

# Germynes and Stannynes with Chelating Anilido–Imine Ligands: Syntheses, Structures and Reactivity

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Germynes and stannynes with anilido–imine ligands were synthesized in high yields by the reaction of group 14 dichlorides ( $\text{Cl}_2\text{Ge}$ -dioxane,  $\text{Cl}_2\text{Sn}$ ) and the lithium salts of the ligands. Complexes were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, and the molecular structure of methoxygermylene was determined by X-ray crystallography. These data indicate the formation of  $N,N'$ -chelate complexes hav-

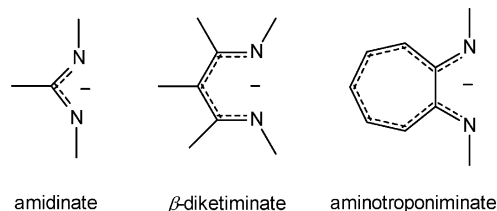
ing three-coordinate germanium or tin atoms and quasiplanar six-membered heterocycles. In the germanium series, cycloaddition reactions with *o*-quinone were performed, and the structures of the cycloadducts were determined by X-ray structure analyses.

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## Introduction

Considerable attention has been focused over the last two decades on the study of amido groups as alternative ligands to cyclopentadienyl ligands in transition-metal coordination chemistry.<sup>[1]</sup> Indeed, this has led to some group 4 and late-transition-metal complexes that are very active catalysts in olefin polymerizations.<sup>[2]</sup> A lower electron density at the metal centre and thus an increase in its electrophilicity could account for this high activity. Consequently, many transition-metal complexes with bi- and multidentate amides and amidinates as ligands have been designed and synthesized.<sup>[1–3]</sup> Amidinates are mono anionic ligands that formally can be considered as a combination of an amido and an imino group (Scheme 1).

The most frequently used patterns are  $\beta$ -diketimines<sup>[4]</sup> with properties tunable by varying the substituent at the  $\gamma$ -carbon of the ligand backbone and aminotroponiminates that consist of a highly delocalized  $10\pi$  electron system.<sup>[5]</sup> More recently, anilido–iminates, new bidentate, monanionic conjugated ligands, have emerged. Many complexes of transition metals, main-group elements and lanthanides con-



Scheme 1.

taining these ligands have been prepared. Some of them have been shown to be effective as either catalysts for olefin polymerization<sup>[6]</sup> or as luminescent materials.<sup>[7]</sup> In addition, these ligands have been also used for the stabilization of unusual oxidation states of transition-metal complexes.<sup>[8]</sup> However, despite these appealing features, their coordination chemistry remains totally unexplored for group 14 divalent elements. The chemistry of germanium(II) and tin(II) compounds have received considerable attention due to their carbene-like properties.<sup>[9]</sup> Such compounds are very reactive and tend to polymerize. They can be stabilized kinetically by incorporating bulky ligands and/or thermodynamically by incorporating electron-donating substituents at the metal 14 centre. In this context, we recently reported the preparation of mono- and bis(ferrocenyl-substituted) group 14 metallocenes (Ge, Sn) showing both properties of chelation and electron donation of the (ferrocenyl)cyclopentadienyl ligand.<sup>[10]</sup> In the course of our investigation to develop new strategies to stabilize low-coordinate group 14 compounds, we introduced anilido–imine ligands instead of cyclopentadienyl ligands on germynes and stannynes. Although a large number of germanium(II) and tin(II) compounds have been isolated, the search for new ligands to stabilize low-coordinate compounds is still important to-

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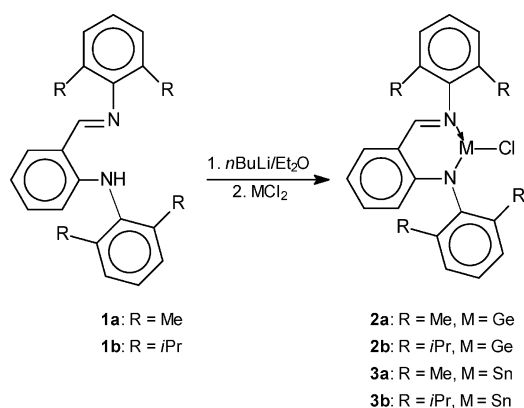
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day. Indeed, an unexpected application of dicyclopentadienyl, amido- and alkoxygermylenes as precursors of nanomaterials has recently been described<sup>[11]</sup> and opens a wide field of investigation. Herein we report the preparation of the first anilido-imine-based germanium(II) and tin(II) complexes and their full characterization including crystal-structure determinations. Also, some reactions were carried out in order to gain insights into the chemical behaviour of these species.

## Results and Discussion

### Synthesis and NMR Spectroscopy of Compounds 2 and 3

For this study, we chose two anilido-iminate ligands: *ortho*-C<sub>6</sub>H<sub>4</sub>(NHAr)(CH=NAr) (**1a**: Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>; **1b**: Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), which were prepared according to literature procedures.<sup>[7a,8]</sup> Germylated and stannylated divalent species **2** and **3**, respectively, were obtained by nucleophilic substitution reactions of Cl<sub>2</sub>Ge·dioxane or Cl<sub>2</sub>Sn with the corresponding lithiated ligands in diethyl ether at low temperature (Scheme 2).



Scheme 2.

Compounds **2** and **3** were isolated in high yields (65–85%) as yellow powders, which are stable under inert atmosphere at room temperature and may be stored for long periods at low temperature (–30 °C). They are soluble in common organic solvents, such as, thf, diethyl ether, toluene and dichloromethane. As often observed, the germynes are more stable in solution than the corresponding stannylenes. All the compounds were perfectly characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic measurements. The <sup>1</sup>H NMR spectrum of **2b** reveals a nonequivalence of the isopropyl units with three signals for the methine protons at  $\delta$  = 3.07, 3.32 and 3.61 ppm and eight signals in the range of 0.90 to 1.41 ppm for the methyl groups (Figure 1). These nonequivalences result not only from initial coordination of the imino nitrogen lone pair of electrons on the metal 14 causing chirality at the germanium atom,<sup>[12]</sup> but also from restricted rotation around the N–C(aryl) bonds, which is slow on the NMR timescale.<sup>[13]</sup> The <sup>1</sup>H NMR spectrum of corresponding stannylene **3b** shows analogous signal sets, which differ only with respect to the chemical shifts. The <sup>13</sup>C

NMR spectrum shows the same complexity with nonequivalence not only of the isopropyl groups, but also of the carbon atoms of the phenyl rings (Figure 2). A complete assignment of these signals was obtained from 2D homonuclear (COSY) and heteronuclear experiments (HSQC and HMBC) and with an additional NOESY experiment. Within the methyl-substituted series, whereas the <sup>1</sup>H NMR spectrum of germylene **2a** exhibited nonequivalence of the methyl groups, the spectrum of analogous stannylene **3a**

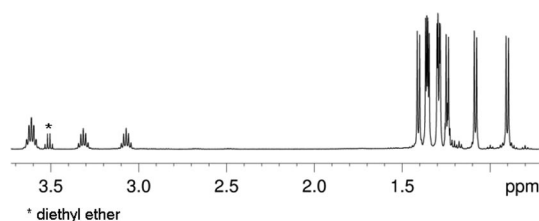


Figure 1. <sup>1</sup>H NMR spectrum of **2b** (500.13 MHz, CDCl<sub>3</sub>, 20 °C). The aromatic region is omitted.

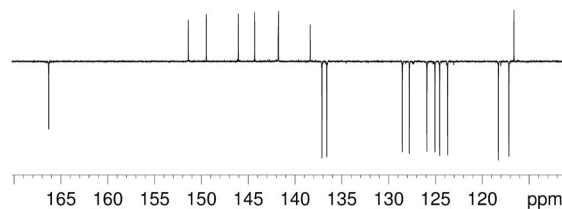


Figure 2. <sup>13</sup>C NMR spectrum of **2b** (125.77 MHz, CDCl<sub>3</sub>, 20 °C). The alkyl region is omitted.

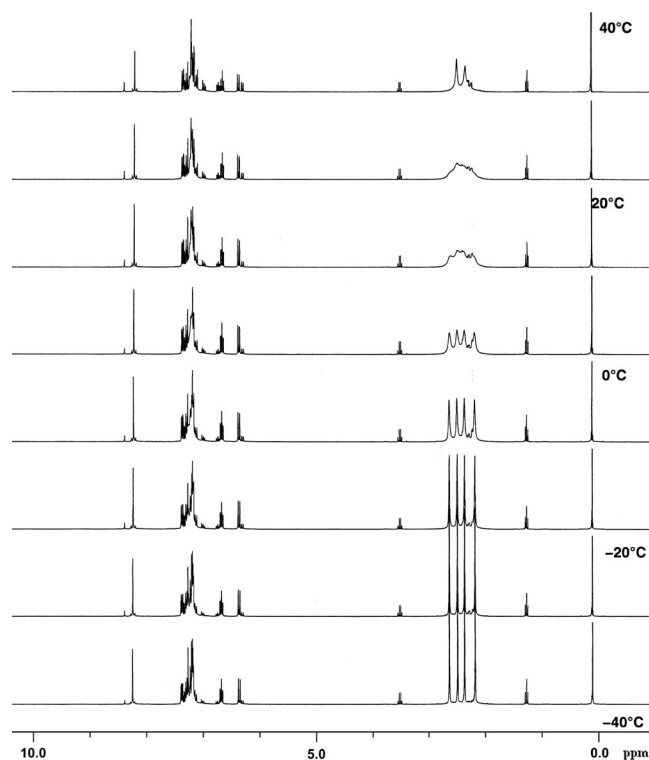


Figure 3. <sup>1</sup>H NMR spectra of **3a** (300 MHz, CDCl<sub>3</sub>) at different temperatures.

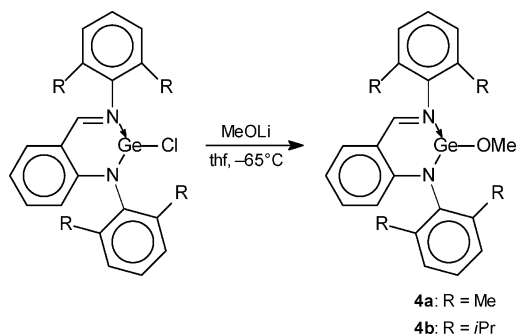
displayed only one broad signal. A dynamic  $^1\text{H}$  NMR experiment in the temperature range between  $-40$  and  $+40$  °C allowed determination of the rotation barrier of the Ar groups around the N–C(aryl) bonds from the evolution of these signals (four singlets at  $-40$  °C and two singlets at  $+30$  °C;  $T_C = 303$  K; Figure 3). This high barrier ( $14.5\text{ kcal mol}^{-1}$ ) reflects the great steric hindrance caused by the large Ar groups.<sup>[14]</sup> The major differences in the profiles of the  $^1\text{H}$  NMR spectra of compounds **2a** and **3a** can be explained both by the greater covalent radius of the tin atom and by the longer Sn–N bond length (Sn–N  $2.10\text{ Å}$ ; <sup>[15]</sup> Ge–N  $1.85\text{ Å}$ <sup>[16]</sup>). These facts account for the deformation of the six-membered heterocycle induced by the group 14 element, which is expected to be greater in the case of tin. Consequently, the diminution of the steric hindrance of the large Ar group allows slow rotation in gear mode that cannot be observed in the case of germanium within the range of temperatures used.

Moreover, the  $^{119}\text{Sn}$  NMR spectra of compounds **3a** and **3b** exhibit signals at  $\delta = -264$  and  $-266$  ppm, respectively, which are in the range typical of three-coordinate tin(II):  $-224$  to  $-246$  ppm for stannylenes containing a diketiminato ligand<sup>[17]</sup> and  $-307$  ppm for  $[\text{H}_2\text{B}(\text{Pz})_2]\text{SnCl}$ .<sup>[18]</sup> The EI mass spectra of **2** and **3** give the corresponding molecular ion peak.

### Derivatives of Compounds **2** and Their Structures

To verify the potential reactivity of the halogen functionality, we tried some nucleophilic reactions. Isoelectronic alkoxy- and aryloxygermylenes have been known for a long time,<sup>[19]</sup> and a few have been examined by X-ray analysis in their monomeric forms,<sup>[20]</sup> but to the best of our knowledge, there is no example in the literature reporting an X-ray study of methoxygermylenes. This prompted us to investigate the preparation of such compounds.

Treatment of **2** with a slight excess of lithium methoxide in thf at low temperature led to methoxygermylenes **4** in moderate yields (25–40%) due to a competitive cleavage reaction of the Ge–N bond to give ligand **1** (Scheme 3).



Scheme 3.

Crystals of **4b** suitable for X-ray structure determination were obtained from a pentane solution. The molecular

structure is shown in Figure 4 and selected bond lengths and angles are given in Tables 1 and 2. The anilido–imine ligand chelates to the germanium centre to form the six-membered chelated ring, and the germanium atom lies  $0.542\text{ Å}$  out of the plane formed by the five other atoms. The three-coordinate germanium atom adopts a pyramidal geometry (the sum of the angles is  $273^\circ$ ) with the bonded oxygen atom approximately orthogonal towards the heterobicyclic plane. The amino C–N bond ( $1.364\text{ Å}$ ) is significantly shorter than the average value of carbon–nitrogen single bonds ( $1.47\text{ Å}$ ),<sup>[12,21]</sup> which indicates partial double bond character. By contrast, the imino C=N bond ( $1.306\text{ Å}$ ) retains its double bond character as observed in various complexes.<sup>[7]</sup> Accordingly, Ge–N bond lengths are different with the Ge–N(imino) bond (Ge1–N2  $2.041\text{ Å}$ ) significantly longer than the Ge–N(amido) bond (Ge1–N1  $1.956\text{ Å}$ ), which corresponds to the simultaneous presence of both coordinate and covalent bonds in the coordination sphere of the metal centre. However, it should be noted that the difference remains low ( $\Delta d = 0.08\text{ Å}$ ) and that such bond lengths are in the normal range of cyclic conjugated bonds observed with aminotroponimate ligands ( $1.96\text{ Å}$ )<sup>[22]</sup> and with diketiminato ligands ( $2.00\text{ Å}$ ),<sup>[23]</sup> this suggests possible delocalization of the electrons on the heterocycle. The Ge–O distance ( $1.840\text{ Å}$ ) is quite close to that observed by Jutzi in [2,4-di-*tert*-butyl-6-((dimethylamino)methyl)phenyl]germanium ethoxide ( $1.844\text{ Å}$ )<sup>[20c]</sup> and is characteristic of a covalent Ge–O bond.<sup>[24]</sup> The  $^1\text{H}$  and  $^{13}\text{C}$  spectroscopic data are in good agreement with the solid-state structure and complete nonequivalence of the isopropyl signals as previously observed for compound **2b**.

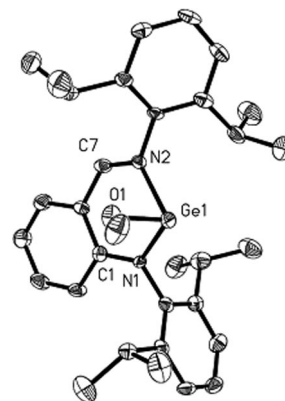


Figure 4. Molecular structure of **4b**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 50% probability.

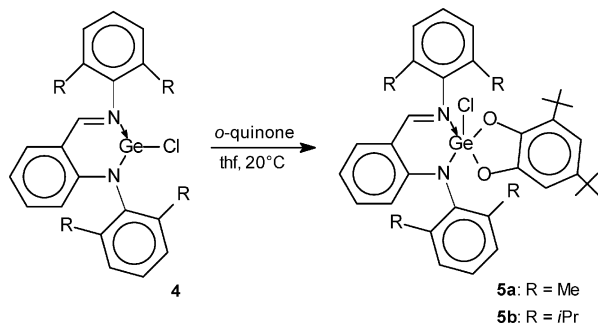
Table 1. Selected bond lengths [Å] for **4b**, **5a** and **5b**.

	<b>4b</b>	<b>5a</b>	<b>5b</b>
C1–N1	1.364(5)	1.407(6)	1.390(4)
C7–N2	1.306(5)	1.291(6)	1.291(4)
Ge1–N1	1.956(3)	1.856(4)	1.864(2)
Ge1–N2	2.041(3)	2.048(4)	2.043(2)
Ge1–O1	1.840(3)	1.813(3)	1.851(2)
Ge1–O2		1.856(4)	1.864(2)
Ge1–Cl		2.174(2)	2.155(1)

Table 2. Selected bond angles [°] for **4b**, **5a** and **5b**.

	<b>4b</b>	<b>5a</b>	<b>5b</b>
O1–Ge1–N1	97.48(13)	133.09(17)	121.80(9)
O1–Ge1–N2	87.12(13)	82.80(17)	82.81(9)
N1–Ge1–N2	88.44(13)	91.42(16)	92.50(10)
O1–Ge1–O2		87.08(16)	87.56(8)
O1–Ge1–Cl1		117.53(12)	128.55(7)
O2–Ge1–N2		169.46(16)	169.53(9)

These data imply that the geometry of the germanium atom is in a good agreement with a nonhybridized system; bonds are formed by using nearly pure p orbitals (sum of the angles 273°), whereas the lone pair of electrons must occupy an orbital with high s character. To verify if these germanium complexes retain their specific character of divalent sites, we also carried out an oxidative cycloaddition reaction with 3,5-di-*tert*-butyl-*ortho*-quinone<sup>[25]</sup> (Scheme 4). Treatment of **2a** or **2b** with *ortho*-quinone at room temperature in thf led to a progressive disappearance of the green colour of *ortho*-quinone.



Scheme 4.

After evaporation of the solvents and treatment by pentane, cycloadducts **5** were isolated as yellow powders that could be crystallized from a thf/toluene solution at –30 °C. The tin(II) compounds did not undergo this type of cycloaddition reaction because of their low stability. The molecular structures of **5a** and **5b** were determined by single-crystal X-ray analysis and are shown in Figures 5 and 6. Selected bond lengths and angles are given in Tables 1 and 2. For both **5a** and **5b**, the chelating character of the ligands to the metal centre as observed for germylene **4b** is conserved. The germanium atoms are pentacoordinate and adopt slightly distorted trigonal bipyramidal geometries with the nitrogen atom of the imino group and one oxygen atom of the quinonic cycle in axial positions. The sums of the bond angles at the germanium atoms are 359.8 and 359.9° for **5a** and **5b**, respectively. As observed in the case of **4b**, the germanium(IV) atoms are not located in the planes of the ligands; they are 0.6270 (for **5a**) and 0.4419 Å (for **5b**) out of the planes. The aryl groups are located in perpendicular planes, which decreases the steric hindrance. As expected, the Ge–N (amino) bonds (1.856 and 1.864 Å for **5a** and **5b**, respectively) are shortened and are in the range of covalent Ge–N bonds (1.85–1.90 Å)<sup>[16]</sup> because of the loss of their conjugated character. Surprisingly, there is

no change in the Ge–N(imino) distances, which indicates comparable chelation of the ligand to both the germanium(II) and germanium(IV) compounds.

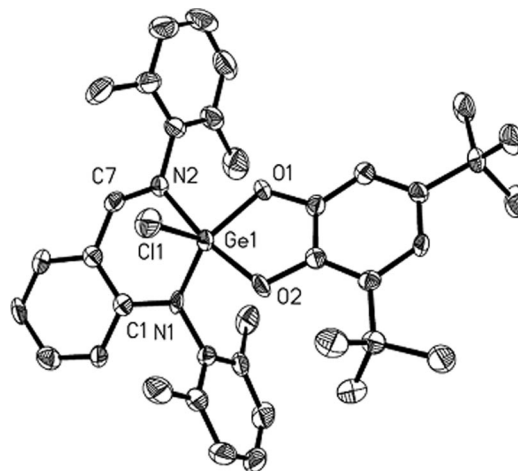


Figure 5. Molecular structure of **5a**. Hydrogen atoms and noncoordinated solvent molecules are omitted for clarity; thermal ellipsoids are drawn at 50% probability.

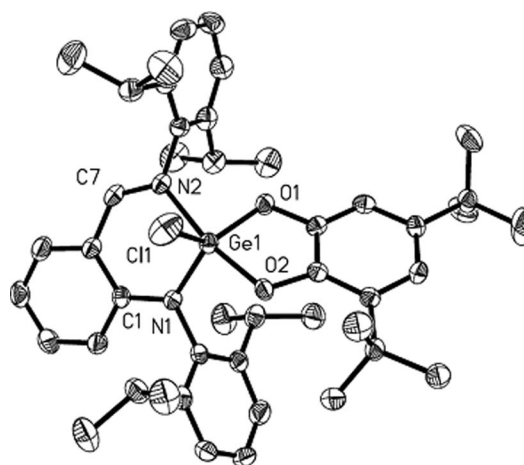


Figure 6. Molecular structure of **5b**. Hydrogen atoms and noncoordinated solvent molecules are omitted for clarity; thermal ellipsoids are drawn at 50% probability.

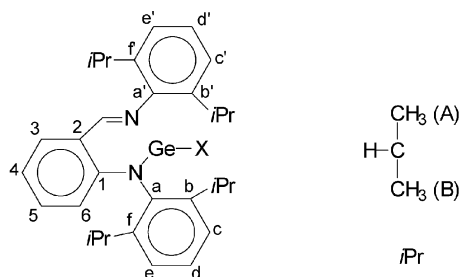
## Conclusions

We demonstrated that anilido-imine ligands are particularly suitable for stabilizing divalent germanium and tin species into their monomeric form. The NMR spectroscopic data, as well as the single-crystal X-ray analysis of the methoxygermylene confirm the perfect chelation of such ligands to the metal centre with formation of three-coordinate germanium. Moreover, these complexes preserve their specific reactivity, as was shown in the nucleophilic substitution of the chloride atom by the methoxy group and in the cycloaddition reaction with *o*-quinone. As a result of these promising results, we are currently testing this mode of stabilization to group 15 electron-rich elements.



## Experimental Section

**General Remarks:** All reactions were carried out under an argon atmosphere by using standard Schlenk techniques. Solvents were dried and distilled according to standard procedures and degassed prior to use. All reagents were purchased from Aldrich and were used without further purification. NMR spectra were recorded with the following spectrometers:  $^1\text{H}$ , Bruker Avance II 300 (300.13 MHz) and Avance II 500 (500.13 MHz);  $^{13}\text{C}$ , Bruker Avance II 300 (75.47 MHz) and Avance II 500 (125.77 MHz) (reference TMS);  $^{119}\text{Sn}$ , Bruker Avance II 300 (111.92 MHz) (reference  $\text{Me}_4\text{Sn}$ ).  $^1\text{H}$  and  $^{13}\text{C}$  NMR assignments of compounds **2a** and **2b** were obtained by COSY ( $^1\text{H}$ – $^1\text{H}$ ), HSQC ( $^1\text{H}$ – $^{13}\text{C}$ ), HMBC ( $^1\text{H}$ – $^{13}\text{C}$ ) and NOESY ( $^1\text{H}$ – $^1\text{H}$ ) experiments. Mass spectra were measured with a Hewlett–Packard HP 5989A in the electron impact mode (70 eV). Melting points were measured with a Leitz microscope or Electrothermal apparatus (capillary). Elemental analyses were done by the Centre de Microanalyse de l'Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques. The ligands *ortho*- $\text{C}_6\text{H}_4\{\text{NH}(\text{C}_6\text{H}_3\text{Me}_2-2,6)\}(\text{CH}=\text{NC}_6\text{H}_3\text{Me}_2-2,6)$ , *ortho*- $\text{C}_6\text{H}_4\{\text{NH}(\text{C}_6\text{H}_3\text{Pr}_2-2,6)\}(\text{CH}=\text{NC}_6\text{H}_3\text{Pr}_2-2,6)$ <sup>[7a,8]</sup> and  $\text{Cl}_2\text{Ge}$ -dioxane<sup>[26]</sup> were prepared according to literature procedures. Atom labelling scheme used in the NMR assignments of **2** and **5** is given below, for example, **2a**.



***ortho*- $\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_3\text{Me}_2-2,6)(\text{CH}=\text{NC}_6\text{H}_3\text{Me}_2-2,6)\text{GeCl}$  (**2a**):** A solution of *n*BuLi (1.02 mmol) in hexane (1.6 mL) was added to a solution of **1a** (0.30 g, 0.91 mmol) in diethyl ether (12 mL) at 0 °C. This mixture was then stirred for 30 min and slowly added to a solution of  $\text{GeCl}_2$ -dioxane (0.21 g, 0.91 mmol) in diethyl ether (10 mL) at –78 °C. After 1 h, the mixture was warmed to room temperature and stirred overnight. The volatiles were removed under reduced pressure, and the residue was extracted with toluene and filtered. The filtrate was concentrated in vacuo to give **2a** (0.26 g, 65%) as a yellow powder. M.p. 167 °C.  $^1\text{H}$  NMR (500.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.15 [s, 3 H, ( $\text{C}_6\text{H}_3\text{CH}_3$ )], 2.38 [s, 3 H, ( $\text{C}_6\text{H}_3\text{CH}_3$ )], 2.51 [s, 3 H, ( $\text{C}_6\text{H}_3\text{CH}_3$ )], 2.66 [s, 3 H, ( $\text{C}_6\text{H}_3\text{CH}_3$ )], 6.45 [d,  $^3J_{\text{H,H}} = 8.8$  Hz, 1 H,  $\text{C}_6\text{-H}$ ], 6.80 [dd,  $^3J_{\text{H,H}} = 7.1$  Hz,  $^3J_{\text{H,H}} = 7.9$  Hz, 1 H,  $\text{C}_4\text{-H}$ ], 7.17 [d,  $^3J_{\text{H,H}} = 7.4$  Hz, 1 H,  $\text{C}_6\text{-H}$ ], 7.20–7.22 (m, 2 H,  $\text{C}_d\text{-H}$ ,  $\text{C}_e\text{-H}$ ), 7.23 (t,  $^3J_{\text{H,H}} = 7.5$  Hz, 1 H,  $\text{C}_d\text{-H}$ ), 7.26–7.28 (m, 1 H,  $\text{C}_e\text{-H}$ ), 7.29 (d,  $^3J_{\text{H,H}} = 7.5$  Hz, 1 H,  $\text{C}_e\text{-H}$ ), 7.39 (ddd,  $^3J_{\text{H,H}} = 8.6$  Hz,  $^3J_{\text{H,H}} = 7.1$  Hz,  $^4J_{\text{H,H}} = 1.3$  Hz, 1 H,  $\text{C}_5\text{-H}$ ), 7.46 (d,  $^3J_{\text{H,H}} = 7.9$  Hz, 1 H,  $\text{C}_3\text{-H}$ ), 8.27 (s, 1 H,  $\text{HC}=\text{N}$ ) ppm.  $^{13}\text{C}$  NMR (125.77 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 19.0 ( $\text{C}_6\text{CH}_3$ ), 19.1 ( $\text{C}_6\text{CH}_3$ ), 19.7 ( $\text{C}_6\text{CH}_3$ ), 19.9 ( $\text{C}_6\text{CH}_3$ ), 116.8 ( $\text{C}_2$ ,  $\text{C}_6$ ), 117.1 ( $\text{C}_4$ ), 126.9 ( $\text{C}_d$ ), 127.8 ( $\text{C}_d$ ), 128.7 ( $\text{C}_e$ ), 129.0 ( $\text{C}_e$ ), 129.4 ( $\text{C}_e$ ), 130.2 ( $\text{C}_e$ ), 131.6 ( $\text{C}_b$ ), 132.9 ( $\text{C}_f$ ), 135.4 ( $\text{C}_b$ ), 136.6 ( $\text{C}_3$ ), 137.6 ( $\text{C}_5$ ), 138.4 ( $\text{C}_f$ ), 141.5 ( $\text{C}_a$ ), 144.71 ( $\text{C}_a$ ), 150.1 ( $\text{C}_1$ ), 166.3 ( $\text{C}=\text{N}$ ) ppm. MS (EI):  $m/z$  = 436 (54) [ $\text{M}]^+$ .  $\text{C}_{23}\text{H}_{23}\text{ClGeN}_2$  (435.49): calcd. C 63.43, H 5.32, N 6.43; found C 62.86, H 5.48, N 6.47.

***ortho*- $\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_3\text{Pr}_2-2,6)(\text{CH}=\text{NC}_6\text{H}_3\text{Pr}_2-2,6)\text{GeCl}$  (**2b**):** By using the same procedure as that described for **2a**, **1b** (1.00 g, 2.27 mmol) in diethyl ether (35 mL) and  $\text{GeCl}_2$ -dioxane (0.53 g,

2.28 mmol) in diethyl ether (35 mL) gave **2b** (0.77 g, 62%) as a yellow powder. M.p. 216 °C.  $^1\text{H}$  NMR (500.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.90 [d,  $^3J_{\text{H,H}} = 6.9$  Hz, 3 H,  $\text{C}_b\text{CH}(\text{CH}_3)_2\text{A}$ ], 1.08 [d,  $^3J_{\text{H,H}} = 6.8$  Hz, 3 H,  $\text{C}_b\text{CH}(\text{CH}_3)_2\text{A}$ ], 1.24 [d,  $^3J_{\text{H,H}} = 6.8$  Hz, 3 H,  $\text{C}_f\text{CH}(\text{CH}_3)_2\text{A}$ ], 1.29 [d,  $^3J_{\text{H,H}} = 6.7$  Hz, 3 H,  $\text{C}_f\text{CH}(\text{CH}_3)_2\text{B}$ ], 1.30 [d,  $^3J_{\text{H,H}} = 6.9$  Hz, 3 H,  $\text{C}_b\text{CH}(\text{CH}_3)_2\text{B}$ ], 1.35 [d,  $^3J_{\text{H,H}} = 6.8$  Hz, 3 H,  $\text{C}_b\text{CH}(\text{CH}_3)_2\text{B}$ ], 1.36 [d,  $^3J_{\text{H,H}} = 6.6$  Hz, 3 H,  $\text{C}_f\text{CH}(\text{CH}_3)_2\text{B}$ ], 1.41 [d,  $^3J_{\text{H,H}} = 6.9$  Hz, 3 H,  $\text{C}_f\text{CH}(\text{CH}_3)_2\text{A}$ ], 3.07 [sept,  $^3J_{\text{H,H}} = 6.9$  Hz, 1 H,  $\text{C}_b\text{CH}(\text{CH}_3)_2$ ], 3.32 [sept,  $^3J_{\text{H,H}} = 6.8$  Hz, 1 H,  $\text{C}_b\text{CH}(\text{CH}_3)_2$ ], 3.61 [sept,  $^3J_{\text{H,H}} = 6.8$  Hz, 2 H,  $\text{C}_f\text{CH}(\text{CH}_3)_2$ ],  $\text{C}_f\text{CH}(\text{CH}_3)_2$ ], 6.47 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 1 H,  $\text{C}_6\text{-H}$ ), 6.79 (dd,  $^3J_{\text{H,H}} = 7.9$  Hz,  $^3J_{\text{H,H}} = 6.9$  Hz, 1 H,  $\text{C}_4\text{-H}$ ), 7.27 (dd,  $^3J_{\text{H,H}} = 7.4$  Hz,  $^4J_{\text{H,H}} = 1.7$  Hz, 1 H,  $\text{C}_e\text{-H}$ ), 7.31 (dd,  $^3J_{\text{H,H}} = 6.7$  Hz,  $^4J_{\text{H,H}} = 2.6$  Hz, 1 H,  $\text{C}_e\text{-H}$ ), 7.37 (ddd,  $^3J_{\text{H,H}} = 8.8$  Hz,  $^3J_{\text{H,H}} = 6.9$  Hz,  $^4J_{\text{H,H}} = 1.9$  Hz, 1 H,  $\text{C}_5\text{-H}$ ), 7.38–7.39 (m, 1 H,  $\text{C}_e\text{-H}$ ), 7.40 (m, 1 H,  $\text{C}_d\text{-H}$ ), 7.41–7.43 (m, 1 H,  $\text{C}_d\text{-H}$ ), 7.42 (d,  $^3J_{\text{H,H}} = 7.9$  Hz, 1 H,  $\text{C}_3\text{-H}$ ), 7.44 (dd,  $^3J_{\text{H,H}} = 7.8$  Hz,  $^4J_{\text{H,H}} = 1.7$  Hz, 1 H,  $\text{C}_e\text{-H}$ ), 8.24 (s, 1 H,  $\text{HC}=\text{N}$ ) ppm.  $^{13}\text{C}$  NMR (125.77 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 23.00 [ $\text{C}_b\text{CH}(\text{CH}_3)_2\text{B}$ ], 24.21 [ $\text{C}_b\text{CH}(\text{CH}_3)_2\text{B}$ ], 24.68 [ $\text{C}_f\text{CH}(\text{CH}_3)_2\text{A}$ ], 24.84 [ $\text{C}_f\text{CH}(\text{CH}_3)_2\text{B}$ ], 25.10 [ $\text{C}_b\text{CH}(\text{CH}_3)_2\text{A}$ ], 25.20 [ $\text{C}_b\text{CH}(\text{CH}_3)_2\text{A}$ ], 26.48 [ $\text{C}_f\text{CH}(\text{CH}_3)_2\text{A}$ ], 26.83 [ $\text{C}_f\text{CH}(\text{CH}_3)_2\text{B}$ ], 27.98 ( $\text{C}_f\text{CH}$ ), 28.29 ( $\text{C}_f\text{CH}$ ), 28.97 ( $\text{C}_b\text{CH}$ ), 30.13 ( $\text{C}_b\text{CH}$ ), 116.61 ( $\text{C}_2$ ), 117.15 ( $\text{C}_4$ ), 118.27 ( $\text{C}_6$ ), 123.70 ( $\text{C}_e$ ), 124.54 ( $\text{C}_e$ ), 125.05 ( $\text{C}_e$ ), 125.91 ( $\text{C}_e$ ), 127.79 ( $\text{C}_d$ ), 128.54 ( $\text{C}_d$ ), 136.61 ( $\text{C}_3$ ), 137.12 ( $\text{C}_5$ ), 138.38 ( $\text{C}_a$ ), 141.77, 141.80 ( $\text{C}_b$ ,  $\text{C}_a$ ), 144.31 ( $\text{C}_f$ ), 146.05 ( $\text{C}_b$ ), 149.47 ( $\text{C}_f$ ), 151.40 ( $\text{C}_1$ ), 166.30 ( $\text{C}=\text{N}$ ) ppm. MS (EI):  $m/z$  = 548 (37) [ $\text{M}]^+$ .  $\text{C}_{31}\text{H}_{39}\text{ClGeN}_2$  (547.70): calcd. C 67.98, H 7.18, N 5.11; found C 67.27, H 7.20, N 4.71.

***ortho*- $\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_3\text{Me}_2-2,6)(\text{CH}=\text{NC}_6\text{H}_3\text{Me}_2-2,6)\text{SnCl}$  (**3a**):** A solution of *n*BuLi (1.02 mmol) in hexane (1.6 mL) was added to a solution of **1a** (0.30 g, 0.91 mmol) in diethyl ether (12 mL) at 0 °C. This mixture was then stirred for 30 min and slowly added to a solution of  $\text{Cl}_2\text{Sn}$  (0.17 g, 0.91 mmol) in diethyl ether (10 mL) at –78 °C. After 1 h, the mixture was warmed to room temperature and stirred for 12 h. The solvents were removed under reduced pressure, and the residue was extracted with toluene and filtered. The filtrate was concentrated in vacuo to give **3a** (0.38 g, 86%) as a yellow powder. M.p. 177 °C.  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  = 1.95–2.60 (m, 12 H,  $\text{CH}_3$ ), 6.32 (d,  $^3J_{\text{H,H}} = 8.6$  Hz, 1 H,  $\text{C}_6\text{-H}$ ), 6.61 (t,  $^3J_{\text{H,H}} = 7.0$  Hz, 1 H,  $\text{C}_4\text{-H}$ ), 7.20–7.30 (m, 8 H,  $\text{C}_3\text{-H}$ ,  $\text{C}_5\text{-H}$ ,  $\text{C}_6\text{H}_3$ ), 8.16 (s,  $J_{\text{Sn,H}} = 11.3$  Hz, 1 H,  $\text{HC}=\text{N}$ ) ppm.  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ , 233 K):  $\delta$  = 2.17 (s, 3 H,  $\text{CH}_3$ ), 2.36 (s, 3 H,  $\text{CH}_3$ ), 2.49 (s, 3 H,  $\text{CH}_3$ ), 2.63 (s, 3 H,  $\text{CH}_3$ ), 6.39 (d,  $^3J_{\text{H,H}} = 8.5$  Hz, 1 H,  $\text{C}_6\text{-H}$ ), 6.70 (t,  $^3J_{\text{H,H}} = 7.9$  Hz, 1 H,  $\text{C}_4\text{-H}$ ), 7.17–7.42 (m, 8 H,  $\text{C}_3\text{-H}$ ,  $\text{C}_5\text{-H}$ ,  $\text{C}_6\text{H}_3$ ), 8.16 (s,  $J_{\text{Sn,H}} = 11.0$  Hz, 1 H,  $\text{HC}=\text{N}$ ) ppm.  $^{13}\text{C}$  NMR (75.48 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 19.18, 19.40 ( $\text{CH}_3$ ), 115.90, 116.54 ( $\text{C}_4$ ,  $\text{C}_6$ ), 117.46 ( $\text{C}_2$ ), 126.23, 127.32, 129.27 ( $\text{C}_6\text{H}_3$ ), 137.01, 138.00 ( $\text{C}_3$ ,  $\text{C}_5$ ), 143.52, 146.27 ( $\text{C}_6\text{H}_3$ , quat.), 152.36 ( $\text{C}_1$ ), 168.23 ( $\text{C}=\text{N}$ ) ppm.  $^{119}\text{Sn}$  NMR (111.92 MHz,  $\text{CDCl}_3$ ):  $\delta$  = –264 ppm. MS (EI):  $m/z$  = 482 (51) [ $\text{M}]^+$ . This compound is not stable in solution and slowly decomposes at room temperature. Reproducible analyses could not be obtained.

***ortho*- $\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_3\text{Pr}_2-2,6)(\text{CH}=\text{NC}_6\text{H}_3\text{Pr}_2-2,6)\text{SnCl}$  (**3b**):** By using the same procedure as that described for **3a**, **1b** (0.30 g, 0.68 mmol) in diethyl ether (12 mL) and  $\text{Cl}_2\text{Sn}$  (0.13 g, 0.68 mmol) in diethyl ether (10 mL) gave **3b** (0.30 g, 75%) as a yellow solid. M.p. 184 °C.  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.96 [d,  $^3J_{\text{H,H}} = 6.9$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.09 [d,  $^3J_{\text{H,H}} = 6.6$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.21 [d,  $^3J_{\text{H,H}} = 6.7$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.24 [d,  $^3J_{\text{H,H}} = 6.7$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.27 [d,  $^3J_{\text{H,H}} = 6.6$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.29 [d,  $^3J_{\text{H,H}} = 6.8$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.35 [d,  $^3J_{\text{H,H}} = 6.8$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.38 [d,  $^3J_{\text{H,H}} = 6.9$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 3.14 [sept,  $^3J_{\text{H,H}} = 6.9$  Hz, 1 H,  $\text{CH}(\text{CH}_3)_2$ ], 3.21 [sept,  $^3J_{\text{H,H}} = 6.7$  Hz, 1 H,

$\text{CH}(\text{CH}_3)_2$ , 3.62 [sept,  $^3J_{\text{H,H}} = 6.6$  Hz, 1 H,  $\text{CH}(\text{CH}_3)_2$ ], 3.68 [sept,  $^3J_{\text{H,H}} = 6.8$  Hz, 1 H,  $\text{CH}(\text{CH}_3)_2$ ], 6.42 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 1 H,  $\text{C}_6\text{-H}$ ), 6.67 (t,  $^3J_{\text{H,H}} = 6.8$  Hz, 1 H,  $\text{C}_4\text{-H}$ ), 7.15–7.45 (m, 8 H,  $\text{C}_3\text{-H}$ ,  $\text{C}_5\text{-H}$ ,  $\text{C}_6\text{H}_3$ ), 8.21 (s,  $J_{\text{Sn,H}} = 10.6$  Hz, 1 H,  $\text{HC}=\text{N}$ ) ppm.  $^{13}\text{C}$  NMR (75.48 MHz,  $\text{CDCl}_3$ ):  $\delta = 22.98, 23.54, 24.44, 24.87, 24.98, 25.12, 26.19, 26.99$  [ $\text{CH}(\text{CH}_3)_2$ ], 27.63, 28.00, 28.71, 30.36 [ $\text{CH}(\text{CH}_3)_2$ ], 117.46 ( $\text{C}_2$ ), 115.98, 118.18 ( $\text{C}_4$ ,  $\text{C}_6$ ), 123.52, 124.56, 124.98, 125.82, 127.09, 128.06 ( $\text{C}_6\text{H}_3$ ), 136.44, 137.95 ( $\text{C}_3$ ,  $\text{C}_5$ ), 138.19, 141.20, 143.65, 145.33, 148.38 ( $\text{C}_6\text{H}_3$ , quat.), 153.69 ( $\text{C}_1$ ), 168.12 ( $\text{C}=\text{N}$ ) ppm.  $^{119}\text{Sn}$  NMR (111.92 MHz,  $\text{CDCl}_3$ ):  $\delta = -266$  ppm. MS (EI):  $m/z = 594$  (80)  $[\text{M}]^+$ . This compound is not stable in solution and slowly decomposes at room temperature. Reproducible analyses could not be obtained.

**ortho- $\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CH}=\text{NC}_6\text{H}_3\text{Me}_2\text{-2,6})\text{GeOMe}$  (4a):** A solution of  $n\text{BuLi}$  (0.32 mmol) in hexane (1.6 mL) was added to a solution of MeOH (0.01 g, 0.31 mmol) in thf (3 mL) at  $-65^\circ\text{C}$ . The reaction mixture was warmed to room temperature and stirred for 30 min. The resulting solution was slowly added to a solution of **2a** (0.14 g, 0.32 mmol) in thf (3 mL) at  $-78^\circ\text{C}$ . The mixture was warmed to room temperature and stirred for 2 h. The volatiles were removed under reduced pressure, and the residue was extracted with toluene (5 mL). The filtrate was removed in vacuo to give a yellow solid.  $^1\text{H}$  NMR spectroscopic analysis showed the formation of **4a** (25%) and the presence of **1a** (75%).  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.03$  (s, 3 H,  $\text{CH}_3$ ), 2.19 (s, 3 H,  $\text{CH}_3$ ), 2.34 (s, 3 H,  $\text{CH}_3$ ), 2.44 (s, 3 H,  $\text{CH}_3$ ), 3.29 (s, 3 H,  $\text{OCH}_3$ ), 6.22 (d,  $^3J_{\text{H,H}} = 8.6$  Hz, 1 H,  $\text{C}_6\text{-H}$ ), 6.51 (t,  $^3J_{\text{H,H}} = 7.1$  Hz, 1 H,  $\text{C}_4\text{-H}$ ), 6.99–7.26 (m, 8 H,  $\text{C}_5\text{-H}$ ,  $\text{C}_3\text{-H}$ ,  $\text{C}_6\text{H}_3$ ), 8.04 (s, 1 H,  $\text{HC}=\text{N}$ ) ppm. MS (EI):  $m/z = 432$  (3)  $[\text{M}]^+$ .

**ortho- $\text{C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-2,6})(\text{CH}=\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6})\text{GeOMe}$  (4b):** By using the same procedure as that described for **4a**, MeOH (0.02 g, 0.62 mmol) in thf (5 mL) and **2b** (0.32 g, 0.56 mmol) in thf (4 mL) gave **4b** as a yellow solid.  $^1\text{H}$  NMR spectroscopic analysis showed the formation of **4b** (40%) and the presence of **1b** (60%). Crystallization from pentane at  $-30^\circ\text{C}$  gave yellow crystals.  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.78$  [d,  $^3J_{\text{H,H}} = 6.8$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 0.94 [d,  $^3J_{\text{H,H}} = 6.8$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.13 [d,  $^3J_{\text{H,H}} = 6.9$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.16 [d,  $^3J_{\text{H,H}} = 7.0$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.19 [d,  $^3J_{\text{H,H}} = 7.3$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.22 [d,  $^3J_{\text{H,H}} = 7.1$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.25 [d,  $^3J_{\text{H,H}} = 6.8$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.27 [d,  $^3J_{\text{H,H}} = 6.6$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 3.09 [sept,  $^3J_{\text{H,H}} = 6.9$  Hz, 1 H,  $\text{CH}(\text{CH}_3)_2$ ], 3.15 [sept,  $^3J_{\text{H,H}} = 6.8$  Hz, 1 H,  $\text{CH}(\text{CH}_3)_2$ ], 3.38 (s, 3 H,  $\text{OCH}_3$ ), 3.53 [sept,  $^3J_{\text{H,H}} = 6.8$  Hz, 2 H,  $\text{CH}(\text{CH}_3)_2$ ], 6.24 (d,  $^3J_{\text{H,H}} = 9.0$  Hz, 1 H,  $\text{C}_6\text{-H}$ ), 6.62 (t,  $^3J_{\text{H,H}} = 7.6$  Hz, 1 H,  $\text{C}_4\text{-H}$ ), 7.06–7.28 (m, 8 H,  $\text{C}_5\text{-H}$ ,  $\text{C}_3\text{-H}$ ,  $\text{C}_6\text{H}_3$ ), 8.04 (s, 1 H,  $\text{HC}=\text{N}$ ) ppm.  $^{13}\text{C}$  NMR (75.48 MHz,  $\text{CDCl}_3$ ):  $\delta = 23.13$  [ $\text{C}_b\text{-CH}(\text{CH}_3)\text{B}$ ], 24.65, 24.86, 25.23, 25.33, 25.46 [ $\text{CH}(\text{CH}_3)\text{A}$ ], 26.43 [ $\text{C}_f\text{-CH}(\text{CH}_3)\text{A}$ ], 27.18 [ $\text{C}_f\text{-CH}(\text{CH}_3)\text{B}$ ], 28.09, 28.15 ( $\text{C}_f\text{-CH}$ ,  $\text{C}_f\text{-CH}$ ), 29.09, 29.74 ( $\text{C}_b\text{-CH}$ ,  $\text{C}_b\text{-CH}$ ), 53.09 ( $\text{OCH}_3$ ), 115.94 ( $\text{C}_4$ ), 116.11 ( $\text{C}_2$ ), 118.43 ( $\text{C}_6$ ), 123.91, 124.85, 124.88, 125.48, 127.46, 128.26 ( $\text{C}_6\text{H}_3$ ), 136.36, 136.97 ( $\text{C}_3$ ,  $\text{C}_5$ ), 140.60, 142.48, 143.91, 144.18, 146.34, 149.10 ( $\text{C}_6\text{H}_3$ , quat.), 152.39 ( $\text{C}_1$ ), 165.17 ( $\text{C}=\text{N}$ ) ppm. MS (EI):  $m/z = 544$  (7)  $[\text{M}]^+$ . This compound is very air sensitive and slowly decomposes at room temperature. Reproducible analyses could not be obtained.

**Reaction of 2a with 3,5-di-*tert*-butyl-*ortho*-quinone:** To a solution of **2a** (0.22 g, 0.50 mmol) in thf (6 mL) was added a solution of *o*-quinone (0.10 g, 0.45 mmol) in thf (4 mL). The mixture was stirred at  $20^\circ\text{C}$  for 2 h. The solvent was evaporated, and the residue was washed with pentane. After filtration and drying, **5a** (0.20 g, 61%) was obtained as a yellow powder. Crystallization from thf/toluene at  $-30^\circ\text{C}$  gave yellow crystals. M.p.  $170^\circ\text{C}$ .  $^1\text{H}$  NMR

(300.13 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.85$  [s, 9 H,  $\text{C}(\text{CH}_3)_3$ ], 1.12 [s, 9 H,  $\text{C}(\text{CH}_3)_3$ ], 1.99 [s, 3 H,  $(\text{CH}_3)$ ], 2.27 [s, 3 H,  $(\text{CH}_3)$ ], 2.48 [s, 3 H,  $(\text{CH}_3)$ ], 2.53 [s, 3 H,  $(\text{CH}_3)$ ], 6.26 (d,  $^4J_{\text{H,H}} = 2.2$  Hz, 1 H,  $\text{C}_6\text{H}_2$ ), 6.40 (d,  $^4J_{\text{H,H}} = 2.2$  Hz, 1 H,  $\text{C}_6\text{H}_2$ ), 6.41 (d,  $^3J_{\text{H,H}} = 8.4$  Hz, 1 H,  $\text{C}_6\text{-H}$ ), 6.80–7.40 (m, 9 H,  $\text{C}_6\text{H}_3$ ,  $\text{C}_6\text{H}_4$ ), 8.24 (s, 1 H,  $\text{HC}=\text{N}$ ) ppm.  $^{13}\text{C}$  NMR (75.48 MHz,  $\text{CDCl}_3$ ):  $\delta = 19.18, 19.68, 19.89, 20.57$  ( $\text{CH}_3$ ), 29.35, 31.68 [ $\text{C}(\text{CH}_3)_3$ ], 33.88, 34.25 [ $\text{C}(\text{CH}_3)_3$ ], 106.63, 112.16 ( $\text{C}_6\text{H}_2$ ), 115.59 ( $\text{C}_2$ ), 117.74, 118.76 ( $\text{C}_4$ ,  $\text{C}_6$ ), 126.89, 127.42, 128.59, 128.77, 128.88, 129.34 ( $\text{C}_6\text{H}_3$ ), 131.67, 132.74, 133.36, 134.81 ( $\text{C}_6\text{H}_3$ ,  $\text{C}_6\text{H}_2$ , quat.), 136.17, 137.04 ( $\text{C}_3$ ,  $\text{C}_5$ ), 139.50, 139.80, 141.80, 146.73, 148.42, 149.98 ( $\text{C}_6\text{H}_3$ ,  $\text{C}_6\text{H}_2$ , quat.), 153.80 ( $\text{C}_1$ ), 172.03 ( $\text{C}=\text{N}$ ) ppm. MS (EI):  $m/z = 656$  (93)  $[\text{M}]^+$ .  $\text{C}_{37}\text{H}_{43}\text{ClGeN}_2\text{O}_2$  (655.80): calcd. C 67.77, H 6.61, N 4.27; found C 68.37, H 7.23, N 3.89.

**Reaction of 2b with 3,5-di-*tert*-butyl-*ortho*-quinone:** By using the same procedure as that described for **5a**, **2b** (0.25 g, 0.45 mmol) in thf (6 mL) and *o*-quinone (0.06 g, 0.30 mmol) in thf (4 mL) gave **5b** (0.20 g, 58%) as a yellow powder. Crystallization from thf/toluene at  $-30^\circ\text{C}$  gave yellow crystals. M.p.  $227^\circ\text{C}$ .  $^1\text{H}$  NMR (300.13 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.73$  [d,  $^3J_{\text{H,H}} = 6.8$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 0.88 [d,  $^3J_{\text{H,H}} = 6.8$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 0.89 [s, 9 H,  $\text{C}(\text{CH}_3)_3$ ], 0.99 [d,  $^3J_{\text{H,H}} = 6.9$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.19 [s, 9 H,  $\text{C}(\text{CH}_3)_3$ ], 1.24 [d,  $^3J_{\text{H,H}} = 6.8$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.32 [d,  $^3J_{\text{H,H}} = 6.9$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.36 [d,  $^3J_{\text{H,H}} = 6.7$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.43 [d,  $^3J_{\text{H,H}} = 6.8$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 1.48 [d,  $^3J_{\text{H,H}} = 6.7$  Hz, 3 H,  $\text{CH}(\text{CH}_3)_2$ ], 3.28 [sept,  $^3J_{\text{H,H}} = 6.8$  Hz, 1 H,  $\text{CH}(\text{CH}_3)_2$ ], 3.33 [sept,  $^3J_{\text{H,H}} = 6.8$  Hz, 1 H,  $\text{CH}(\text{CH}_3)_2$ ], 3.36 [sept,  $^3J_{\text{H,H}} = 6.8$  Hz, 1 H,  $\text{CH}(\text{CH}_3)_2$ ], 3.88 [sept,  $^3J_{\text{H,H}} = 6.7$  Hz, 1 H,  $\text{CH}(\text{CH}_3)_2$ ], 6.43 (d,  $^4J_{\text{H,H}} = 3.0$  Hz, 1 H,  $\text{C}_6\text{H}_2$ ), 6.52 (d,  $^4J_{\text{H,H}} = 3.0$  Hz, 1 H,  $\text{C}_6\text{H}_2$ ), 6.44 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 1 H,  $\text{C}_6\text{-H}$ ), 6.91 (t,  $^3J_{\text{H,H}} = 9.0$  Hz, 1 H,  $\text{C}_4\text{-H}$ ), 7.11–7.45 (m, 8 H,  $\text{C}_3\text{-H}$ ,  $\text{C}_5\text{-H}$ ,  $\text{C}_6\text{H}_3$ ), 8.29 (s, 1 H,  $\text{HC}=\text{N}$ ) ppm.  $^{13}\text{C}$  NMR (75.48 MHz,  $\text{CDCl}_3$ ):  $\delta = 21.98, 22.25, 23.99, 24.41, 25.02, 25.37, 25.75, 25.79$  [ $\text{CH}(\text{CH}_3)_2$ ], 28.31, 28.40, 29.09, 29.96 [ $\text{CH}(\text{CH}_3)_2$ ], 29.44, 31.65 [ $\text{C}(\text{CH}_3)_3$ ], 33.96, 34.14 [ $\text{C}(\text{CH}_3)_3$ ], 106.45, 112.55 ( $\text{C}_6\text{H}_2$ ), 114.26 ( $\text{C}_2$ ), 118.67, 119.27 ( $\text{C}_4$ ,  $\text{C}_6$ ), 123.25, 124.20, 124.66, 125.22, 127.64, 128.08 ( $\text{C}_6\text{H}_3$ ), 132.43 ( $\text{C}_6\text{H}_2$ , quat.), 136.23, 136.42 ( $\text{C}_3$ ,  $\text{C}_5$ ), 138.89, 139.51, 141.67, 143.29, 144.30, 144.80, 145.45, 145.61, 148.01 ( $\text{C}_6\text{H}_3$ ,  $\text{C}_6\text{H}_2$ , quat.), 155.28 ( $\text{C}_1$ ), 171.86 ( $\text{C}=\text{N}$ ) ppm. MS (EI):  $m/z = 769$  (42)  $[\text{M} + \text{H}]^+$ .  $\text{C}_{45}\text{H}_{59}\text{ClGeN}_2\text{O}_2$  (768.01): calcd. C 70.38, H 7.74, N 3.65; found C 69.64, H 7.35, N 3.58.

**X-ray Structure Determination:** All data for all structures represented in this paper were collected at low temperature by using an oil-coated shock-cooled crystal with a Bruker-AXS CCD 1000 diffractometer with Mo- $K_\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods<sup>[27]</sup> and all non-hydrogen atoms were refined anisotropically by using the least-squares method on  $F^2$ .<sup>[28]</sup>

**4b:**  $\text{C}_{32}\text{H}_{42}\text{GeN}_2\text{O}$ ,  $M = 543.27$ , monoclinic,  $a = 9.7264(3)$  Å,  $b = 26.3655(8)$  Å,  $c = 11.3724(3)$  Å,  $\beta = 95.577(2)^\circ$ ,  $V = 2902.6(2)$  Å<sup>3</sup>,  $T = 173(2)$  K, space group  $P2_1/n$ ,  $Z = 4$ ,  $\mu = 1.081$  mm<sup>-1</sup>, 16713 reflections measured, (4086 independent,  $R_{\text{int}} = 0.0775$ ) were collected. Largest diff. peak and hole: 0.453 and  $-0.672$  e Å<sup>-3</sup>.  $R_1$  [ $I > 2\sigma(I)$ ] = 0.0464 and  $wR_2 = 0.0966$  (all data) with  $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$  and  $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{0.5}$ . **5a:**  $\text{C}_{51}\text{H}_{59}\text{ClGeN}_2\text{O}_2$ ,  $M = 840.04$ , monoclinic,  $a = 11.463(1)$  Å,  $b = 15.005(2)$  Å,  $c = 26.655(3)$  Å,  $\beta = 101.518(2)^\circ$ ,  $V = 4492.3(8)$  Å<sup>3</sup>,  $T = 173(2)$  K, space group  $P2_1/n$ ,  $Z = 4$ ,  $\mu = 0.782$  mm<sup>-1</sup>, 19574 reflections measured, (6374 independent,  $R_{\text{int}} = 0.1163$ ) were collected. Largest diff. peak and hole: 0.758 and  $-0.800$  e Å<sup>-3</sup>.  $R_1$  [ $I > 2\sigma(I)$ ] = 0.0599 and  $wR_2 = 0.1402$  (all data). **5b:**  $\text{C}_{52}\text{H}_{67}\text{ClGeN}_2\text{O}_2$ ,  $M = 860.12$ , monoclinic,  $a = 17.376(1)$  Å,  $b = 16.349(1)$  Å,  $c =$

18.004(1) Å,  $\beta = 109.386(1)^\circ$ ,  $V = 4824.8(5) \text{ Å}^3$ ,  $T = 173(2) \text{ K}$ , space group  $P2_1/n$ ,  $Z = 4$ ,  $\mu = 0.730 \text{ mm}^{-1}$ , 21073 reflections measured, (6843 independent,  $R_{\text{int}} = 0.0558$ ) were collected. Largest diff. peak and hole: 0.417 and  $-0.298 \text{ e Å}^{-3}$ .  $R_1 [I > 2\sigma(I)] = 0.0382$  and  $wR_2 = 0.0866$  (all data).

CCCD-695220 (for **4b**), -695221 (for **5a**) and -695222 (for **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Supporting Information** (see footnote on the first page of this article): Details of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data for **2a** and **2b**.

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