STUDIA UBB CHEMIA, LVII, 2, 2012 (p. 119 - 127)

NOVEL PHOSPHAGERMAPROPENES, PRECURSORS FOR HETEROALLENES STABILIZED THROUGH INTRAMOLECULAR COORDINATION

PETRONELA M. PETRAR[a], RALUCA SEPTELEAN[a], AGOTA BARTOK[a], NOEMI DEAK[a], GABRIELA NEMES[a]

ABSTRACT. Potential precursors of phosphagermaallenes based on the use of dimethyl-benzyl-amine as a substituent on the group 14 element were designed. The proper orientation of the lone pair on the nitrogen towards the germanium atom could enhance the electron density around the germanium, thus stabilizing the –P=C=Ge< unit. Three novel phosphagermapropenes have been obtained and evidenced through NMR spectroscopy. The solid state structure of a novel organometallic germanium derivatives is also discussed.

Keywords: *phosphagermapropenes, heteroallenes, 2-substituted (N,N-dimethyl-aminobenzyl ligands, organogermanium derivatives*

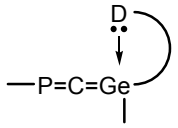
INTRODUCTION

The synthesis of compounds in which two, or even three carbon atoms of an allene are formally replaced by heavier elements of group 14 or 15, has constituted a new challenge in organometallic chemistry [1-4]. Due to the presence of two unsaturations, such heteroallenes were thought to possess a rich and versatile chemistry and to be very useful building blocks in organometallic chemistry.

Unlike the 1,3-dimetallaallenes $>E_{14}=C=E_{14}<$, their phosphorus counterparts, 1,3-phosphametallaallenes $–P=C=E_{14}<$, have been experimentally investigated [5]. The recent studies reveal that for the stabilization of the P=C=Ge framework a greater steric shielding is required [6]. This was achieved by grafting bulky organic groups on the germanium atom. The 1,3-phosphagermaallene Mes*P=C=GeTip(*t*Bu) (Tip=2,4,6-tri-*iso*-propyl-phenyl), the first stable heteroallene that contains two heavy double-bonded group 14 and 15 elements, was obtained quantitatively as an orange solid by the dehalogenation of dihalophosphagermapropene with *tert*-butyllithium at -80 °C [5c].

[a] "Babeş-Bolyai" University of Cluj-Napoca, Faculty of Chemistry and Chemical Engineering, Arany Janos Street 11, 400028 Cluj-Napoca, Romania

While exploring new ways to further stabilize the -P=C=Ge< unit in phosphagermaallenes, we have envisaged the increase of the electron density on the germanium atom through its coordination with an electron-donor atom (scheme 1). The electronic influence, combined with the steric hindrance afforded by the coordinating atom can be enhanced by a chelate effect.

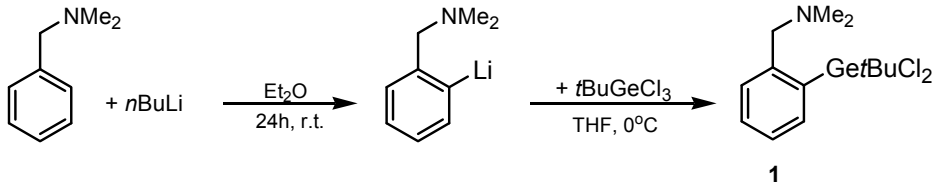


Scheme 1

This can be attained by functionalizing the germanium precursor with a pendant arm ligand containing a nitrogen atom as the electron-donor atom and it has already been used in the stabilization of various doubly-bonded compounds of germanium such as germathiones >Ge=S [7], germaselones >Ge=Se [8] and germatellones >Ge=Te [8].

RESULTS AND DISCUSSIONS

In order to obtain new products containing stable P=C-Ge or P=C=Ge units, the dimethyl-benzylamine group can be employed as a pendant arm ligand. To this purpose the synthesis of 2-(*tert*-butyldichlorogermyl)phenyl)-*N,N*-dimethylmethanamine **1** has been carried out through the series of reactions represented in scheme 2. The *ortho*-lithium N,N-dimehyl-benzylamine was first prepared according to the method of Noltes [9]. The selectivity of the *ortho*-lithiation was explained by a strong coordination between the nitrogen and lithium atoms. Addition to *t*BuGeCl$_3$ [10] afforded **1** in a good yield.



1

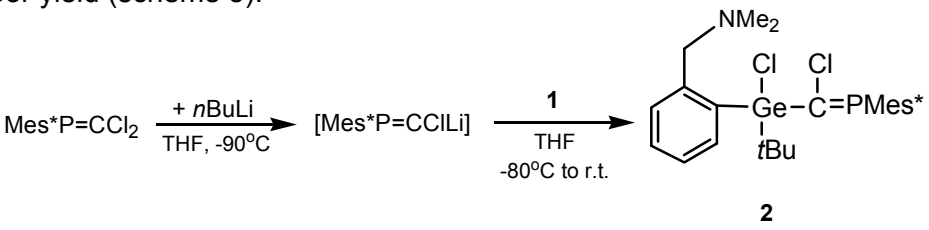
Scheme 2

A by-product of the reaction depicted in scheme 2 was the germane ($Me_2NCH_2C_6H_4)_2$(*t*Bu)GeCl **4**, for which the solid state structure was determined and will be discussed herein.

Derivative **1** was characterized through its proton and carbon NMR spectra. From the available data, it was impossible to determine if the nitrogen atom was coordinated to the germanium atom since in both cases

(coordination or lack of thereof) the two Me group and the two methylenic protons are equivalent.

Reaction of the dichlorogermane **1** with the lithium derivative of $Mes^*P=CCl_2$ at low temperature led to the phosphagermapropene **2** in a poor yield (scheme 3).



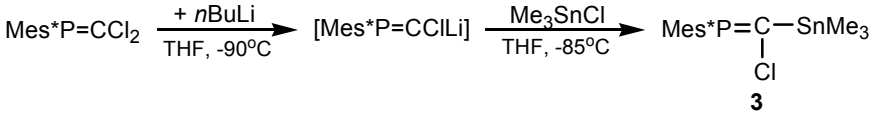
2

Scheme 3

One of the major by-products was Mes*P=C(Cl)H, due to the final hydrolysis of Mes*P=C(Cl)Li which had not reacted with **1**. The formation of **2** was evidenced through ^{31}P NMR spectroscopy. The signal appears at 300.4 ppm, as expected for a phosphagermapropene, along with the characteristic peak for Mes*P=C(Cl)H, in a 3.6:1 ratio. Although attempts to isolate compound **2** failed, its ^{1}H NMR spectrum shows a broad signal for the methylene protons on the pendant arm indicating in this case the coordination of the nitrogen atom to the germanium.

The N→Ge coordination should be less favorable in **2** than **1** for two reasons: the greater steric congestion which can prevent the approach of the NMe_2 moiety and the less electrophilic character of the germanium atom substituted by only one chlorine atom instead of two. As the coordination was proved in the case of **2**, we can reasonably postulate that such coordination also exists in **1** [11].

An alternative synthetic route involved the preparation of Mes*P=C($SnMe_3$)Cl **3**, as indicated in scheme 4, to obtain the phosphagermaallene precursor Mes*P=C($SnMe_3$)-Ge($Me_2NCH_2C_6H_4$)(*t*Bu)Cl. The latter could eliminate Me_3SnCl to afford the P=C=Ge unit without using a lithium compound.

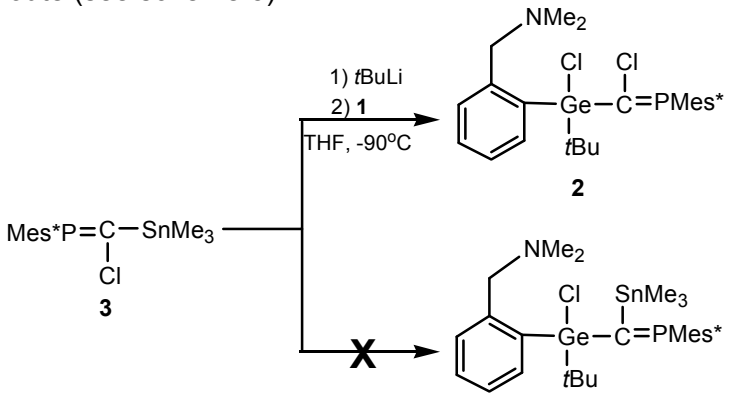


3

Scheme 4

Mes*P=C($SnMe_3$)Cl **3** was evidenced by ^{31}P NMR (with a chemical shift at 280.5 ppm) and the resulting reaction mixture was used without further purification. Treatment with *t*BuLi and the subsequent addition of ($Me_2NCH_2C_6H_4$)(*t*Bu)$GeCl_2$ does not lead to the expected stannylated-

phosphagermapropene, but affords a mixture of **2** and Mes*P=C(Cl)H, in about the same ratio as observed in the case of the previously described synthetic route (see scheme 5).



Scheme 5

The formation of **2** can be explained by the preliminary cleavage reaction of the weak C-Sn bond by *t*BuLi, leading to Me_3SnBu and Mes*P=C(Cl)Li followed by the subsequent reaction with **1** and/or hydrolysis.

Study of germane $(Me_2NCH_2C_6H_4)_2tBuGeCl$ 4

The structure of compound **4**, obtained as a by-product in the reaction between $C_6H_4(Li)CH_2NMe_2$ and $tBuGeCl_3$, was determined by X-ray diffraction (figure 1), showing that two halogen atoms of *t*BuGeCl$_3$ have been replaced by two $Me_2NCH_2C_6H_4$ moieties. The Ge(1)-C(1) (1.919(11) Å) and Ge(1)-C(10) (1.931(10) Å) distances lie in the normal range for such bonds between a germanium atom and the *ipso*-carbon of an aromatic ring. By contrast, the Ge(1)-C(19) distance was slightly elongated to 1.993(14) Å) due to the steric hindrance of the *t*Bu group.

The most interesting feature was the presence of a distorted tetrahedral geometry around the germanium atom: the sum of angles C(1)Ge(1)C(10), C(1)Ge(1)C(19) and C(10)Ge(1)C(19) was 350.5°, not too far from 360° for a planar geometry. In a tetrahedral structure, the sum of these angles should be 327.7°. The distance of the Ge atom to the C(1)C(10)C(19) plane was only 0.35 Å. Thus, the four atoms C(1), C(10), C(19) and Ge(1) are roughly in a plane. The Ge(1)-Cl(1) bond length (2.253 Å) is slightly elongated compared to standard Ge-Cl distances (2.09 to 2.21 Å) [14b]. The nitrogen atom N(1) is far from the germanium atom (4.724 Å), but the nitrogen atom N(2) is closer (3.107 Å). Even if the distance is long for an interaction between the Ge and N(2) atoms, the elongated Ge-Cl bond and the tendency to a planar geometry for the GeC_3 skeleton are in agreement with a weak coordination.

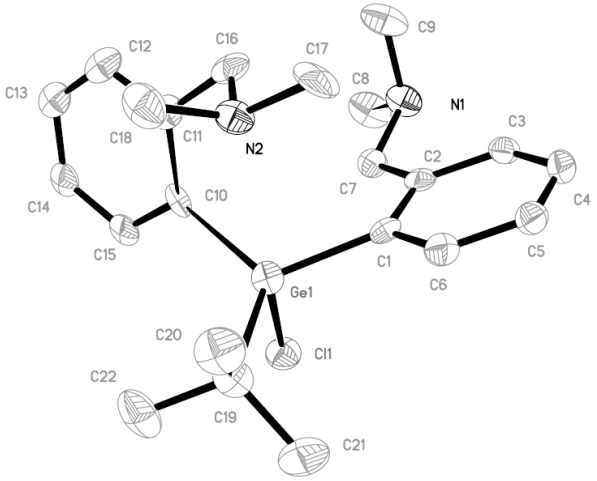


Figure 1. Molecular structure of **4** (thermal ellipsoids drawn at the 50% probability level); hydrogen atoms are omitted for clarity; selected bond lengths (Å) and angles (°).

Ge(1)-C(10): 1.919(11); Ge(1)-C(1): 1.931(10); Ge(1)-C(19): 1.993(14); Ge(1)-Cl(1) 2.253(4); C(2)-C(7): 1.515(14); C(7)-N(1): 1.451(16); C(11)-C(16): 1.517(15); C(16)-N(2); 1.473(14); C(10)-Ge(1)-C(1): 117.5(5); C(10)-Ge(1)-C(19): 117.3(5); C(1)-Ge(1)-C(19): 115.7(5); C(10)-Ge(1)-Cl(1): 100.6(4); C(1)-Ge(1)-Cl(1): 100.8(3); C(19)-Ge(1)-Cl(1): 99.6(4); Ge(1)-N(1): 4.724; Ge(1)-N(2): 3.107.

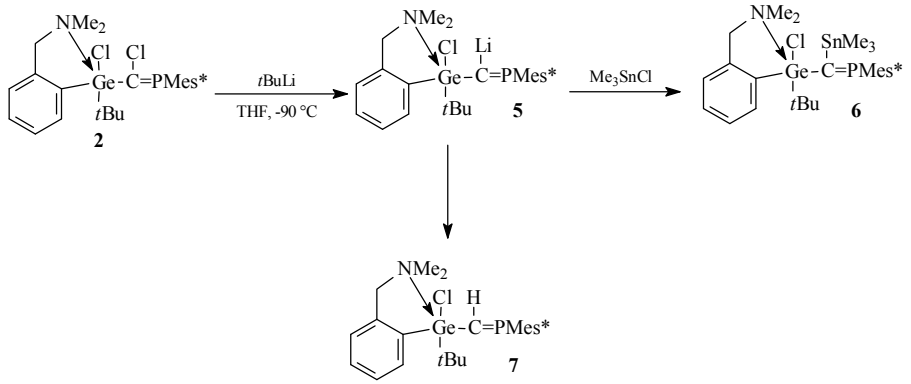
Action of tBuLi on derivative 2

The reaction of **2** with *tert*-butyllithium was followed by ^{31}P NMR techniques. After the addition of the lithium reagent and warming up to room temperature, the signal corresponding to the phosphagermapropene **2** disappears and two other peaks appear at 403.3 and 322.2 ppm (d, J_{PH} = 24.85 Hz). The more deshielded signal at 403 ppm could reasonably be assigned to the lithium compound **5** (scheme 6), stabilized by a possible interaction with the amino group (such a deshielded signal like the one at 441.4 ppm was observed in a phosphasilapropenyl derivative with a similar structure Mes*P=C(Li)SiCl [12].

When the reaction mixture was kept under an inert atmosphere, the amount of the compound corresponding to the signal at 322 ppm increased.

Although attempts to separate the mixture and further analyze the two derivatives are still in progress, we have assigned the signal at 322 ppm to **7**, the hydrolysis product of **5**, which can also be used as a precursor in the synthesis of the desired phosphagermaallene.

Subsequent treatment of **5** with Me_3SnCl led to the shift of the signal to a higher field (392.6 ppm), which could be explained by the formation of **6** (scheme 6).



Scheme 6

A signal at this field was characteristic of a Mes*P=C derivative, with two electropositive groups on the doubly bonded carbon atom. For example Mes*P=C($SiMe_3$)$_2$ with two $SiMe_3$ group which have about the same electronic proprieties as Me_3Sn and R(*t*Bu)ClGe gives a signal at 393 ppm [13] and the rather similar derivative Mes*P=C($SnMe_3$)$_2$ gives a signal at 386.7 ppm [14].

Heating **5** or **6** to get the expected phosphagermaallene by elimination of LiCl or Me_3SnCl was unsuccessful. However, new attempts will be made using other solvents or involving heating in a sealed tube.

CONCLUSIONS

Several routes to obtain phosphagermaallenes stabilized through electronic effects induced by the presence of a pendant arm ligand on the germanium atom were investigated. The increased reactivity of the phosphagermapropenes and their lithium derivatives leads to poor yields and the reaction parameters are yet to be perfected, but three novel precursors in the synthesis of phosphagermaallenes, Mes*P=C(Cl)Ge(Me_2NR)*t*BuCl **2**, Mes*P=C($SnMe_3$)Ge(Me_2NR)*t*BuCl **6** and Mes*P=C(H)-Ge(Me_2NR)*t*BuCl **7** (R=$CH_2C_6H_4$) have been obtained and evidenced through NMR spectroscopy. A new organometallic derivative of germanium, ($Me_2NCH_2C_6H_4$)$_2$*t*BuGeCl **4**, has also been characterized and its structure in solid state has been determined through X-ray diffraction.

EXPERIMENTAL PART

General procedures

All experiments were carried out in flame-dried glassware under an argon atmosphere using high-vacuum-line techniques. Solvents were dried and freshly distilled on drying agents and carefully deoxygenated on a

vacuum line by several “freeze-pump-thaw” cycles. NMR spectra were recorded in $CDCl_3$ on the following spectrometers: ^{1}H, Bruker Avance 300 (300.13 MHz) and Avance 400 (400.13 MHz); $^{13}C\{^{1}H\}$, Bruker Avance 300 (75.47 MHz) and Avance 400 (100.62 MHz) (reference TMS), ^{31}P, Bruker AC200 at 81.02 MHz (reference H_3PO_4). Melting points were determined on a Wild Leitz-Biomed apparatus. Mass spectra were obtained on a Hewlett-Packard 5989A spectrometer by EI at 70 eV.

Synthesis of 2-(tert-butyldichlorogermyl)phenyl)-N,N-dimethylmethan-amine 1

To 4.5 ml (4 g, 29 mmol, 10% excess) of $PhCH_2NMe_2$ in 30 ml of ether, 16.25 ml *n*BuLi 1.6 M (26 mmol) were added dropwise and then the reaction mixture was stirred at room temperature for 24 hours, when a white precipitate appeared, and then it was cooled down to 0 °C. A solution of 6.25 g of *t*BuGeCl_3 (26 mmol) in 40 ml of THF was cooled to 0 °C and then cannulated drop by drop to the lithium derivative of the amine. The mixture was allowed to react for ½ hours and then the solvents were removed under vacuum and replaced with 40 ml of pentane. Lithium salts were separated by filtration and the solution was stored at -25 °C for 24 hours. The solution was concentrated until **1** precipitates as a white solid (7 g, η = 60 %).

δ **^{1}H** (300 MHz): 1.33 (s, 9H, *t*Bu, C($\underline{C}H_3$)$_3$); 2.17 (s, 6H, methyl, $\underline{C}H_3$); 3.61 (s, 2H, methylene, $\underline{C}H_2$); 7.39-8 (m, 4H, arom H)

δ **^{13}C** (75.5 MHz): 27.08 (*t*Bu, C($\underline{C}H_3$)$_3$) 38.26(*t*Bu, $\underline{C}$(CH_3)$_3$); 45.35 (Me, $\underline{C}H_3$); 63.43(methylene, $\underline{C}H_2$); 127.30-144.84 (arom C)

Transparent crystals are obtained from the pentane solution stored at room temperature and were later identified by X-ray crystallography as derivative **4**.

δ **^{1}H** (300 MHz, C_6D_6): 1.48 (s, 9H, *t*Bu, C($\underline{C}H_3$)$_3$), 1.70 (s, 12H, N$\underline{C}H_3$), 2.92 (d, 2H, $\underline{C}H_2$, $^{2}J_{HH}$ = 12 Hz), 3.26 (d, 2H, $\underline{C}H_2$, $^{2}J_{HH}$ = 12 Hz), 7.15-7.20, 8.13-8.19 (broad signals, 8H, arom H)

Synthesis of ($Me_2NCH_2C_6H_4$)tBuGe(Cl)C(Cl)=PMes 2*

To 2.6 g (7.2 mmol) of Mes*P=CCl_2 in 40 mL of THF cooled at -95 °C, 4.95 mL of *n*BuLi 1.6 M in hexane (10% excess) were added dropwise. The reaction mixture was stirred at low temperature (-75 °C) for 45 minutes. A solution of 2.4 g of **1** in 30 ml of THF was cannulated slowly on to the lithium derivative, after it had been previously cooled down to -70 °C. The reaction mixture was then allowed to gradually warm up to room temperature and THF was removed under vacuum. Replacement with pentane allowed for the precipitation and separation of the lithium salts. ^{31}P-NMR spectra indicates the formation of **2**, which could not be separated from the by-product Mes*P=CHCl. The estimated yield (in ^{31}P NMR) was 40%.

δ **^{31}P** (121.5 MHz): 300.3 ppm

*Attempted Synthesis of ($Me_2NCH_2C_6H_4$)tBuGe(Cl)C($SnMe_3$)=PMes**

To a solution of 2.6 ml of Mes*P=CClLi in 20 ml THF, prepared as described above, 10 ml of a THF solution of Me_3SnCl_2 (0.52 g, 2.6 mmol) were added dropwise at -70 °C. The resulting mixture was used without any further purification; as Mes*PCCl($SnMe_3$) was identified by ^{31}P NMR to form in almost quantitative yield. 2 ml of *t*BuLi 1.5M in hexane were then added at low temperature and after 15 minutes, 0.9 g (2.6 mol) of **1** in 15 ml THF were cannulated. The solution was allowed to slowly warm up at room temperature. The formation of the expected Mes*P=C($SnMe_3$)Ge($Me_2NCH_2C_6H_4$)(Cl)*t*Bu was not evidenced, instead, derivative **1** was formed (δ^{31}**P** :300.3 ppm).

Action of tBuLi on 2

To the THF solution of a mixture of **2** and Mes*P=CHCl (1.55 g, in a 3.6:1 molar ratio), 2 ml *t*BuLi 1.5M in pentane were added at -90 °C. The solution was allowed to warm up to room temperature, and then the reaction products were characterized by ^{31}P-NMR and the lithium derivative **5** was assigned the peak at 403 ppm. At room temperature, only the hydrolysis product of the lithioderivative, compound **7**, was observed in phosphorus NMR (δ ppm: 322.2 ppm (d, J_{PH} = 24.85 Hz)). Upon adding an excess of Me_3SnCl to a sample solution of **5**, the signal shifted at higher fields, which was consistent with the formation of **6**.
δ^{31}**P** (121.5 MHz): 147 ppm

ACKNOWLEDGEMENTS

The authors wish to thank Dr Jean Escudié for useful discussions. R.S. thanks CNCSIS for funding through project PD-438. A.L. is funded by a Ph.D. scholarship through contract no. POSDRU/88/1.5/S/60185 **–** "Innovative Doctoral Studies in a Knowledge Based Society" Babeş-Bolyai University, Cluj-Napoca, Romania.

N.D. thanks Babeş-Bolyai University for the awarded scholarship**.**

REFERENCES

[1] J. Escudié, H. Ranaivonjatovo, *Organometallics*, **2007**, *26,* 1542.

[2] For reviews on heteroallenes, see refs: (a) J. Escudié, H. Ranaivonjatovo, L. Rigon, *Chem. Rev.,* **2000**, *100*, 3639. (b) B. Eichler, R. West, *Adv. Organomet. Chem.,* **2001**, *46*, 1. (c) M. Yoshifuji, K. Toyota, in *The Chemistry of Organosilicon Compounds*; Z. Rappoport, Y. Apeloig, Eds.; Wiley: Chichester, U.K., **2001**; Vol. 3, p. 491. (d) J. Escudié, H. Ranaivonjatovo, M. Bouslikhane, Y. El Harouch, L. Baiget, G. Cretiu Nemes, *Russ. Chem. Bull.,* **2004**, *53*, 1020.

[3] R. Appel, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Georg Thieme Verlag: Stuttgart, Germany, **1990**, p. 157.

[4] J. Escudié, G. Nemes, *Comptes Rendus Chimie*, **2010**, *13*, 954.

[5] (a) L. Rigon, H. Ranaivonjatovo, J. Escudié, A. Dubourg, J.-P. Declercq, *Chem. Eur. J.,* **1999**, *5*, 774. (b) H. Ramdane, H. Ranaivonjatovo, J. Escudié, S. Mathieu, N. Knouzi, *Organometallics,* **1996**, *15*, 3070. (c) Y. El Harouch, H. Gornitzka, H. Ranaivonjatovo, J. Escudié, *J. Organomet. Chem.,* **2002**, *643-644*, 202.

[6] D. Ghereg, E. Andre, H. Gornitzka, J. Escudie, F. Ouhsaine, N. Saffon, K. Miqueu, J.M. Sotiropoulos, *Chem. Eur. J.*, **2011**, *45*, 12763. (b) D. Ghereg, H. Gornitzka, J. Escudie, *Eur. J. Inorg. Chem.*, **2011**, *2*, 281. (c) D. Ghereg, H. Gornitzka, J. Escudie, S. Ladeira, *Inorg. Chem.*, **2010**, *49*, 10497. (e) G. Dumitru, E. Andre, J. M. Sotiropoulos, K. Miqueu, H. Gornitzka, J. Escudie, *Angew. Chem. Int. Ed. Engl.*, **2010**, *49*, 8704. (f) P.M. Petrar, G. Nemes, I. Silaghi-Dumitrescu, H. Ranaivonjatovo, H. Gornitzka, J. Escudie, *Chem. Commun.*, **2007**, 4149.

[7]. a) W.-P. Leung, K.-H. Chong, Y.-S. Wu, C.-W. So, T.C.W. Mak, *Eur. J. Inorg. Chem.*, **2006**, *4*, 808. (b) W.-P. Leung, K.-H. Chong, Z.-Y. Zhou, T.C.W. Mak, *Organometallics*, **2000**, *19*, 293. (c) M. Veith, A. Rammo, Z. *Anorg. Allg. Chem.*, **1997**, *623*, 861.

[8] G. Ossig, A. Meller, C. Brönneke, O. Müller, M. Schafer, R. Herbst-Irmer, *Organometallics*, **1997**, *16*, 2116.

[9] G. Van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, W.M.G.F. Pontenagel, J. Kroon, A.L. Spek, *J. Am. Chem. Soc.*, **1978**, *100*, 5021.

[10]. H. Puff, S. Franken, W. Schuh, W. Schwab, *J. Organomet. Chem.*, **1983**, *254*, 33.

[11] C. Brelière, F. Carré, R.J.P. Corriu, A. De Saxce, M. Poirier, G. Royo, *J. Organomet. Chem.*, **1981**, *205*, C1.

[12] G. Nemes, H. Ranaivonjatovo, J. Escudié, I. Silaghi-Dumitrescu, L. Silaghi-Dumitrescu, H. Gornitzka, *Eur. J. Inorg. Chem.*, **2005**, 1109.

[13] A.H. Cowley, R.A. Jones, J.G. Lasch, N.C. Norman, C.A. Stewart, A.L. Stuart, J.L. Atwood, W.E. Hunter, H.-M. Zhang, *J. Am. Chem. Soc.*, **1985**, *106*, 7015.

[14] S.I. Goede, F. Bickelhaupt, *Chem. Ber.*, **1991**, *124*, 2677.