Novel Heteroleptic Germanium(II) Compounds from [2,4-Di-*tert*-butyl-6-((dimethylamino)methyl)phenyl]germanium Chloride: Synthesis, Structure, and Derivatization

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The synthesis of novel heteroleptic germanium(II) compounds starting from [2,4-di-*tert*-butyl-6-((dimethylamino)methyl)phenyl]germanium chloride, MamxGeCl (**1**), is reported. **1** reacts with potassium alkoxides to give the alkoxy-substituted compounds MamxGeO-*t*-Bu (**2**), MamxGeO-*i*-Pr (**3**), MamxGeOEt (**4**), and MamxGeOMe (**5**). The ethynyl-substituted species MamxGe(C≡CPh) (**6**) and MamxGe(C≡CH) (**7**) are obtained by the reaction of **1** with LiC≡CPh and NaC≡CH, respectively. The alkyl-substituted germanium(II) species MamxGeR (R = *t*-Bu (**8**), *n*-Bu (**9**), Me (**10**)) are formed by the reaction of **1** with the corresponding alkyllithium compounds. Derivatization of **8**−**10** with MeI leads to the formation of compounds containing the germyl cations [MamxGe(*t*-Bu)(Me)]$^+$ (**11a**), [MamxGe(*n*-Bu)(Me)]$^+$ (**12a**), and [MamxGe(Me)$_2$]$^+$ (**13a**), respectively. All new species have been characterized by NMR, MS, and microanalytical data. X-ray crystal structure determinations are presented for **3, 4, 6, 7**, and **11**.

Introduction

The synthesis of stable germylenes—the germanium analogues of the carbenes—has attracted much attention over the last 20 years.[1] Germylenes having small substituents are unstable toward oligomerization. They can be stabilized kinetically by the use of bulky ligands and/or thermodynamically by donor substituents, which reduce the electron deficiency at the germanium(II) center. Up to now a rather large number of germanium(II) compounds has been isolated using these concepts.[2,3]

The 2,4-di-*tert*-butyl-6-((dimethylamino)methyl)phenyl ligand, abbreviated Mamx (Mamx = **m**ethyl**a**mino**m**ethyl-*m*-**x**ylyl), was introduced by Yoshifuji and coworkers in 1994.[4] This ligand combines the steric features of a supermesityl group[2c,e] and the electronic properties of the 2-((dimethylamino)methyl)phenyl system.[5] In 1998 we reported the first results concerning the application of this ligand in germanium chemistry.[6] The synthesis of the monomeric MamxGeCl (**1**) from GeCl$_2$·(dioxane) and 1 equiv of MamxLi as well as the treatment of **1** with various nucleophiles, leading to the formation of novel diarylgermanium(II) compounds, was described.

Here we report the synthesis and structural characterization of heteroleptic germanium(II) species containing the Mamx substituent and sterically unpretentious ligands, which are so far nearly unknown in the chemistry of monomeric germanium(II) compounds. We present the alkoxy-substituted compounds MamxGeO-*t*-Bu (**2**), MamxGeO-*i*-Pr (**3**), MamxGeOEt (**4**), and MamxGeOMe (**5**) as well as the ethynyl-substituted species MamxGe(C≡CPh) (**6**) and MamxGeC≡CH (**7**). Furthermore, we report on the synthesis of the alkyl-substituted germanium(II) compounds MamxGe-*t*-Bu (**8**), MamxGe-*n*-Bu (**9**), and MamxGeMe (**10**) and their derivatization with MeI under formation of the ionic compounds [MamxGe(*t*-Bu)(Me)]$^+$I$^-$ (**11**), [MamxGe(*n*-Bu)(Me)]$^+$I$^-$ (**12**), and [MamxGe(Me)$_2$]$^+$I$^-$ (**13**).

Results and Discussion

1. Germanium(II) Compounds with Small Alkoxy Substituents (MamxGeOR). Stabilization of alkoxy-

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[1] (1) See for example: (a) Rivière, P.; Rivière-Baudet, M.; Satgé, J. In *Comprehensive Organometalic Chemistry*; Pergamon: Oxford, U.K., 1982; Vol. 2, Chapter 10. (b) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311. (c) Barrau, J.; Rima, G. *Coord. Chem. Rev.* **1998**, *178*, 593.

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[3] (3) (a) Scibelli, J. V.; Curtis, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 924. (b) Jutzi, P.; Kohl, F.; Hofmann, P.; Krüger, C. Tsay, Y.-H. *Chem. Ber.* **1980**, *113*, 757. (c) Karsch, H. H. *Russ. Chem. Bull. (Engl. Transl.)* **1993**, *42*, 1937 and references cited therein. (d) Jutzi, P. Schmidt, H.; Neumann, B.; Stammler, H.-G. *J. Organomet. Chem.* **1995**, *499*, 7. (e) Dias, H. V. R.; Wang, Z. *J. Am. Chem. Soc.* **1997**, *119*, 4650. (f) Foley, S. R.; Bensimon, C.; Richeson, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 10359. (g) Ossig, G.; Meller, A.; Brönneke, C.; Müller, O.; Schäfer, M.; Herbst-Irmer, R. *Organometallics* **1997**, *16*, 2116. (h) Leung, W.-P.; Kwok, W.-H.; Weng, L.-H.; Law, L. T. C.; Zhou, Z. Y.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1997**, 4301. (i) Drohst, C.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J.-M. *J. Chem. Soc., Chem. Commun.* **1997**, 1141. (j) Karsch, H. H.; Schlüter, P. A.; Reisky, M. *Eur. J. Inorg. Chem.* **1998**, 433. (k) Benet, S.; Cardin, C. J.; Cardin, D. J.; Constantine, S. P., Heath, P.; Rashid, H.; Teixeira, S.; Thorpe, J. H.; Todd, A. K. *Organometallics* **1999**, *18*, 389.

[4] (4) Yoshifuji, M.; Kamijo, K.; Toyota, K. *Tetrahedron Lett.* **1994**, *35*, 3971.

[5] (5) (a) Corriu, P.; Lanneau, G.; Priou, C.; Soulairol, F.; Auner, N.; Probst, R.; Conlin, R.; Tan, C. *J. Organomet. Chem.* **1994**, *466*, 55. (b) Belzner, J.; Schär, D.; Kneisel, B. O.; Herbst-Irmer, R. *Organometallics* **1995**, *14*, 1840.

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10.1021/om990557r CCC: $18.00

Scheme 1

$$\mathbf{1} + \mathrm{NaOR} \xrightarrow[\text{15-crown-5}]{\text{toluene}} \mathrm{MamxGeOR} \quad (\mathbf{2}\text{-}\mathbf{5})$$

R = *t*-Bu (**2**)
i-Pr (**3**)
Et (**4**)
Me (**5**)

and aryloxygermylenes in a monomeric form has proved to be difficult, because the formation of dimers or polymers is favored.[7] Therefore, only a few monomeric alkoxy- and aryloxygermylenes have been reported in the literature,[8] and even fewer have been completely characterized. The first structurally characterized monomeric diaryloxygermylene, $Ge\{O(2,6\text{-}(t\text{-}Bu)_2\text{-}4\text{-}Me\text{-}C_6H_2\}_2$,[9] and dialkoxygermylene, $Ge\{OC(t\text{-}Bu)_3\}_2$, were reported by Lappert et al.[10] The synthesis of intramolecularly base stabilized aryloxygermylenes has been reported by Barrau et al. only recently.[1c,11]

Treatment of MamxGeCl (**1**) with an excess of the respective potassium alkoxide (1:4) in the presence of 15-crown-5 in toluene at ambient temperature led to the formation of the germanium(II) compounds MamxGeO-*t*-Bu (**2**), MamxGeO-*i*-Pr (**3**), MamxGeOEt (**4**), and MamxGeOMe (**5**) (Scheme 1).

After removal of the solvent and of the crown ether by distillation, the remaining compounds **2**−**5** were purified by sublimation in vacuo. They could be isolated in good yields as colorless powders, which are soluble in common organic aprotic solvents. In the absence of 15-crown-5, no reaction was observed. The high thermal stability of **2**−**5** is noteworthy. For example, the potentially most unstable germanium(II) compound **5** can be treated either in solution or as a solid at 80−100 °C for hours without decomposition.

Crystals suitable for an X-ray structure analysis of **3** and **4** were obtained from a *n*-hexane solution. The molecular structures of **3** and **4** are shown in Figures 1 and 2. Crystallographic data are given in Table 1; selected bond lengths and angles are presented in Table 2.

In the structures of **3** and **4**, the germanium atom is three-coordinate, forming one σ-bond to each substituent and an additional N→Ge donor bond. The $Ge-C_{aryl}$ bond length is 2.039(3) Å for **3** and 2.037(4) Å for **4**; typical $Ge^{II}-C_{\sigma}$ bond distances vary between 1.98 and 2.14 Å.[12] The Ge−O bond length is 1.856(2) Å in **3** and 1.844(3) Å in **4**; these values are in the same range as those observed in $Ge[OC(t\text{-}Bu)_3]_2$ (1.896(6) and 1.832(11) Å)[10] or in the aryloxygermylene $Ge[O(2,6\text{-}(t\text{-}Bu)_2\text{-}4\text{-}Me\text{-}(C_6H_2)]_2$ (1.802(8) and 1.812(7) Å).[9] The Ge−N bond length is 2.149(2) Å for **3** and 2.123(3) Å for **4**, which is slightly elongated in comparison to that for **1** (2.093(6) Å)[6] but shortened compared to the distances found for other base-stabilized germylenes such as $Cp{\wedge}GeCl$ (2.29 Å)[3d] and $Ge[2\text{-}\{(Me_3Si)_2C\}\text{-}C_5H_4N)]_2$ (2.27 Å).[3h] In **3** and **4**, the geometry at the germanium atom is worth mentioning. In both compounds the bond angles at the metal center are in the same range: The angle α ($C_{aryl}-Ge-N$) is 81.3° in **3** and 82.4° in **4**; the angles β ($C_{aryl}-Ge-OR$) and γ ($RO-Ge-N$) are nearly rectangular ($\beta \cong 93°$, $\gamma \cong 92°$). The degree of hybridization of the germanium atom can be inferred from these data; hence, it follows that the germanium atom in **3** and **4** is almost not hybridized. The lone pair occupies an orbital with high s character, and the σ-bonds to the ligands are formed by using p orbitals at the germanium center. The nitrogen atom of the coordinating amino side chain is oriented nearly perpendicular to the $C_{aryl}-Ge-O$-plane, allowing ideal interaction with the vacant Ge(p) orbital.

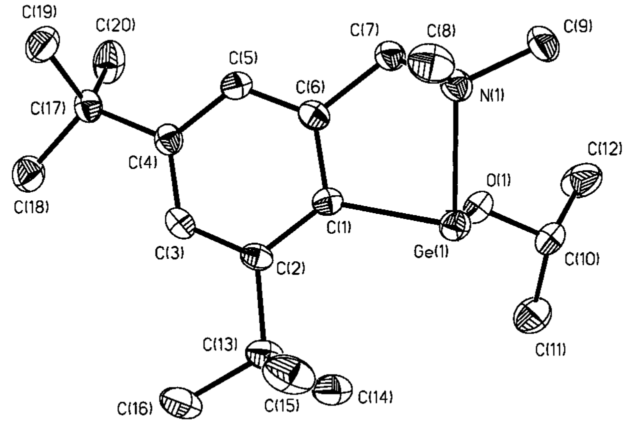

Figure 1. Molecular structure of **3**.

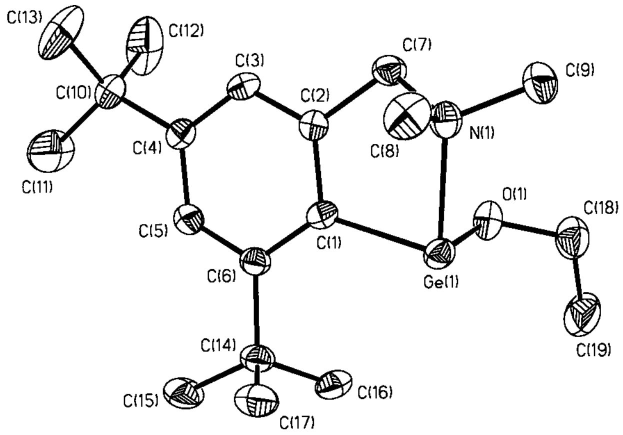

Figure 2. Molecular structure of **4**.

The solution NMR data of **3** and **4** are in accord with the solid-state structures. The benzylic as well as the methyl protons of the (dimethylamino)methyl side chain are diastereotopic due to the chirality of the germanium center (Chart 1); thus, the ^1H NMR spectra show doublets for the methylene protons and two singlets for the $N(CH_3)_2$ groups. A permanent coordination of the amino group is observed even at high temperatures, indicating a very strong N→Ge interaction.

2. Germanium(II) Compounds with Ethynyl Substituents (MamxGeC≡CR). Species with ethynyl substituents constitute a novel class of heteroleptic germanium compounds. In silicon chemistry, various ethynylsi-

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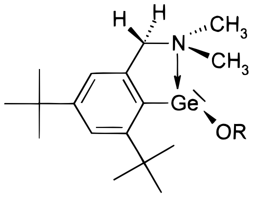
Table 1. Crystallographic Data for 3, 4, 6, 7, and 11

	3	**4**	**6**	**7**	**11**
empirical formula	$C_{20}H_{35}GeNO$	$C_{19}H_{33}GeNO$	$C_{25}H_{33}GeN$	$C_{19}H_{29}GeN$	$C_{26}H_{48}NOI$
fw	378.08	364.05	420.11	344.02	590.14
cryst color, habit	colorless, plates	colorless, plates	colorless, needles	colorless, rhombic	colorless, plates
cryst size, mm^3	0.7 × 0.5 × 0.15	0.80 × 0.40 × 0.20	0.8 × 0.3 × 0.1	0.4 × 0.4 × 0.1	0.4 × 0.3 × 0.02
temp, K			173(2)		
radiation (λ, Å)			Mo Kα (0.71073 Å), graphite monochromator		
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
unit cell dimens					
a, Å	11.237(3)	17.215(5)	15.248(8)	9.820(2)	16.230(3)
b, Å	15.818(4)	9.551(2)	13.836(7)	15.818(3)	12.357(2)
c, Å	11.864(3)	12.006(3)	11.133(7)	12.165(3)	14.941(3)
α, deg	90	90	90	90	90
β, deg	99.49(2)	91.01(2)	99.60(5)	102.63(2)	105.12(2)
γ, deg	90	90	90	90	90
V, Å^3	2079.9(9)	1973.7(9)	2516(2)	1843.9(7)	2892.7(9)
Z	4	4	4	4	4
density (calcd), Mg/m^3	1.207	1.225	1.205	1.239	1.355
θ range for data collecn, deg	1.84−27.49	2.37−27.50	2.37−27.03	2.13−27.06	2.10−28.5
no. of rflns collected	5017	4759	5314	4279	7615
no. of indep rflns	4781 (R_{int} = 0.0323)	4535 (R_{int} = 0.0333)	5047 (R_{int} = 0.0425)	4047 (R_{int} = 0.0745)	7339 (R_{int} = 0.0531)
abs cor	empirical	none	empirical	empirical	empirical
final R indices ($I > 2\sigma(I)$)					
R_F	0.0451	0.0548	0.0595	0.0652	0.0666
R_{F^2}	0.0918	0.1216	0.1152	0.1231	0.1440
no. of rflns used for R indices	3408	3048	3342	2429	4507
no. of params	218	221	252	198	271
largest diff peak and hole, e/Å^3	0.418, −0.423	0.965, −0.891	0.884, −0.709	0.796, −0.659	0.915, −1.185
diffractometer used	Siemens R3m/V	Siemens P2(1)	Siemens P2(1)	Siemens P2(1)	Siemens P2(1)
programs used			Siemens SHELXTL plus SHELXL-97		
structure refinement			full-matrix least squares on F^2		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3 and 4

	3	**4**
Ge(1)−O(1)	1.856(2)	1.844(3)
Ge(1)−C(1)	2.039(3)	2.037(4)
Ge(1)−N(1)	2.149(2)	2.123(3)
O(1)−Ge(1)−C(1)	92.94(10)	92.56(13)
O(1)−Ge(1)−N(1)	91.32(9)	91.62(13)
C(1)−Ge(1)−N(1)	81.26(10)	82.26(13)

Chart 1



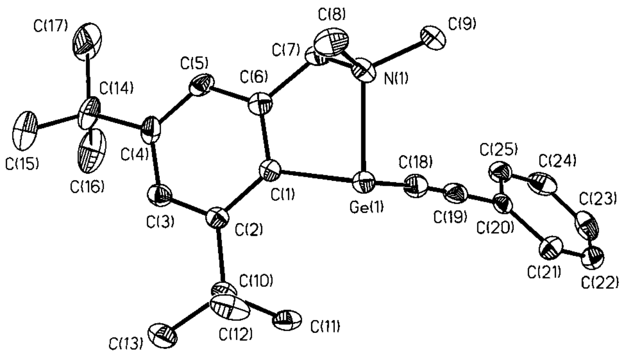
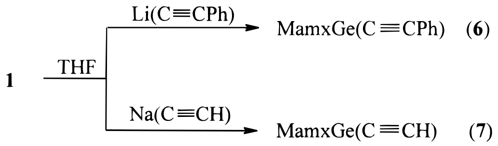


Figure 3. Molecular structure of **6**.

Scheme 2



lylenes have been prepared in matrixes,[13] but comparable germanium compounds are unknown.

Reaction of **1** with Li(C≡CPh) in THF at −60 °C furnished the heteroleptic germanium(II) compound MamxGe(C≡CPh) (**6**), whereas the ethynyl-substituted species MamxGe(C≡CH) (**7**) was synthesized by stirring a suspension of **1** and Na(C≡CH) in THF at ambient temperature for 3 days (Scheme 2).

Crystals suitable for an X-ray structure analysis were obtained from a toluene solution. The molecular structures of **6** and **7** are depicted in Figures 3 and 4. Crystal structure parameters are given in Table 1, and selected bond lengths and angles are collected in Table 3.

In compounds **6** and **7** the structural features at the germanium center are quite similar to those found for **3** and **4**; again, the Mamx ligand is coordinated in a bidentate fashion. The C_{aryl}−Ge−$C_{ethynyl}$ and the $C_{aryl/ethynyl}$−Ge−N angles are nearly rectangular (Table 3). The Ge−C_{aryl} bond length is 2.035(4) Å for **6** and 2.026(5) Å for **7.** The Ge−N bond distances are almost identical and are again elongated in comparison to **1** (2.126(4) Å (**6**) and 2.124(4) Å (**7**)). The Ge−$C_{ethynyl}$ bond

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[13] Apeloig, Y.; Karni, M.; West, R.; Welsh, K. *J. Am. Chem. Soc.* **1994**, *116*, 9719.

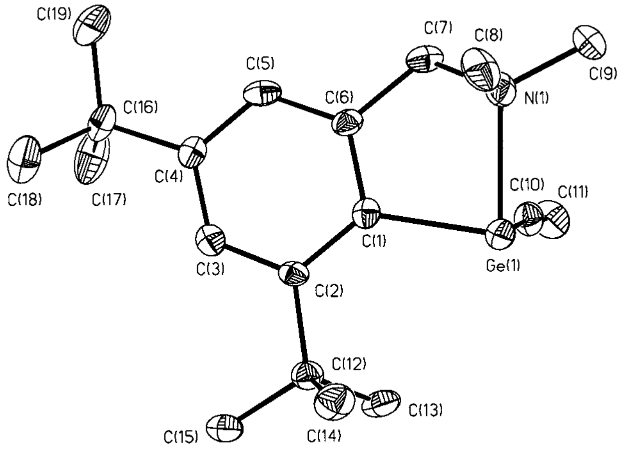


Figure 4. Molecular structure of **7**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 6 and 7

	6	7
Ge(1)−$C_{ethynyl}$	2.001(4)	1.989(6)
Ge(1)−C(1)	2.035(4)	2.026(5)
Ge(1)−N(1)	2.126(2)	2.124(4)
$C_{ethynyl}$−$C_{ethynyl}$	1.209(6)	1.191(8)
$C_{ethynyl}$−Ge(1)−C(1)	97.90(16)	95.4(2)
$C_{ethynyl}$−Ge(1)−N(1)	91.97(16)	92.9(2)
C(1)−Ge(1)−N(1)	82.70(15)	82.04(18)
$C_{ethynyl}$−$C_{ethynyl}$−Ge(1)	165.6(4)	171.1(5)

length is 2.001(4) Å for **6** and 1.989(6) Å for **7**. The CC triple-bond distance is 1.209(6) Å in **6** and 1.191(8) Å in **7**. The C−C bond length in acetylene is 1.204 Å,[1414] which is slightly elongated compared to that in **6** and shortened in comparison with that in **7**. The Ge−C−C angle is 165.6(4)° in **6** and 171.1(5)° in **7**, respectively.

The structures of **6** and **7** found in the solid state are also present in solution; the permanent coordination of the amino group to the germanium(II) center is observed even at high temperatures (80 °C). Thus, again doublets for the methylene protons and two singlets for the dimethylamino protons are detected in the ^{1}H NMR spectra of **6** and **7**. In the ^{13}C NMR spectra the signals for the acetylenic carbon atoms are observed at 109.6 and 111.2 ppm for **6** and 97.8 and 103.6 ppm for **7**, respectively; this means a low-field shift of approximately 30 ppm in comparison with phenylacetylene (78.6, 84.6 ppm) and acetylene (71.9 ppm).[15]

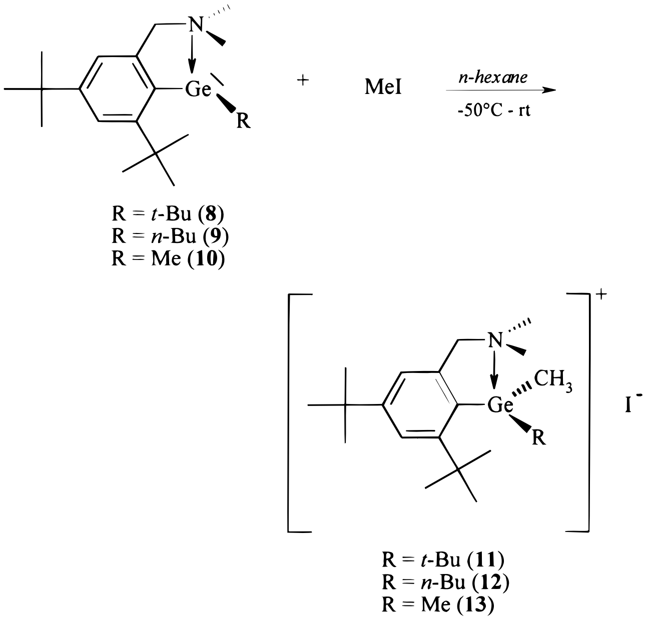
3. Germanium(II) Compounds with Alkyl Substituents (MamxGeR) and Germyl Cations. Up to now several kinetically substituted stable dialkylgermylenes and arylalkylgermylenes have been reported in the literature.[1−3] The Mamx ligand is able to stabilize germanium(II) species containing nonbulky alkyl ligands, as demonstrated by the synthesis of MamxGe-*t*-Bu (**8**), MamxGe-*n*-Bu (**9**), and MamxGeMe (**10**). Compounds **8**−**10** were obtained by reaction of **1** with 1 equiv of the corresponding alkyllithium reagent in *n*-hexane at −60 °C. After filtration and removal of all volatiles in vacuo, **8**−**10** were isolated as yellow solids (**8, 9**) and as a yellow viscous oil (**10**), respectively (Scheme 3).[16]

Scheme 3

$$\mathbf{1} + \mathrm{LiR} \xrightarrow[-60^\circ\mathrm{C\ -\ rt}]{n\text{-hexane}} \mathrm{MamxGeR}\ (\mathbf{8\text{-}10})$$

R = *t*-Bu (**8**)
R = *n*-Bu (**9**)
R = Me (**10**)

Scheme 4



Compounds **8**−**10** are stable at room temperature in *n*-hexane solution and in the solid state, but slow decomposition is observed in solution at 80 °C. The NMR data of **8**−**10** are in accordance with those of all other germanium(II) compounds containing the Mamx ligand; a permanent coordination of the amino side chain is observed. Compounds **8**−**10** were characterized by standard CI-MS techniques; the molecular ions were observed, and no dimeric or other oligomeric species were found.

Keeping in mind the fact that reaction of MeI with diarylgermanium(II) compounds MamxGeAr (Ar = Mamx, 2,4,6-$(C_3H_7)_3$-C_6H_2) afforded ionic species containing germyl cations,[6] alkylation of **8**−**10** should also be possible. Reaction of **8**−**10** with 1 equiv of MeI in *n*-hexane led to the colorless compounds **11**−**13**, which contain the germyl cations $[\mathrm{MamxGe}(t\text{-Bu})(\mathrm{Me})]^+$ **(11a)**, $[\mathrm{MamxGe}(n\text{-Bu})(\mathrm{Me})]^+$ **(12a),** and $[\mathrm{MamxGe}(\mathrm{Me})_2]^+$ **(13a)**, respectively, and the counteranion I^- (Scheme 4).

Crystals of **11**, suitable for an X-ray structure analysis, were obtained from THF solution. The molecular structure of **11a** is shown in Figure 5. Crystallographic data for **11** are given in Table 1, and selected bond lengths and angles are collected in Table 4.

In compound **11**, the closest Ge−I distance is 4.887 Å, which excludes any bonding interactions. In **11a**, the germanium atom is surrounded by the three carbon atoms (C_{aryl}, C_{t-Bu}, C_{Me}) in a nearly perfect trigonal-planar fashion; the angle sum is 351.5°. The Ge−C bond lengths do not vary significantly. The Ge−C_{Me} bond length (1.938(6) Å) is in accordance with the distances

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(14) *CRC Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, 1979.

(15) Hesse, M.; Meier, H.; Zeeh, B. *Spectroscopic Methods in Organic Chemistry*; Thieme Verlag: Stuttgart, Germany, 1984.

(16) Purification of the alkylgermylenes by crystallization, sublimation, or distillation was not successful; therefore, no elemental analyses could be performed.

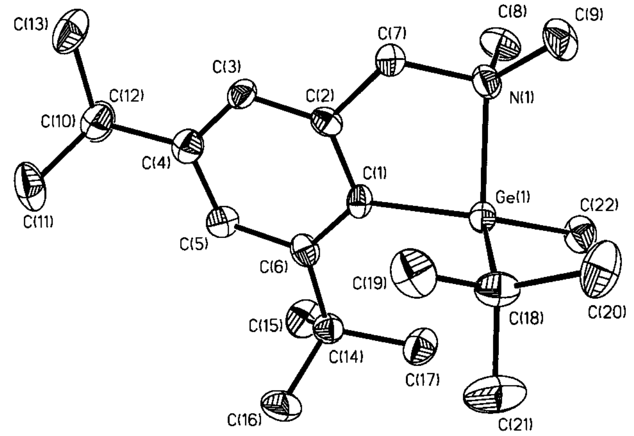

Figure 5. Molecular structure of **11a**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 11

Ge(1)−C(22)	1.938(6)	Ge(1)−N(1)	2.014(6)
Ge(1)−C(1)	1.962(6)	Ge(1)−I(1)	4.887
Ge(1)−C(18)	1.983(7)		
C(22)−Ge(1)−C(1)	126.3(3)	C(22)−Ge(1)−N(1)	102.8(3)
C(22)−Ge(1)−C(18)	111.8(3)	C(1)−Ge(1)−N(1)	86.9(2)
C(1)−Ge(1)−C(18)	113.4(3)	C(18)−Ge(1)−N(1)	110.7(3)

found for germyl cations presented in our previous work.[6] The $C_{aryl}C_{t-Bu}C_{Me}$ plane and the Ge−N bond vector form an angle of 75.7°; the Ge−N bond length is shortened compared to that of other germylenes with the Mamx ligand.

The ^1H NMR spectra of **11**−**13** demonstrate the large effect the alkylation has on the germanium center. Thus, the spectra show an enormous low-field shift of up to 2 ppm of the NCH_3 as well as of the CH_2 protons in comparison with **8** and **9**; hence, it follows that the N→Ge interaction is strengthened in the germyl cations. In **13** the germanium center is no longer chiral, and as a result the methyl and methylene protons of the amino side chain are not diastereotopic, as indicated by one singlet for the NCH_3 and one singlet for the CH_2 protons.

Conclusions

It has been demonstrated that the chloro species MamxGeCl (**1**) is a useful precursor for novel heteroleptic germanium(II) compounds. Starting from **1**, we have prepared and structurally characterized several alkoxy-substituted germanium(II) compounds (**2**−**5**) as well as the ethynyl species **6** and **7**. Additionally we synthesized the alkyl-substituted species MamxGeR (R = *t*-Bu (**8**), *n*-Bu (**9**), Me (**10**)). The nucleophilic character of the germanium center has been pointed out by reaction of **8**−**10** with MeI leading to ionic compounds containing germyl cations. All these compounds show a high stability, which can be referred to the unique characteristics of the Mamx ligand. (i) Due to the fact that the *tert*-butyl group in the ortho position of the C_{aryl} atom shields the germanium atom, nucleophilic attack on the metal center is rendered to be more difficult; therefore, further nucleophilic substitution at these germanium(II) species only takes place with strong nucleophiles. (ii) A permanent coordination of the amino side chain is observed even at high temperatures. This leads to a thermodynamic stabilization of the germanium(II) center; due to the strong N→Ge bond, alkylation takes place at the germanium and not at the nitrogen atom. (iii) By coordination of the amino side chain a five-membered ring ($GeNC_3$) with low ring strain is formed. The C_{aryl}−Ge−N angle in all compounds is almost rectangular (≅83°). For this reason nearly ideal interaction between the nitrogen atom and the vacant Ge(p) orbital is observed.

A characteristic feature of a germylene (singlet ground state) is the presence of an electron lone pair and of a vacant p orbital at the germanium center. In the compounds mentioned above the p(Ge) orbital is not vacant and, as shown, interaction takes place between the nitrogen and the germanium atom. Therefore, we wish to describe the species presented in this work and in general germanium compounds containing the Mamx ligand not as germylenes, but as monomeric germanium(II) compounds.

Experimental Section

General Data. All manipulations were carried out under a purified argon atmosphere using standard vacuum techniques. The solvents were commercially available, purified by conventional means, and distilled immediately prior to use. 15-Crown-5, *t*-BuLi (1.6 M solution in pentane), *n*-BuLi (1.6 M solution in hexane), MeLi (1.6 M solution in Et_2O), MeI, phenylacetylene, and potassium acetylide were commercially available. MamxGeCl,[6] NaO-*t*-Bu, NaO-*i*-Pr, NaOEt, and NaOMe were prepared according to the literature. Elemental analyses were performed by the Microanalytical Laboratory of Universität Bielefeld. The NMR spectra were recorded using a Bruker Avance DRX 500 spectrometer (^1H, 500.1 MHz; $^{13}C\{^1H\}$, 125.8 MHz). Chemical shifts are reported in ppm and are referenced to the solvent as an internal standard. Mass spectrometry was performed using a VG Autospec spectrometer. Only characteristic fragments and isotopes of the highest abundance are listed.

General Procedure for the Preparation of the Alkoxygermanium(II) Compounds 2−**5.** The sodium alkoxide (16 mmol) NaOR (**2**, R = *t*-Bu; **3**, R = *i*-Pr; **4**, R = Et; **5**, R = Me) was added to a solution of 3.95 mmol (1.40 g) of **1** and 3.95 mmol of 15-crown-5 (0.87 g, 0.78 mL) in toluene (25 mL) at ambient temperature. The reaction mixture was stirred for 24 h at that temperature. After filtration and removal of the solvent and of the crown ether by distillation (93 °C, 0.05 mbar), the germanium(II) species **2**−**5** were purified by sublimation in vacuo.

MamxGeO-*t*-Bu (**2**): Yield: 1.05 g (2.67 mmol, 68%). ^1H NMR (C_6D_6): δ 1.32, 1.50, 1.68 (3s, 9H, *t*-Bu), 1.85, 2.15 (2s, 3H, $N(CH_3)_2$), 2.96, 4.28 (2d, 1H, $-CH_2-$, $^2J = 13$ Hz), 6.95, 7.49 (2s, 1H, aryl H). ^{13}C NMR (C_6D_6): δ 31.7, 34.0 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 35.0 ($OC(CH_3)_3$), 38.1 ($C(CH_3)_3$), 43.6, 45.2 ($N(CH_3)_2$), 66.6 ($OC(CH_3)_3$), 67.2 ($-CH_2-$), 118.5, 121.0 (tertiary aryl C), 144.4, 149.5, 150.7, 157.0 (quaternary aryl-C). MS (CI; m/z (I_{rel})): 393 (100, M^+), 320 (15, $MamxGe^+$). Anal. Calcd for $C_{21}H_{37}GeNO$ ($M_r = 392.17$): C, 64.31; H, 9.50; N, 3.57. Found: C, 64.10; H, 9.30; N, 3.59.

MamxGeO-*i*-Pr (**3**). Recrystallization of the sublimate from *n*-hexane yielded 0.97 g (2.56 mmol, 65%) of **3** as colorless crystals. ^1H NMR (C_6D_6): δ 1.34 (s, 9H, *t*-Bu), 1.36, 1.41 (2d, 3H, $OCH(CH_3)_2$, $^3J = 6$ Hz), 1.66 (s, 9H, *t*-Bu), 1.82, 2.17 (2s, 3H, $N(CH_3)_2$), 2.92, 4.32 (2d, 1H, $-CH_2-$, $^2J = 13$ Hz), 4.41 (pseudo-septet), 1H, $OCH(CH_3)_2$), 6.95, 7.49 (2s, 1H, aryl H). ^{13}C NMR (C_6D_6): δ 27.6, 27.9 ($OCH(CH_3)_2$), 31.7, 33.8 ($C(CH_3)_3$), 34.8, 37.9 ($C(CH_3)_3$), 43.4, 44.6 ($N(CH_3)_2$), 67.3 ($-CH_2-$), 68.0 ($OCH(CH_3)_2$), 118.4, 120.9 (tertiary aryl C), 144.8, 150.0, 156.5, 156.9 (quaternary aryl C). MS (CI; m/z (I_{rel})): 379 (48, M^+), 364 (23, $M^+ - CH_3$), 320 (87, $MamxGe^+$). Anal. Calcd for

$C_{20}H_{35}GeNO$ (M_r = 378.14): C, 63.52; H, 9.32; N, 3.70. Found: C, 63.30; H, 9.18; N, 3.41.

MamxGeOEt (**4**). Recrystallization of the sublimate from *n*-hexane yielded 0.96 g (2.63 mmol, 67%) of **4** as colorless crystals. ^{1}H NMR (C_6D_6): δ 1.35 (s, 9H, *t*-Bu), 1.41 (t, 3H, CH_2CH_3, ^3J = 7 Hz), 1.67 (s, 9H, *t*-Bu), 1.81, 2.14 (2s, 3H, $N(CH_3)_2$), 2.92 (d, 1H, $-CH_2-$, ^2J = 13 Hz), 4.17 (m, 2H, CH_2CH_3), 4.30 (d, 1H, $-CH_2-$, ^2J = 13 Hz), 6.97, 7.51 (2s, 1H, aryl H). ^{13}C NMR (C_6D_6): δ 20.9 (OCH_2CH_3), 31.7, 33.7 ($C(CH_3)_3$), 34.8, 38.0 ($C(CH_3)_3$), 43.5, 44.7 ($N(CH_3)_2$), 62.9 (OCH_2CH_3), 67.5 ($-CH_2-$), 118.3, 123.6 (tertiary aryl C), 144.9, 149.9, 156.3, 157.0 (quaternary aryl C). MS (CI; m/z (I_{rel})): 365 (60, M^+), 350 (12, $M^+ - CH_3$), 320 (64, $MamxGe^+$). Anal. Calcd for $C_{19}H_{33}GeNO$ (M_r= 364.12): C, 62.67; H, 9.13; N, 3.84. Found: C, 62.40; H, 9.39; N, 3.83.

MamxGeOMe (**5**). Yield: 0.73 g (2.08 mmol, 53%). ^{1}H NMR (C_6D_6): δ 1.35, 1.65 (2s, 9H, *t*-Bu), 1.81, 2.13 (2s, 3H, $N(CH_3)_2$), 2.95 (d, 1H, $-CH_2-$, ^2J = 13 Hz), 3.95 (s, 3H, OCH_3), 4.27 (d, 1H, $-CH_2-$, ^2J = 13 Hz), 6.97, 7.50 (2s, 1H, aryl H). ^{13}C NMR (C_6D_6): δ 31.7, 33.6 ($C(CH_3)_3$), 34.8, 37.9 ($C(CH_3)_3$), 43.5, 44.6 ($N(CH_3)_2$), 55.4 (OCH_3), 67.6 ($-CH_2-$), 118.2, 120.9 (tertiary aryl C), 144.9, 150.1, 156.1, 157.1 (quaternaryaryl-C). MS (CI; m/z (I_{rel})): 351 (80, M^+), 336 (22, $MamxGeO^+$), 320 (100, $MamxGe^+$). Anal. Calcd for $C_{18}H_{31}GeNO$ (M_r = 350.09): C, 61.75; H, 8.92; N, 4.00. Found: C, 61.31; H, 9.14; N, 3.92.

Preparation of MamxGe(C≡CPh) (6). Within 3 min 1.25 mL of a 1.6 M solution of *n*-BuLi in *n*-hexane was added to a stirred solution of phenylacetylene (0.20 g, 2.00 mmol) in THF (10 mL) at −60 °C. After the mixture was warmed to room temperature within 3 h, it was added to a solution of **1** (0.71 g, 2.00 mmol) in THF (15 mL) at −60 °C. The reaction mixture turned immediately yellow, and the solution was warmed to room temperature. The solvent was removed in vacuo, and the residue was extracted with toluene. Cooling the liquid yielded 0.64 g (76%) of **6** as colorless crystals.^{1}H NMR (C_6D_6): δ 1.35, 1.66 (2s, 9H, *t*-Bu), 1.83, 2.40 (2s, 3H, $N(CH_3)_2$), 3.05, 4.52 (2d, 1H, $-CH_2-$, ^2J = 13 Hz), 6.92 (m, 3H, *m*,*p*-Ph), 7.01 (s, 1H, aryl H Mamx), 7.41 (d, 2H, *o*-Ph, ^3J = 7 Hz), 7.54 (s, 1H, aryl H Mamx). ^{13}C NMR (THF-d_8): δ 31.9, 33.0 ($C(CH_3)_3$), 35.2, 37.9 ($C(CH_3)_3$), 46.1, 46.8 ($N(CH_3)_2$), 70.6 ($-CH_2-$), 109.6, 111.2 ($-CCPh$), 118.8, 121.4 (tertiary aryl C, Mamx), 126.6, 127.4, 128.6, 131.8 (aryl C, Ph) 144.4, 149.8, 154.2, 156.5 (quaternary aryl C, Mamx). MS (CI; m/z (I_{rel})): 422 (8, $M^+ + H$), 320 (16, $MamxGe^+$). Anal. Calcd for $C_{25}H_{33}GeN$ (M_r = 420.18): C, 71.46; H, 7.92; N, 3.33. Found: C, 70.26; H, 7.78; N, 3.18.

Preparation of MamxGe(C≡CH) (**8**). To a suspension of sodium acetylide (0.11 g, 2.29 mmol, purified by washing three times with pentane) in THF (30 mL) was added a solution of **1** (0.81 g, 2.29 mmol) in THF (15 mL) at ambient temperature within 5 min. The reaction mixture was stirred at that temperature for 3 days. The solvent was removed in vacuo, and the residue was dissolved in toluene. Cooling the solution to −30 °C after filtration and concentration yielded 0.47 g (60%) of **8** as colorless crystals. ^{1}H NMR (C_6D_6): δ 1.34, 1.62 (2s, 9H, *t*-Bu), 1.77, 2.33 (2s, 3H, $N(CH_3)_2$), 2.64 (s, 1H, $-CCH$), 2.99, 4.47 (2d, 1H, $-CH_2-$, ^2J = 13 Hz), 6.98, 7.51 (2s, 1H, aryl H).^{13}C NMR (C_6D_6): δ 31.7, 32.9 ($C(CH_3)_3$), 34.7, 37.6 ($C(CH_3)_3$), 45.4, 46.0 ($N(CH_3)_2$), 69.7 ($-CH_2-$), 97.8 ($-CCH$), 103.6 ($-CCH$), 118.2, 121.3 (tertiary aryl C), 143.5, 149.5, 153.6, 156.6 (quaternary aryl C). MS (CI; m/z (I_{rel})): 346 (100, $M^+ + H$), 320 (38, $MamxGe^+$). Anal. Calcd for $C_{19}H_{29}GeN$ (M_r = 344.09): C, 66.32; H, 8.49; N, 4.07. Found: C, 66.02; H, 8.85; N, 3.80.

General Procedure for the Preparation of the Alkylgermanium(II) Compounds 8−10. A solution of an equimolar amount of the alkyllithium reagent (*t*-BuLi **(8)**, *n*-BuLi **(9)**, MeLi **(10)**) was added slowly to a suspension of **1** in *n*-hexane at −60 °C. The mixture was stirred at that temperature for 4 h and then warmed to room temperature. After the mixture was stirred for another 12 h at that temperature, the LiCl was filtered off and the solvent was removed in vacuo.

MamxGe-*t*-Bu (**8**). Reaction of **1** (0.39 g, 1.10 mmol) in *n*-hexane (20 mL) with *t*-BuLi (1.7 M solution in pentane, 0.65 mL, 1.10 mmol) at −60 °C afforded **6** as a yellow solid. ^{1}H NMR (C_6D_6): δ 1.21, 1.35, 1.62 (3s, 9H, *t*-Bu), 2.00, 2.05 (2s, 3H, $N(CH_3)_2$), 2.95, 4.13 (2d, 1H, $-CH_2-$, ^2J = 14 Hz), 6.99, 7.55 (2s, 1H, aryl H). ^{13}C NMR (C_6D_6): δ 31.7, 31.8, 34.5 ($C(CH_3)_3$), 33.1, 34.6, 38.1 ($C(CH_3)_3$), 45.5, 49.2 ($N(CH_3)_2$), 69.4 ($-CH_2-$), 117.8, 122.1 (tertiary aryl C), 143.5, 148.5, 157.0, 157.6 (quaternary aryl C). MS (CI; m/z (I_{rel})): 378 (87, $M^+ + H$), 320 (100, $MamxGe^+$).

MamxGe-*n*-Bu (**9**). Reaction of **1** (0.69 g, 1.96 mmol) in *n*-hexane (30 mL) with *n*-BuLi (1.6 M solution in hexane, 1.23 mL, 1.96 mmol) at −60 °C afforded **7** as a yellow solid. ^{1}H NMR (C_6D_6): δ 1.03 (t, 3H, *n*-Bu CH_3, ^3J = 7 Hz), 1.07−1.61 (broad m, 6H, $-(CH_2)_3-$), 1.37, 1.59 (2s, 9H, *t*-Bu), 1.95, 2.01 (2s, 3H, $N(CH_3)_2$), 2.95, 3.96 (2d, 1H, $-CH_2-$, ^2J = 14 Hz), 6.99, 7.52 (2s, 1H, aryl H). ^{13}C NMR (C_6D_6): δ 14.36 ($-CH_3$), 26.1, 27.4, 31.4 ($-(CH_2)_3-$), 31.4, 33.2 ($C(CH_3)_3$), 34.7, 37.9 ($C(CH_3)_3$), 44.4, 48.1 ($N(CH_3)_2$), 68.5 ($-CH_2-$), 117.8, 121.0 (tertiary aryl C), 142.2, 148.5, 156.3, 158.9 (quaternary aryl C). MS (CI; m/z (I_{rel})): 377 (95, M^+), 335 (18, $M^+ - CH_3$), 320 (100, $MamxGe^+$).

MamxGeMe (**10**). Reaction of **1** (0.32 g, 0.91 mmol) in *n*-hexane (30 mL) with MeLi (1.6 M in diethyl ether, 0.57 mL, 0.91 mmol) at −60 °C afforded **8** as a yellow oil. ^{1}H NMR (C_6D_6): δ 0.68 (s, 3H, $GeCH_3$), 1.38, 1.60 (2s, 9H, *t*-Bu), 1.89, 1.98 (2s, 3H, $N(CH_3)_2$), 2.97, 3.95 (2d, 1H, $-CH_2-$, ^2J = 14 Hz), 7.00, 7.52 (2s, 1H, aryl-H). ^{13}C NMR (C_6D_6): δ 9.4 ($-CH_3$), 31.4, 33.2 ($C(CH_3)_3$), 34.6, 38.2 ($C(CH_3)_3$), 44.1, 45.5 ($N(CH_3)_2$), 65.4 ($-CH_2-$), 120.9, 123.9 (tertiary aryl C), 136.5, 144.3, 150.7, 158.7. MS (CI; m/z (I_{rel})): 335 (100, M^+), 320 (52, $MamxGe^+$).

General Procedure for the Preparation of the Ionic Compounds 11−13. One equivalent of MeI was added to a freshly prepared solution of the alkylgermanium(II) species (**8**−**10**) in *n*-hexane at −50 °C. The reaction mixture was warmed to room temperature, giving a colorless suspension. Evaporation of the solvent and recrystallization of the residue from THF yielded the ionic compounds **11**−**13** as colorless crystals.

[MamxGe(*t*-Bu)(Me)]$^+$I$^-$ (**11**). Reaction of **8** (0.86 mmol) in *n*-hexane (15 mL) with MeI (0.12 g, 0.05 mL, 0.86 mmol) yielded 0.25 g (57%) of colorless crystals. ^{1}H NMR (THF-d_8): δ 1.29, 1.34, 1.39 (3s, 9H, *t*-Bu), 1.50 (s, 3H, $Ge-CH_3$), 3.18, 3.69 (2s, 3H, $N(CH_3)_2$), 4.67, 5.27 (2d, 1H, $-CH_2-$, ^2J = 16 Hz), 7.42, 7.64 (2s, 1H, aryl H). ^{13}C NMR (THF-d_8): δ 1.8 ($Ge-CH_3$), 28.4, 31.4 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 33.0 ($C(CH_3)_3$), 35.6, 37.4 ($C(CH_3)_3$), 48.9, 49.1 ($N(CH_3)_2$), 67.6 ($-CH_2-$), 121.9, 124.4 (tertiary aryl C), 126.2, 142.8, 154.9, 158.0 (quaternary aryl C). MS (CI, M^+ = MamxGe(*t*-Bu)(Me)$^+$; m/z (I_{rel})): 392 (5, M^+), 378 (100, $M^+ + H - CH_3$), 320 (71, $MamxGe^+$). Anal. Calcd for $C_{22}H_{40}GeNI$ (M_r = 518.06): C, 51.00; H, 7.78; N, 2.70. Found: C, 50.80; H, 7.99; N, 2.59.

[MamxGe(*n*-Bu)(Me)]$^+$I$^-$ (**12**). Reaction of **9** (1.18 mmol) in *n*-hexane (20 mL) with MeI (0.17 g, 0.07 mL, 1.18 mmol) yielded 0.30 g (49%) of a colorless powder. ^{1}H NMR (C_6D_6): δ 0.93 (t, 3H, $-CH_3$, ^3J = 7 Hz), 1.07, 1.19 (2s, 9H, *t*-Bu), 1.32 (s, 3H, $Ge-CH_3$), 1.50−2.00 (broad multipletts, 6H, $-(CH_2)_3-$), 3.61, 3.87 (2s, 3H, $N(CH_3)_2$), 5.11, 5.53 (2d, 1H, $-CH_2-$, ^2J = 15 Hz), 7.41, 7.47 (2s, 1H, aryl H). ^{13}C NMR (C_6D_6): δ 1.9 ($Ge-CH_3$), 13.8 ($-CH_3$), 18.6, 26.0, 26.8 ($-(CH_2)_3)-$), 31.2, 32.2 ($C(CH_3)_3$), 35.1, 36.3 ($C(CH_3)_3$), 47.8, 48.0 ($N(CH_3)_2$), 66.4 ($-CH_2-$), 121.4, 123.6 (tertiary aryl C), 126.1, 142.2, 154.7, 156.3 (quaternary aryl C). MS (CI, M^+ = MamxGe(*n*-Bu)(Me)$^+$; m/z (I_{rel})): 392 (17, M^+), 376 (38, $M^+ - CH_4$), 320 (20, $MamxGe^+$). Anal. Calcd for $C_{22}H_{40}GeNI$ (M_r = 518.06): C, 51.00; H, 7.78; N, 2.70. Found: C, 50.40; H, 7.33; N, 2.43.

[MamxGe(Me)$_2$]$^+$I$^-$ (**13**). Reaction of **10** (1.40 mmol) in *n*-hexane (40 mL) with MeI (0.20 g, 0.09 mL, 1.40 mmol) yielded 0.38 g (58%) of colorless needles.^{1}H NMR (CD_3CN): δ 1.10 (s, 6H, $Ge(CH_3)_2$), 1.31, 1.34 (2s, 9H, *t*-Bu), 2.85 (s, 6H, $N(CH_3)_2$), 4.36 (s, 2H, $-CH_2-$), 7.29, 7.61 (2s, 1H, aryl H). ^{13}C

NMR (DMSO-d_6): δ 1.12 (Ge(CH_3)$_2$), 30.9, 32.0 (C(CH_3)$_3$), 34.8, 36.3 (C(CH_3)$_3$), 46.3 (N(CH_3)$_2$), 65.6 ($-CH_2-$), 120.0, 123.7 (tertiary aryl C), 125.6, 140.9, 154.0, 156.2 (quaternary aryl-C). MS (CI, M^+ = MamxGe(Me)$_2$$^+$; m/z (I_{rel})): 350 (4, M^+), Anal. Calcd for $C_{19}H_{34}GeNI$ (M_r = 476.03): C, 47.94; H, 7.19; N, 2.94. Found: C, 47.92; H, 7.20; N, 2.90.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and selected bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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