [1] For reviews on heteroallenes, see a) J. Escudié, H. Ranaivonjatovo, L. Rigon, *Chem. Rev.* **2000**, *100*, 3639–3696; b) B. Eichler, R. West, *Adv. Organomet. Chem.* **2001**, *46*, 1–46; c) J. Escudié, H. Ranaivonjatovo, *Organometallics* **2007**, *26*, 1542–1559; d) R. Appel in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**, pp. 157–219; e) M. Yoshifuji, *J. Chem. Soc. Dalton Trans.* **1998**, 3343–3349.
- [2] Stable $\text{R}^1\text{R}^2\text{Si}=\text{C}=\text{CR}^3\text{R}^4$: a) G. Miracle, J. L. Ball, D. R. Powell, R. West, *J. Am. Chem. Soc.* **1993**, *115*, 11598–11599; b) M. Trommer, G. E. Miracle, B. E. Eichler, D. R. Powell, R. West, *Organometallics* **1997**, *16*, 5737–5747; c) B. E. Eichler, G. E. Miracle, D. R. Powell, R. West, *Main Group Met. Chem.* **1999**, *22*, 147–162; d) M. Ichinohe, T. Tanaka, A. Sekiguchi, *Chem. Lett.* **2001**, 1074–1075; e) S. Spirk, F. Belaj, J. H. Albring, R. Pietschnig, *Organometallics* **2010**, *29*, 2981–2986.
- [3] Stable $\text{R}^1\text{R}^2\text{Ge}=\text{C}=\text{CR}^3\text{R}^4$: a) B. E. Eichler, D. R. Powell, R. West, *Organometallics* **1998**, *17*, 2147–2148; B. E. Eichler, D. R. Powell, R. West, *Organometallics* **1999**, *18*, 540–545; b) K. Kishikawa, N. Tokitoh, R. Okazaki, *Organometallics* **1997**, *16*, 5127–5129; c) N. Tokitoh, K. Kishikawa, R. Okazaki, *Chem. Lett.* **1998**, 811–812.
- [4] a) Transient $\text{R}^1\text{R}^2\text{Si}=\text{C}=\text{PR}^3$: L. Rigon, H. Ranaivonjatovo, J. Escudié, A. Dubourg, J.-P. Declercq, *Chem. Eur. J.* **1999**, *5*, 774–781; b) Transient $\text{R}^1\text{R}^2\text{Ge}=\text{C}=\text{PR}^3$: H. Ramdane, H. Ranaivonjatovo, J. Escudié, S. Mathieu, N. Knouzi, *Organometallics* **1996**, *15*, 3070–3075; c) stable $\text{R}^1\text{R}^2\text{Ge}=\text{C}=\text{PR}^3$: Y. El Harouch, H. Gornitzka, H. Ranaivonjatovo, J. Escudié, *J. Organomet. Chem.* **2002**, *643–644*, 202–208.
- [5] The only exceptions are the phosphallenes $\text{RP}=\text{C}=\text{X}$, which react sometimes by the phosphorus lone pair (1acde), and SiCN (6ab) derivatives, which can behave as silylenes $>\text{Si}$ and isocyanides $\text{C}=\text{NR}$ owing to their intermediary structure between azasilaallenes $\text{R}^1\text{N}=\text{C}=\text{SiR}^2\text{R}^3$ and silylene–isonitrile

- complexes $R^1N=C \rightarrow SiR^2R^3$. The same phenomenon has been reported for the $SnCN$ analogues.^[6c]
- [6] a) N. Takeda, H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, *J. Am. Chem. Soc.* **1997**, *119*, 1456–1457; b) T. Abe, T. Iwamoto, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **2006**, *128*, 4228–4229; c) H. Grützmacher, S. Freitag, R. Herbst-Irmer, G. M. Sheldrick, *Angew. Chem.* **1992**, *104*, 459; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 437–438.
- [7] D. Martin, A. Baceiredo, H. Gornitzka, W. W. Schoeller, G. Bertrand, *Angew. Chem.* **2005**, *117*, 1728–1731; *Angew. Chem. Int. Ed.* **2005**, *44*, 1700–1703.
- [8] Reviews: a) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704–724; b) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731–1770; c) F. Kakiuchi, S. Murai, *Acc. Chem. Res.* **2002**, *35*, 826–834; d) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633–639.
- [9] Gaussian09 (Revision A.02): M. J. Frisch et al. (see the Supporting Information).
- [10] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
- [11] The triplet state lies 22.6 kcal mol^{−1} higher in energy.
- [12] T. Kato, H. Gornitzka, A. Baceiredo, A. Savin, G. Bertrand, *J. Am. Chem. Soc.* **2000**, *122*, 998–999.
- [13] a) K. M. Baines, W. G. Stibbs, *Coord. Chem. Rev.* **1995**, *145*, 157–200; b) C. E. Holloway, M. Melnik, *Main Group Met. Chem.* **2002**, *25*, 185–266.
- [14] a) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926; b) J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218.
- [15] NBO calculations on the non-cyclic carbene did not show this stabilizing interaction. The presence of a cycle favors a better orbital overlap.
- [16] This mechanism does not take into account steric effects. It should be noted that the reintroduction of the real substituents into the TS structure calculated for the parent compound shows that the steric hindrance should not significantly modify the approach between **1** and the acetylene derivative.
- [17] In a previous work, calculations have shown that the geometric and electronic structures of **1** and **1H** were similar: F. Ouhsaine, E. André, J. M. Sotiropoulos, J. Escudié, H. Ranaivonjatovo, H. Gornitzka, N. Saffon, K. Miqueu, M. Lazraq, *Organometallics* **2010**, *29*, 2566–2578.
- [18] a) J. Krysiak, C. Lyon, A. Baceiredo, H. Gornitzka, M. Mikolajczyk, G. Bertrand, *Chem. Eur. J.* **2004**, *10*, 1982–1986; b) J. Krysiak, T. Kato, H. Gornitzka, A. Baceiredo, M. Mikolajczyk, G. Bertrand, *J. Org. Chem.* **2001**, *66*, 8240–8242; c) S. Goumri-Magnet, T. Kato, H. Gornitzka, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **2000**, *122*, 4464–4470.