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Halogermanium(II) Complexes Having Phenylamidinate As Supporting Ligands: Syntheses, Characterizations, and Reactivities

Dimitri Matioszek,[†] Nadia Katir,[†] Nathalie Saffon,[‡] and Annie Castel*[,†]

[†] *Laboratoire Hétérochimie Fondamentale et Appliquée, UMR/CNRS 5069, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex 09, France, and* [‡] *Structure Fédérative Toulousaine en Chimie Moléculaire (FR2599), Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex 09, France*

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Novel germylenes [{$Me_3SiNC(Ph)NSiMe_3$}GeX] (X = Cl, Br, I) and [{$Me_3SiNC(Ph)NSiMe_3$}$_2$Ge] with the bidentate phenylamidinato ligand have been synthesized in high yields by a salt metathesis reaction between $Cl_2Ge\cdot$dioxane or I_2Ge and the lithium salt of the ligand. They were characterized by ^1H and ^{13}C NMR and mass spectrometry and single-crystal X-ray structure analyses, which confirmed N-chelation and a three-coordinate germanium center. The cycloaddition reactions with *o*-quinone led to cycloadducts, whose structures were determined by X-ray analyses. The chelation of the ligand to the metal center was conserved, affording penta- and hexacoordinated germanium(IV) atoms. Complexation reactions with [codW(CO)$_4$] and [nbdMo(CO)$_4$] resulted in trinuclear bis(germanium(II)) transition-metal complexes in "*trans*" octahedral geometry.

Introduction

During the last three decades, the stabilization and isolation of compounds with group 14 elements in unusual or low oxidation states has received considerable attention, particularly since the discovery of the Arduengo-type carbene in 1991.[1] The rapid development of the chemistry of N-heterocyclic carbenes (NHC) and their use in transition-metal catalysis[2] and more recently as organocatalysts[3] have increased interest in their higher congeners, NHGe or NHSn, although they had been discovered earlier.[4] Since these initial reports, the chemistry of stable NHGe has largely been developed.[5] Besides the divalent NHGe featuring two normal covalent Ge−N bonds, the tricoordinated species having amino/imino ligands with a covalent Ge−N bond and a coordinative Ge→N bond have also been reported. Examples of such ligands include amidinates,[5b] aminotroponiminates,[6] and *β*-diketiminates.[5d] In this context, we have recently reported the preparation of new germylenes and stannylenes with chelating anilido-imine ligands showing both the chelating and electron donor properties of these ligands.[7] Although a large number of germanium(II) compounds have been isolated, the search for new ligands able to stabilize low-coordinate compounds is still very important today. Indeed, an unexpected application of dicyclopentadienyl, amido, and alkoxy germylenes as precursors of nanomaterials has recently been described and opens a wide field of investigation.[8] Likewise, amidinate ligands have been emphasized as convenient precursors for CVD methods.[9] They are bidentate, three-atom-bridging moieties with the general formula $[R'NC(R)NR']^-$. Another characteristic is the possibility of modifying their steric and electronic properties by changing the organic substituents at the nitrogen atom as well at the bridging carbon atom. Only a few chlorogermylenes with amidinate or guanidinate ligands[10] and with alkyl or aryl substituents at nitrogen atoms[5d,e,11] have been reported so far. With the bulky trimethylsilyl group as substituent, only the mixed amidinato amido complex [{$Me_3SiNC(t\text{-}Bu)NSiMe_3$}Ge{$N(SiMe_3)_2$}] was obtained because of a rearrangement of the lithium amidinate salt.[12] 1,3

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*To whom correspondence should be addressed. E-mail: castel@chimie.ups-tlse.fr.

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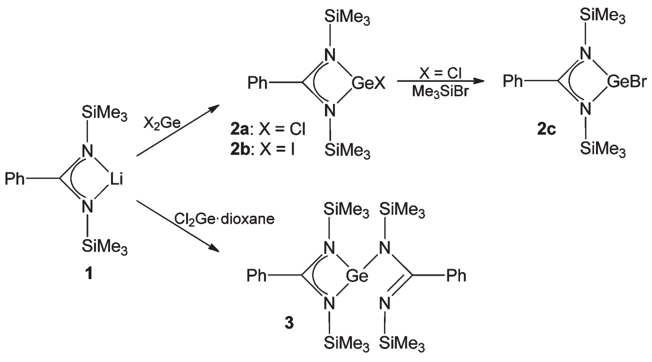
Scheme 1



Trimethylsilyl shifts within the amidinate framework were suggested to lose *t*-BuCN and generate $(Me_3Si)_2NLi$, which in turn reacted with the transient chlorogermylene. Changing a *tert*-butyl to a methyl group partially stabilizes the lithium salt. With a phenyl group at the methine carbon, while the unstable amidonato chlorosilylene decomposed into a six-coordinate $[\{Me_3SiNC(Ph)NSiMe_3\}_2SiCl_2]$,[13] the corresponding tin analogue was obtained by treatment in situ with lithium hexamethyldisilazide.[14] However to the best of our knowledge, this ligand remains unknown in germanium chemistry. Thus, our study in this area will explore the use of a phenylamidinato ligand to stabilize halogermanium(II) species and investigate its effect on their reactivity.

The present work reports the preparation of novel phenylamidinate-based germanium(II) complexes and their full characterization including single-crystal X-ray diffraction structure determinations. In order to gain insights into the chemical behavior of these species, oxidative cycloadditions with *o*-quinone and complexation with transition-metal complexes will be described.

Results and Discussion

Ge(II) Complexes of the $[(Me_3SiNC(Ph)NSiMe_3)]^-$ Anion. The lithium amidinate salt **1** was prepared by treatment of benzonitrile with $(Me_3Si)_2NLi$ in diethyl ether according to the method previously described.[15] Stoichiometric reactions of **1** with $Cl_2Ge\cdot$dioxane and with I_2Ge led to the formation of new halogermylenes **2a** and **2b** in almost quantitative yields, 95% and 98%, respectively. No trace of the amidinato amido complex was detected in the crude reaction product, confirming the stability of **1**. In addition, the reaction is highly selective without forming bis(amidinate)germylene **3** which could be easily prepared using two equivalents of **1** (Scheme 1). Note that it is the first example of such selectivity in the group 14 series. Recently, Gibson et al. reported that the nature of the group on methine carbon highly regulates such reactions.[16] By using the methyl group, a mixture of chloromonoamidinate [{ArNC(Me)NAr}SnCl] and bis(amidinate) tin(II) complexes $[\{ArNC(Me)NAr\}_2Sn]$ (Ar = 2,6-*i*-$Pr_2C_6H_3$) was obtained, whereas the bulkier *tert*-butyl ligand gave the monochloride complex [{ArNC(*t*-Bu)NAr}SnCl] exclusively. In our case, the combination of trimethylsilyl and phenyl substituents on the amidinato moieties allowed stabilization of both the amidinate salt **1** and halogermylenes without preventing access to **3**.

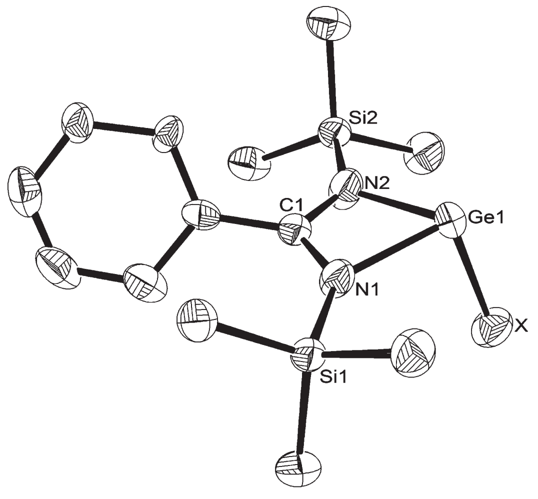


Figure 1. Molecular structures of **2a** (X = Cl) and **2c** (X = Br). Thermal ellipsoids are set at 50% probability. Hydrogen atoms and disordered atoms have been omitted for clarity. Selected bond distances [Å] and bond angles [deg] for **2a**: Ge(1)−Cl(1) 2.2632(18); Ge(1)−N(1) 2.031(4); Ge(1)−N(2) 2.059(4); C(1)−N(1) 1.337(6); C(1)−N(2) 1.326(6); N(1)−Ge(1)−N(2) 65.56(16); N(1)−Ge(1)−Cl(1) 95.69(13); N(2)−Ge(1)−Cl(1) 97.27(15). Selected bond distances [Å] and bond angles [deg] for **2c**: Ge(1)−Br(1) 2.4239(12); Ge(1)−N(1) 2.049(6); Ge(1)−N(2) 2.037(5); C(1)−N(1) 1.316(8); C(1)−N(2) 1.351(8); N(1)−Ge(1)−N(2) 66.0(2); N(1)−Ge(1)−Br(1) 97.55(17); N(2)−Ge(1)−Br(1) 95.81(16).

Addition of an excess of Me_3SiBr to **2a** at room temperature led to bromogermylene **2c** quantitatively.

These germanium(II) species were isolated as pale yellow powders which are stable under inert atmosphere and can be stored for long periods at low temperature (−30 °C). They show high solubility in organic solvents such as pentane, hexanes, diethyl ether, THF and toluene. Their stability in solution decreases rapidly from **2a**, **2c**, **3** to **2b**. All attempts to crystallize **2b** failed, and only the salt $[\{H(Me_3Si)NC(Ph)N(SiMe_3)H\}^+ I^-]$[17] was isolated and its structure elucidated by X-ray diffraction method. All the compounds were perfectly characterized by ^1H and ^{13}C NMR, and mass spectrometry. In all cases, only a single methyl group signal was observed in the NMR spectra. When a dynamic ^1H NMR experiment was performed in the temperature range +20 °C to −80 °C for **3**, a singlet was always observed indicating fluxional behavior with equivalent nitrogen atoms and the existence of a symmetrical coordination at the germanium center on the NMR time-scale.

To establish the geometries of these germanium(II) compounds, X-ray crystal structure determinations were done. The halogermylenes **2a** and **2c** are isomorphous and their structures are very similar to those recently described for chloroamidinato[11a] and guanidinato germylenes.[10] Structures of **2a** and **2c** are given in Figure 1 together with selected bond lengths and angles. The amidinato ligand chelates to the germanium center to form a four membered ring with the

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(17) Molecular structure of $[\{H(Me_3Si)NC(Ph)N(SiMe_3)H\}^+I^-]$ are given in the Supporting Information.

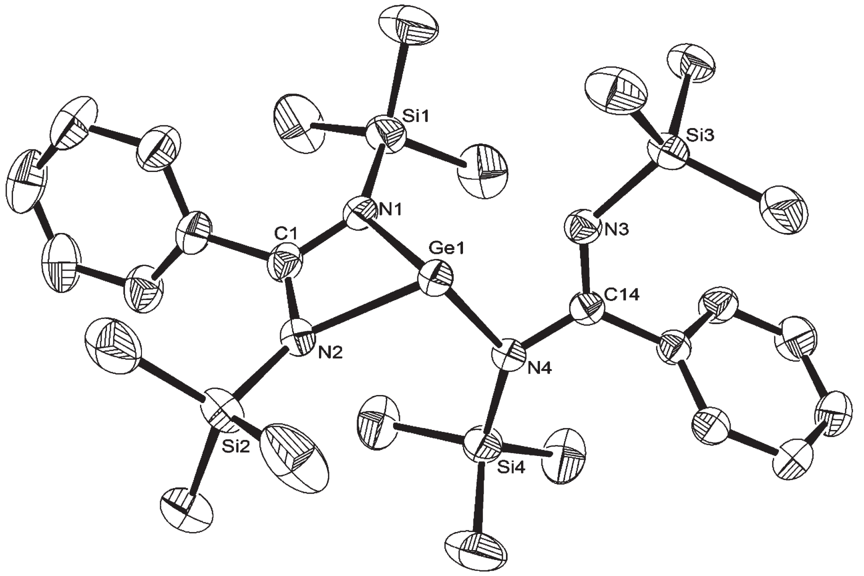
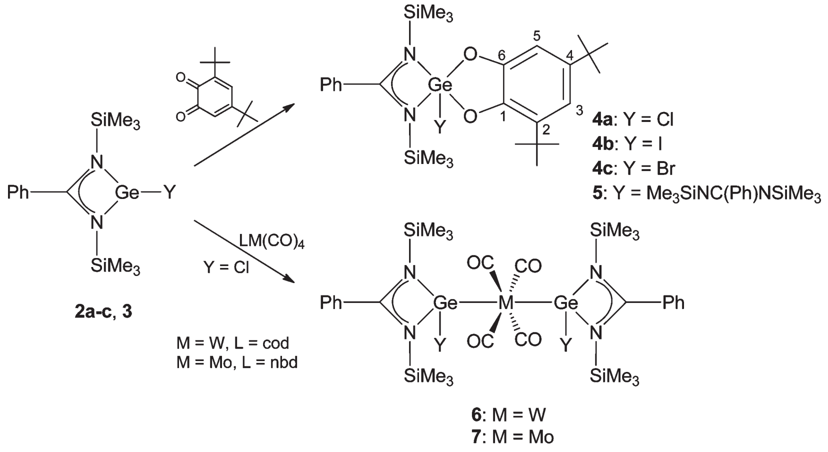


Figure 2. ORTEP view of compound **3** (50% probability level for the thermal ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and bond angles [deg]: Ge(1)−N(1) 2.0106(18); Ge(1)−N(2) 2.1948(19); Ge(1)···N(3) 2.3397(18); Ge(1)−N(4) 2.0121(18); C(1)−N(1) 1.346(3); C(1)−N(2) 1.322(3); C(14)−N(3) 1.308(3); C(14)−N(4) 1.348(3); N(1)−Ge(1)−N(2) 64.21(7); N(1)−Ge(1)−N(3) 100.68(7); N(1)−Ge(1)−N(4) 98.22(8); N(2)−Ge(1)−N(3) 155.07(7); N(2)−Ge(1)−N(4) 99.04(7); N(3)−Ge(1)−N(4) 62.01(7).

Scheme 2



germanium atom lying 0.38 Å (**2a**) and 0.39 Å (**2c**) out of the plane defined by the other three atoms. The three-coordinate germanium atom adopts a significantly distorted pyramidal geometry (the sums of the bond angles are 258° and 259° for **2a** and **2c**, respectively) with the Ge−halogen bond approximately orthogonal to the cycle. The Ge−Cl distance (2.2632(18) Å) is very close to that observed by Roesky et al. in [{*t*-BuNC(Ph)N*t*-Bu}GeCl] (2.2572(13) Å)] which also has a phenyl group in the bridging carbon.[11a] The Ge−Br bond length (2.4239(12) Å) lies in the range of standard Ge−Br bonds.[18] Regarding the bis(amidinate)germylene **3** (Figure 2), we observed two amidinato systems, one presenting a chelated ring with the Ge−N distances (2.0106(18) and 2.1948(19) Å) in the range of those observed previously[10] and the second with a more distorted structure having two different Ge−N distances, the Ge−N(4) (2.0121(18) Å) being significantly shorter than the Ge−N(3) (2.3397(18) Å). The latter value is between that of the axial Ge−N bond (2.300(2) Å) found in [{*i*-PrNC(Me)N*i*-Pr}$_2$Ge],[19] which displays a four-coordinate germanium center and that of the Ge−N interaction (2.474 Å) in the complex [{CyNC(Me)NCy}$_2$Ge][20,21] having three-coordinate germanium. In our case, the slight shortening of the neighboring N−C bond, C(14) −N(3) (1.308(3) Å), the lack of symmetry of the molecule and a sum of angles at germanium atom (261°) which approximates the ideal trigonal pyramid geometry (270°), are consistent with a three-coordinate germanium center with one bidentate and one monodentate amidinate ligand. Accordingly, the Me$_3$Si groups are different in the solid-state structure, but in solution a rapid exchange between the two amidinato moieties

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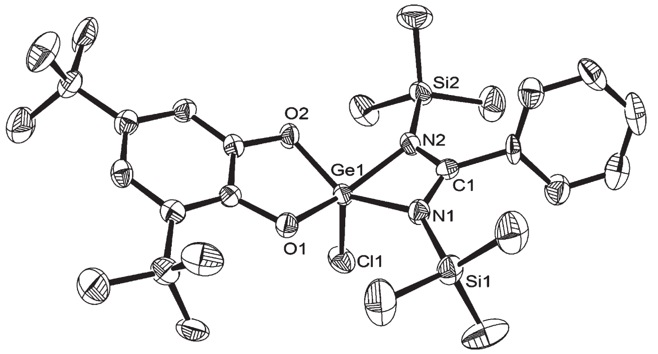

Figure 3. ORTEP view of compound **4a** (50% probability level for the thermal ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and bond angles [deg]: Ge(1)−Cl(1) 2.1556(8); Ge(1)−N(1) 1.978 (3); Ge(1)−N(2) 1.969(3); C(1)−N(1) 1.342(4); C(1)−N(2) 1.319(4); Ge(1)−O(1) 1.8326(19); Ge(1)−O(2) 1.823(2); N(1)−Ge(1)−N(2) 68.04(10); N(1)−Ge(1)−Cl(1) 105.44(8); N(2)−Ge(1)−Cl(1) 101.69(8); O(1)−Ge(1)−Cl(1) 103.17(7); O(2)−Ge(1)−Cl(1) 108.50(7); O(1)−Ge(1)−N(1) 97.05(10); O(1)−Ge(1)−N(2) 153.74(10); O(2)−Ge(1)−N(1) 143.15(10); O(2)−Ge(1)−N(2) 91.18(10); O(1)−Ge(1)−O(2) 88.92(9).

could explain the equivalence of these substituents in the ^{1}H and ^{13}C NMR spectra as previously mentioned.

Reactivity. These structural results imply that the geometry of the germanium atom is in good agreement with a nonhybridized system with bonds formed by using nearly pure p orbitals while the lone-pair must occupy an orbital with high s character. To verify whether these germanium complexes retain their specific character of a divalent species, an oxidative cycloaddition reaction with 3,5-di-*tert*-butyl-*ortho*-quinone was examined.[22]

Oxidative Cycloaddition. Treatment of **2a**−**c** and **3** with *ortho*-quinone at room temperature in toluene (or diethyl ether for **3**) led to a progressive disappearance of the green color of *ortho*-quinone. After evaporation of the solvents, the cycloadducts **4a**−**c** and **5** were isolated as powders which could be crystallized from toluene (or diethylether for **5**) at −24 °C (Scheme 2).

While the ^{1}H NMR spectra of **4a**−**c** revealed the equivalence of the two Me$_3$Si groups, the four Me$_3$Si groups in **5** are nonequivalent and four signals were observed at −0.10, 0.00, 0.14, and 0.19 ppm probably because of the steric hindrance of the molecule. ^{13}C and ^{29}Si NMR spectra showed the same nonequivalence of trimethylsilyl groups. A complete assignment of these signals was obtained by 2D homonuclear (COSY) and heteronuclear experiments (HSQC and HMBC).

Molecular structures of **4a** and **5** were determined by single-crystal X-ray analysis and are shown in Figures 3 and 4, respectively with selected bond lengths and angles. In **4a**, the chelating character of the ligand to the metal center, as was observed for the corresponding germylene, is conserved. The germanium atom is penta-coordinate and the geometry around this atom is in between a distorted trigonal bipyramidal geometry with one nitrogen atom of the amidinato group N(2) and one oxygen atom O(1) of the quinonic cycle in axial positions as we previously observed with anilido-imine ligands[7] and a distorted square pyramid with the chlorine atome on the top. A comparable structure was recently reported for a monosilaepoxide stabilized by amidinato ligand.[23] As expected, the Ge−N bond distances (1.969(3) and 1.978(3) Å) are shortened compared to those of the germanium(II) starting compound because of the loss of their conjugated character.[7,20] The X-ray analysis of **5** reveals a six coordinate germanium center that has distorted octahedral coordination geometry with the four nitrogen atoms of the amidinato ligands and with the two oxygen atoms of the quinonic cycle. By contrast with the corresponding germylene **3**, the two amidinate ligands exhibit only a very slight difference in the Ge−N bond lengths (in the range from 2.004 to 2.065 Å) and are almost perfectly chelated to the germanium atom in spite of the increased steric hindrance compared to the germanium(II) compound **3**. As a consequence of this steric congestion, the Ge−O distances (1.860(3) and 1.868(3) Å) are longer than those of the chloromonoamidinate germanium(IV) **4a** (1.8326(19) and 1.823(2) Å) but still lie in the range of covalent Ge−O bonds.[7,24] ^{1}H and ^{13}C NMR

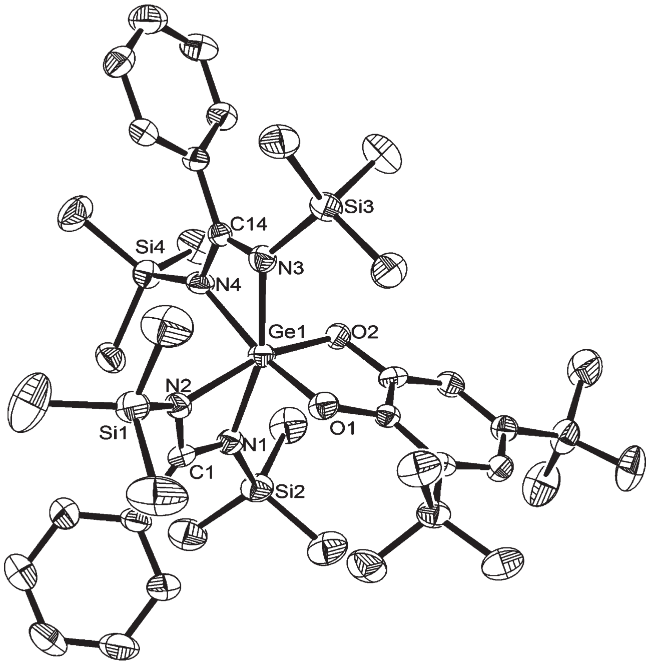

Figure 4. ORTEP view of compound **5** (50% probability level for the thermal ellipsoids). Hydrogen atoms and disordered atoms have been omitted for clarity. Selected bond distances [Å] and bond angles [deg]: Ge(1)−N(1) 2.023(4); Ge(1)−N(2) 2.025(4); Ge(1)−N(3) 2.004(4); Ge(1)−N(4) 2.065(3); C(1)−N(1) 1.332(5); C(1)−N(2) 1.342(5); C(14)−N(3) 1.332(5); C-(14)−N(4) 1.338(5); Ge(1)−O(1) 1.860(3); Ge(1)−O(2) 1.868(3); N(1)−Ge(1)−N(2) 66.85(13); N(1)−Ge(1)−N(3) 162.67(14); N(1)−Ge(1)−N(4) 99.37(14); N(2)−Ge(1)−N(3) 102.46(14); N(2)−Ge(1)−N(4) 94.57(14); N(3)−Ge(1)−N(4) 66.96(14); O(1)−Ge(1)−N(1) 93.73(14); O(1)−Ge(1)−N(2) 88.10(13); O(1)−Ge(1)−N(3) 99.67(14); O(1)−Ge(1)−N(4) 166.63(13); O(2)−Ge(1)−N(1) 96.73(14); O(2)−Ge(1)−N(2) 162.91(14); O(2)−Ge(1)−N(3) 94.62(12); O(2)−Ge(1)−N(4) 92.77(12); O(1)−Ge(1)−O(2) 88.31(12).

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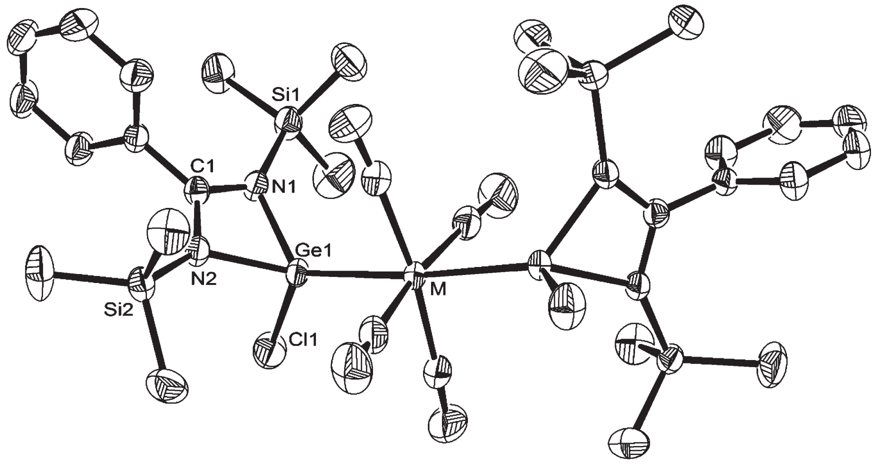

Figure 5. Molecular structures of **6** (M = W) and **7** (M = Mo). Thermal ellipsoids are set at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and bond angles [deg] for **6**: Ge(1)−Cl(1) 2.2124(10); Ge(1)−N(1) 1.988(2); Ge(1)−N(2) 1.979(2); C(1)−N(1) 1.335(4); C(1)−N(2) 1.330(4); Ge(1)−W(1) 2.4984(3); N(1)−Ge(1)−N(2) 67.77(10); N(1)−Ge(1)−Cl(1) 99.67(8); N(2)−Ge(1)−Cl(1) 99.58(8); N(1)−Ge(1)−W(1) 124.61(8); N(2)−Ge(1)−W(1) 126.34(8); Cl(1)−Ge(1)−W(1) 124.01(3). Selected bond distances [Å] and bond angles [deg] for **7**: Ge(1)−Cl(1) 2.2156(6); Ge(1)−N(1) 1.9886(15); Ge(1)−N(2) 1.9810(17); C(1)−N(1) 1.327(2); C(1)−N(2) 1.338(2); Ge(1)−Mo(1) 2.49901(19); N(1)−Ge(1)−N(2) 67.63(6); N(1)−Ge(1)−Cl(1) 99.34(5); N(2)−Ge(1)−Cl(1) 99.31(5); N(1)−Ge(1)−Mo(1) 124.89(5); N(2)−Ge(1)−Mo(1) 126.47(5); Cl(1)−Ge(1)−Mo(1) 124.146(18).

data are in good agreement with the solid-state structure and the observation of distinct trimethylsilyl and phenyl groups.

Ge(II) Complexes with Transition Metals. Like N-heterocyclic carbenes, the NHGe are usually regarded as σ-donors, although the weakness of the N→Ge π-donation could involve the π-acceptor strength when used as ligands for transition metals. With amidinate as ligand, the p-orbital of germanium is filled by the coordinative bond from the imino nitrogen atom which diminishes the Lewis character of these tricoordinate germylenes. In order to test their ability to coordinate with transition-metal, complexations of **2a** with [codW(CO)$_4$] (cod = 1,5-cyclooctadiene) and [nbdMo(CO)$_4$] (nbd = 2,5-norbornadiene) were examined. Displacement of the ligand (cod or nbd) by two germanium(II) species **2a** occurred easily in THF solution (Scheme 2).

Complexes **6** and **7** were isolated as pale yellow powders in moderate yields, 22% and 24%, respectively. They were crystallized from toluene at low temperature to give analytically pure colorless crystals. Their ^{1}H and ^{13}C NMR spectra showed only small differences from the spectra of the corresponding germylene except for a slight shift of the signals of the trimethylsilyl group ($\Delta\delta \sim 0.20$ ppm, ^{1}H NMR). However, it is noteworthy that in the^{13}C NMR spectrum there is only one carbonyl resonance (210.4 and 210.2 ppm) for **6** and **7**, respectively. Furthermore a strong band in the IR spectrum (1894 and 1903 cm^{-1}) indicates a "*trans*" octahedral geometry for these complexes.[25] An X-ray structure study confirmed the "*trans*" orientation of the two chloroamidinato germanium fragments in both cases (Figure 5). Compounds **6** and **7** are the first di(amidinatogermylene)-tungsten and -molybdenum complexes to be isolated and structurally characterized. The germanium atom adopts a distorted tetrahedral geometry, and the transition metals (W, Mo) are octahedrally coordinated with almost linear Ge−M−Ge bond angles, 174° both for **6** and **7**. The W−Ge bond length (2.4984(3) Å) is very similar to that in the closely related chelated complex [{ArNC(*t*-Bu)NAr}-Ge(Cl)W(CO)$_5$] (2.5564(6) Å) (Ar = C$_6$H$_3$*i*-Pr$_2$-2,6)[10] and to that observed with the β-diketiminato ligand.[25] The same small variations were observed for the Mo−Ge bond length (2.4990 Å) compared to those of the five-membered N-heterocyclic germylene complex [(NHGe)$_3$Mo(CO)$_3$] (2.5285(2), 2.5445(2), and 2.5452(3) Å).[26] The two Ge−N bonds are shorter (Δ = 0.044−0.081 Å) than those of the starting chlorogermylene. Recently, molybdenum complexes of benzaannulated bisstannylenes were reported.[27] In this last case, the two tin(II) centers lie in neighboring positions probably because of the presence of an alkyl bridging group through the ring nitrogen atoms.

These results are very encouraging and open up new perspectives for the involvement of these germanium(II) compounds as valuable ligands for transition-metal complexes and their applications as new catalysts.

Conclusion

The first bromide and iodide amidinatogermanium(II) species have been isolated and characterized. Besides the steric hindrance of the trimethylsilyl groups on the nitrogen atoms, the presence of a phenyl group on the bridging carbon is significant. It not only stabilizes the germylenes into their monomeric forms but also induces a perfect selectivity of the metalation reaction on Cl$_2$Ge·dioxane, giving either mono-amidinato or diamidinato compounds according to the stoichiometry used. NMR spectroscopic data and single-crystal X-ray analyses confirm the perfect chelation of this ligand to the metal center, forming three-coordinate germanium. Moreover, these complexes preserve their specific reactivity, as was shown in the cycloaddition reaction with

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o-quinone. Their σ-donor character was highlighted by their easy complexation with transition-metal complexes. For the first time, two trinuclear bis(germanium(II)) tungsten and molybdenum complexes were prepared and their structures elucidated by X-ray single-crystal diffraction studies.

Experimental Section

General Procedures. All manipulations with air-sensitive materials were performed in a dry and oxygen-free atmosphere of argon by using standard Schlenk-line and glovebox techniques. Solvents were purified with the MBraun SBS-800 purification system except THF, which was distilled on Na/benzophenone. Benzonitrile and hexamethyldisilazane were distilled on potassium hydroxyde and degassed using three consecutive freeze−pump−thaw cycles and vacuum before storage on molecular sieves (4 Å). NMR spectra were recorded with the following spectrometers: ^{1}H, Bruker Avance II 300 (300.13 MHz) and Avance II 500 (500.13 MHz); ^{13}C, Bruker Avance II 300 (75.47 MHz) and Avance II 500 (125.77 MHz); ^{29}Si, Bruker Avance II 300 (59.63 MHz) at 298 K. Mass spectra were measured with a Hewlett-Packard 5989A in the electron impact mode (70 eV). Melting points were measured with a capillary electrothermal apparatus. Elemental analyses were done on a Perkin Elmer 2400. IR spectra were measured on a Varian 640-IR FT-IR spectrometer. The germanium(II) derivatives $Cl_2Ge\cdot$dioxane[28] and I_2Ge[29] were prepared according to literature procedures.

[{Me$_3$SiNC(Ph)NSiMe$_3$}GeCl] (2a). A solution of freshly prepared lithium benzamidinate [{Me$_3$SiNC(Ph)NSiMe$_3$}Li] (6.20 mmol) in diethyl ether (7 mL) was added to a suspension of $Cl_2Ge\cdot$dioxane (1.44 g, 6.20 mmol) in diethyl ether (5 mL) at −78 °C. The reaction mixture was warmed to room temperature, stirred for 2.5 h, and then refluxed for 4 h. The solvents were removed under reduced pressure, and the residue was extracted with toluene (50 mL). After filtration on Celite, the filtrate was concentrated in vacuo to give **2a** as a pale yellow solid. Yield: 2.20 g (95%). Crystallization from a mixture of toluene/THF at −24 °C gave colorless crystals suitable for X-ray study. Mp: 60 °C. ^{1}H NMR (300.13 MHz, C_6D_6): δ (ppm) −0.06 (s, 18H, SiMe$_3$); 6.90−7.03 (m, 5H, C_6H_5). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6): δ (ppm) 0.3 (SiMe$_3$); 125.9 (C_{ortho}); 128.1 (C_{meta}); 129.7 (C_{para}); 137.3 (C_{ipso}); 181.8 (C_6H_5-*C*). ^{29}Si NMR (59.63 MHz, C_6D_6): δ (ppm) 3.0 (SiMe$_3$). MS *m*/*z* (%): $[M]^+$ = 372 (13); $[M - Cl]^+$ = 337 (6); $[M - GeCl]^+$ = 263 (13); $[SiMe_3]^+$ = 73 (100). Anal. Calcd for $C_{13}H_{23}ClGeN_2Si_2$: C, 42.02; H, 6.24; N, 7.54. Found: C, 41.52; H, 6.19; N, 7.07.

[{Me$_3$SiNC(Ph)NSiMe$_3$}GeI] (2b). By using the same procedure as that described for **2a**, [{Me$_3$SiNC(Ph)NSiMe$_3$}Li] (6.20 mmol) in diethyl ether (7 mL) and I_2Ge (2.03 g, 6.20 mmol) in diethyl ether (15 mL) gave **2b** as a yellow solid. Yield: 2.83 g (98%). Mp: 82 °C. ^{1}H NMR (300.13 MHz, C_6D_6): δ (ppm) −0.03 (s, 18H, SiMe$_3$); 6.87-6.98 (m, 5H, C_6H_5). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6): δ (ppm) 0.0 (SiMe$_3$); 125.5 (C_{ortho}); 127.8 (C_{meta}); 129.5 (C_{para}); 137.0 (C_{ipso}); 180.4 (C_6H_5-*C*). ^{29}Si NMR (59.63 MHz, C_6D_6): δ (ppm) 4.0 (SiMe$_3$). MS *m*/*z* (%): $[M]^+$ = 464 (1); $[M - I]^+$ = 337 (25); $[M - GeI]^+$ = 263 (17); $[SiMe_3]^+$ = 73 (100). Anal. Calcd for $C_{13}H_{23}GeIN_2Si_2$: C, 33.72; H, 5.01; N, 6.05. Found: C, 33.93; H, 5.19; N, 5.45.

[{Me$_3$SiNC(Ph)NSiMe$_3$}GeBr] (2c). An excess of trimethylsilyl bromide (0.20 mL, 1.50 mmol) was added to a suspension of **2a** (0.20 g, 0.54 mmol) in toluene (5 mL). The mixture was stirred for 24 h. The volatiles were removed in vacuo, giving quantitatively **2c** as a white solid. Crystallization from toluene at −24 °C gave colorless crystals. Mp: 53 °C. ^{1}H NMR (300.13 MHz, C_6D_6): δ (ppm) −0.04 (s, 18H, SiMe$_3$); 6.92−6.99 (m, 5H, C_6H_5). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6): δ (ppm) 0.3 (SiMe$_3$); 125.9 (C_{ortho}); 128.1 (C_{meta}); 129.7 (C_{para}); 137.3 (C_{ipso}); 181.6 (C_6H_5-*C*). ^{29}Si NMR (59.63 MHz, C_6D_6): δ (ppm) 3.5 (SiMe$_3$). MS *m*/*z* (%): $[M]^+$ = 416 (32); $[M - Br]^+$ = 337 (58); $[M - GeBr]^+$ = 263 (16); $[SiMe_3]^+$ = 73 (100). Anal. Calcd for $C_{13}H_{23}BrGeN_2Si_2$: C, 37.53; H, 5.57; N, 6.73. Found: C, 36.93; H, 5.23; N, 6.18.

[{Me$_3$SiNC(Ph)NSiMe$_3$}$_2$Ge] (3). By using the same procedure as that described for **2a**, except the reaction time (20 h at room temperature then refluxed for 8 h), [{Me$_3$SiNC(Ph)NSiMe$_3$}Li] (4.10 mmol) in diethyl ether (10 mL) and $Cl_2Ge\cdot$dioxane (0.48 g, 2.07 mmol) gave **3** as a yellow, sticky solid, which was crystallized in toluene at −24 °C. Yield: 1.22 g (98%). ^{1}H NMR (300.13 MHz, C_6D_6): δ (ppm) 0.16 (s, 36H, SiMe$_3$); 6.98-7.03 (m, 6H, C_{meta}H and C_{para}H); 7.20 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.8 Hz, 4H, C_{ortho}H). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6): δ (ppm) 1.8 (SiMe$_3$); 127.2 (C_{ortho}); 127.8 (C_{meta}); 128.7 (C_{para}); 141.6 (C_{ipso}); 174.1 (C_6H_5-*C*). ^{29}Si NMR (59.63 MHz, C_6D_6): δ (ppm) −1.0 (SiMe$_3$). MS *m*/*z* (%): $[M]^+$ = 600 (12); $[M - CH_3]^+$ = 585 (6); $[SiMe_3]^+$ = 73 (100). Anal. Calcd for $C_{26}H_{46}GeN_4Si_4$: C, 52.08; H, 7.73; N, 9.34. Found: C, 51.86; H, 8.42; N, 8.94.

Reactivity of 3,5-Di-*tert*-butylorthoquinone toward 2a (4a). To a solution of **2a** (0.19 g, 0.51 mmol) in toluene (3 mL) was added a solution of 3,5-di-*tert*-butylorthoquinone (0.11 g, 0.51 mmol) in toluene (2 mL). The solution was stirred for 30 min. The solvent was removed in vacuo to yield **4a** as a light brown powder. Yield: 0.30 g (99%). Crystallization from a mixture of toluene/THF at −24 °C gave colorless crystals. Mp: 160 °C. ^{1}H NMR (300.13 MHz, C_6D_6): δ (ppm) 0.07 (s, 18H, SiMe$_3$); 1.33 (s, 9H, C_4-C(CH$_3$)$_3$); 1.66 (s, 9H, C_6-C(CH$_3$)$_3$); 6.77 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, C_{ortho}H); 6.88 (t, $^3J_{HH}$ = 7.5 Hz, 2H, C_{meta}H); 6.94−6.99 (m, 1H, C_{para}H); 7.05 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_5H); 7.25 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_3H). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6): δ (ppm) 0.5 (SiMe$_3$); 29.8 (C_6-C(*C*H$_3$)$_3$); 31.8 (C_4-C(*C*H$_3$)$_3$); 34.4 (C_4-*C*(CH$_3$)$_3$); 34.7 (C_6-*C*(CH$_3$)$_3$); 108.2 (C_3); 113.3 (C_5); 126.3 (C_{ortho}); 128.2 (C_{meta}); 130.1 (C_{para}); 131.9 (C_{ipso}); 133.4 (C_6); 141.1 (C_4); 143.4 (C_1); 147.6 (C_2); 178.8 (C_6H_5-*C*). ^{29}Si NMR (59.63 MHz, C_6D_6): δ (ppm) 6.2 (SiMe$_3$). MS *m*/*z* (%): $[M]^+$ = 592 (15); $[M - CH_3]^+$ = 577 (6); $[M - Cl]^+$ = 557 (1); $[SiMe_3]^+$ = 73 (100). Anal. Calcd for $C_{27}H_{43}$-$GeClN_2O_2Si_2$: C, 54.79; H, 7.32; N, 4.73. Found: C, 54.54.25; H, 7.15; N, 4.32.

Reactivity of Di-*tert*-butylorthoquinone toward 2b (4b). By using the same procedure as that described for **4a**, **2b** (0.38 g, 0.83 mmol) in toluene (4 mL) and 3,5-di-*tert*-butylorthoquinone (0.18 g, 0.83 mmol) in toluene (3 mL) gave **4b** as a brown powder. Yield: 0.56 g (99%). Mp: 77 °C. ^{1}H NMR (300.13 MHz, C_6D_6): δ (ppm) 0.10 (s, 18H, SiMe$_3$); 1.33 (s, 9H, C_4-C(CH$_3$)$_3$); 1.70 (s, 9H, C_6-C(CH$_3$)$_3$); 6.79−6.80 (m, 2H, C_{ortho}H); 6.85-6.94 (m, 2H, C_{meta}H); 6.99−7.03 (m, 1H, C_{para}H); 7.12 (d, $^4J_{HH}$ = 2.2 Hz, 1H, C_5H); 7.32 (d, $^4J_{HH}$ = 2.2 Hz, 1H, C_3H). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6): δ (ppm) 0.7 (SiMe$_3$); 29.9 (C_6-C(*C*H$_3$)$_3$); 31.7 (C_4-C(*C*H$_3$)$_3$); 34.4 (C_4-*C*(CH$_3$)$_3$); 34.8 (C_6-*C*(CH$_3$)$_3$); 108.3 (C_3); 113.5 (C_5); 126.3 (C_{ortho}); 128.2 (C_{meta}); 129.9 (C_{para}); 132.1 (C_{ipso}); 133.5 (C_6); 141.2 (C_4); 143.3 (C_1); 147.5 (C_2); 177.7 (C_6H_5-*C*). ^{29}Si NMR (59.63 MHz, C_6D_6): δ (ppm) 6.4 (SiMe$_3$). MS *m*/*z* (%): $[M - I]^+$ = 557 (4); $[SiMe_3]^+$ = 73 (100). Anal. Calcd for ($C_{27}H_{43}GeIN_2O_2Si_2$): C, 47.46; H, 6.34; N, 4.10. Found: C, 47.67; H, 6.41; N, 3.71.

Reactivity of Di-*tert*-butylorthoquinone toward 2c (4c). By using the same procedure as that described for **4a**, except the reaction time (40 min), **2c** (0.21 g, 0.50 mmol) in toluene (3 mL) and 3,5-di-*tert*-butylorthoquinone (0.11 g, 0.50 mmol) in toluene (3 mL) gave **4c** quantitatively as a yellow-green powder. Mp: 154 °C. ^{1}H NMR (300.13 MHz, C_6D_6): δ (ppm) 0.10 (s, 18H, SiMe$_3$); 1.35 (s, 9H, C_4−C(CH$_3$)$_3$); 1.72 (s, 9H, C_6−C(CH$_3$)$_3$); 6.74−6.84 (m, 4H, C_{ortho}H, C_{meta}H); 6.88−6.94 (m, 1H, C_{para}H); 7.12 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_5H); 7.33 (d, $^4J_{HH}$ = 2.3 Hz, 1H, C_3H). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6): δ

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Table 1. Crystal Data and Structure Refinements of Complexes 2a,c, 3, 4a, and 5−7

	2a	**2c**	**3**	**4a**
empirical formula	$C_{13}H_{23}ClGeN_2Si_2$	$C_{13}H_{23}BrGeN_2Si_2$	$C_{26}H_{46}GeN_4Si_4$	$C_{27}H_{43}ClGeN_2O_2Si_2$
fw (g/mol)	371.55	416.01	599.62	591.85
temp (K)	193(2)	193(2)	193(2)	193(2)
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/\mathrm{c}$	$P2_1/c$	$P2_12_12_1$	$Pna2_1$
a (Å)	12.4571(3)	12.5760(6)	11.4651(2)	18.8621(3)
b (Å)	10.7366(2)	10.7725(6)	12.8058(2)	14.8137(2)
c (Å)	14.8710(3)	15.0109(8)	23.5802(4)	11.2794(2)
α (deg)	90	90	90	90
β (deg)	110.190(1)	110.286(3)	90	90
γ (deg)	90	90	90	90
volume (Å^3)	1866.73(7)	1907.46(17)	3462.04(10)	3151.66(9)
Z	4	4	4	4
density calcd (g/cm^3)	1.322	1.449	1.150	1.247
absorp coeff (mm^{-1})	1.903	3.817	1.043	1.157
F(000)	768	840	1272	1248
$\theta_{\max}$ (deg)	28.28	26.37	28.28	25.34
reflns collected/unique	34 119/4602	29 815/3870	56 792/8489	29 818/5678
R_{merge}	0.0551	0.1011	0.0608	0.0537
data/restraints/params	4602/207/252	3870/238/252	8489/0/328	5678/1/328
goodness-of-fit	1.221	1.224	0.991	1.019
R indices [I > 2(σ)I]	$wR_2 = 0.1478$ $R_1 = 0.0631$	$wR_2 = 0.1341$ $R_1 = 0.0587$	$wR_2 = 0.0678$ $R_1 = 0.0333$	$wR_2 = 0.0718$ $R_1 = 0.0326$
R indices (all data)	$wR_2 = 0.1538$ $R_1 = 0.0825$	$wR_2 = 0.1454$ $R_1 = 0.0946$	$wR_2 = 0.0727$ $R_1 = 0.0484$	$wR_2 = 0.0759$ $R_1 = 0.0420$
largest diff peak and hole (e Å^{-3})	0.401, −0.860	0.571, −0.502	0.331, −0.193	0.436, −0.257

	5	**6**	**7**
empirical formula	$C_{40}H_{66}GeN_4O_2Si_4$	$C_{30}H_{46}Cl_2Ge_2N_4O_4\ Si_4W$	$C_{30}H_{46}Cl_2Ge_2MoN_4O_4Si_4$
fw (g/mol)	819.92	1039.00	951.09
temp (K)	193(2)	193(2)	193(2)
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$Pna2_1$	$C2/c$	$C2/c$
a (Å)	19.9585(6)	29.3454(5)	29.3886(5)
b (Å)	21.4419(6)	9.2756(2)	9.2725(2)
c (Å)	11.2036(3)	19.3970(3)	19.4268(4)
α (deg)	90	90	90
β (deg)	90	124.3860(10)	124.4100(10)
γ (deg)	90	90	90
volume (Å^3)	4794.6(2)	4357.15(14)	4367.56(15)
Z	4	4	4
density calcd (g/cm^3)	1.136	1.584	1.446
absorp coeff (mm^{-1})	0.773	4.272	1.918
F(000)	1752	2056	1928
$\theta_{\max}$ (deg)	26.37	30.03	30.51
reflns collected/unique	72 086/9718	28508/6304	34 688/6623
R_{merge}	0.1568	0.0459	0.0482
data/restraints/parameters	9718/37/503	6304/0/219	6623/0/219
goodness-of-fit	1.009	1.014	1.008
R indices [$I > 2(\sigma)I$]	$wR_2 = 0.0827$ $R_1 = 0.0504$	$wR_2 = 0.0632$ $R_1 = 0.0300$	$wR_2 = 0.0707$ $R_1 = 0.0303$
R indices (all data)	$wR_2 = 0.0982$ $R_1 = 0.0997$	$wR_2 = 0.0688$ $R_1 = 0.0451$	$wR_2 = 0.0787$ $R_1 = 0.0480$
largest diff. peak and hole (e Å^{-3})	0.287, −0.329	1.760, −0.543	0.572, −0.400

(ppm) 0.5 (SiMe$_3$); 29.8 (C_6-C(*C*H$_3$)$_3$); 31.7 (C_4-C(*C*H$_3$)$_3$); 34.4 (C_4-*C*(CH$_3$)$_3$); 34.8 (C_6-*C*(CH$_3$)$_3$); 108.3 (C_3); 113.5 (C_5); 126.4 (C_{ortho}); 128.1 (C_{meta}); 129.9 (C_{para}); 132.1 (C_{ipso}); 133.6 (C_6); 141.3 (C_4); 143.4 (C_1); 147.5 (C_2); 178.3 (C_6H_5-*C*). ^{29}Si NMR (59.63 MHz, C_6D_6): δ (ppm) 6.2 (SiMe$_3$). MS m/z (%): $[M]^+ = 636$ (50); $[M - CH_3]^+ = 621$ (21); $[SiMe_3]^+ = 73$ (100). Anal. Calcd for $C_{27}H_{43}BrGeN_2O_2Si_2$: C, 50.96; H, 6.81; N, 4.40. Found: C, 50.92; H, 6.99; N, 4.22.

Reactivity of Di-*tert*-butylorthoquinone toward 3 (5). By using the same procedure as that described for **4a**, except the reaction time (1 h), **3** (0.27 g, 0.44 mmol) in diethyl ether (4 mL) and 3,5-di-*tert*-butylorthoquinone (0.10 g, 0.44 mmol) in diethyl ether (3 mL) gave quantitatively **5** as a green powder. Mp: 170 °C. ^{1}H NMR (300.13 MHz, C_6D_6): δ (ppm) −0.10, 0.00, 0.14, and 0.19 (s, 36H, SiMe$_3$); 1.43 (s, 9H, C_4-C(CH$_3$)$_3$); 1.87 (s, 9H, C_6-C(CH$_3$)$_3$); 6.95-6.99 (m, 6H, C_6H_5); 7.01 (d, $^4J_{HH} = 2.3$ Hz, 1H, C_5H); 7.21 (d, $^4J_{HH} = 2.2$ Hz, 1H, C_3H); 7.26-7.32 (m, 3H, C_6H_5); 7.43-7.45 (m, 1H, C_6H_5). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6): δ (ppm) 1.0, 1.5, 1.7 (SiMe$_3$); 31.8 (C_6-C(*C*H$_3$)$_3$); 31.9 (C_4-C(*C*H$_3$)$_3$); 34.3 (C_4-*C*(CH$_3$)$_3$); 35.0 (C_6-*C*(CH$_3$)$_3$); 109.3 (C_3); 111.4 (C_5); 126.2, 126.6, 126.7, 126.8, 127.9, 128.1, 128.3, 128.4, 128.9, 129.1 (C_6H_5); 131.3 (C_6); 136.2 and 136.3 (C_{ipso}); 138.9 (C_4); 147.6 (C_1); 149.8 (C_2); 176.6 and 178.1 (C_6H_5-*C*). ^{1}H NMR (THF-d_8): δ (ppm) −0.40 (s, 9H, Si$_a$Me$_3$), -0.21 (s, 9H, Si$_b$Me$_3$), 0.04 (s, 9H, Si$_c$Me$_3$), 0.09 (s, 9H, Si$_d$Me$_3$); 1.26 (s, 9H, C_4-C(CH$_3$)$_3$); 1.50 (s, 9H, C_6-C(CH$_3$)$_3$); 6.57 (d, $^4J_{HH} = 2.3$ Hz, 1H, C_5H); 6.67 (d, $^4J_{HH} = 2.3$ Hz, 1H, C_3H); 7.27−7.22 (m, 10H, C_6H_5). $^{13}C\{^1H\}$ NMR (75.47 MHz, THF-d_8): δ (ppm) 1.5 (Si$_a$Me$_3$); 2.0 (Si$_b$Me$_3$); 2.1 and 2.3 (Si$_{c,d}$Me$_3$); 31.3 (C_6-C-(*C*H$_3$)$_3$); 32.6 (C_4-C(*C*H$_3$)$_3$); 35.1 (C_4-*C*(CH$_3$)$_3$); 35.7 (C_6-*C*-(CH$_3$)$_3$); 109.7 (C_3); 111.8 (C_5); 127.7, 128.1, 128.2, 128.9, 129.1, 129.1, 129.4, 129.5, 130.3, 130.6 (C_6H_5); 131.9 (C_6); 137.2 and 137.3 (C_{ipso}); 139.2 (C_4); 148.5 (C_1); 150.6 (C_2); 177.8 and 179.5 (C_6H_5-*C*). ^{29}Si NMR (59.63 MHz, C_6D_6): δ

(ppm) 0.4, 0.6, 1.1, 3.0 ($SiMe_3$). MS *m*/*z* (%): $[M]^+ = 820$ (27); $[M - CH_3]^+ = 805$ (1); $[SiMe_3]^+ = 73$ (100). HRMS $C_{40}H_{66}GeN_4O_2Si_4$: calcd mass 820.3484, measured mass 820.3479.

[{{Me$_3$SiNC(Ph)NSiMe$_3$}Ge(Cl)}$_2$W(CO)$_4$] (6). A solution of tetracarbonyl(1,5-cyclooctadiene)tungsten (0.22 g, 0.54 mmol) in THF (10 mL) was added to a solution of **2a** (0.40 g, 1.08 mmol) in THF (10 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred at 60 °C for 4 h. The volatiles were removed under reduced pressure, leading to **6** after crystallization from toluene at 4 °C to give yellow crystals. Yield: 0.12 g (22%). Mp: 190 °C. ^1H NMR (300.13 MHz, C_6D_6): δ (ppm) 0.14 (s, 36H, $SiMe_3$); 6.82−6.86 (m, 4H, C_6H_5); 6.88−6.91 (m, 3H, C_6H_5); 6.95−6.99 (m, 3H, C_6H_5). ^1H NMR (500.13 MHz, THF-d_8): δ (ppm) 0.10 (s, 36H, $SiMe_3$); 7.49−7.51 (m, 4H, C_6H_5); 7.52−7.54 (m, 3H, C_6H_5); 7.56−7.57 (m, 3H, C_6H_5). $^{13}C\{^1H\}$ NMR (125.77 MHz, THF-d_8): δ (ppm) −0.5 ($SiMe_3$); 126.7 (C_{ortho}); 128.5 (C_{meta}); 130.6 (C_{para}); 134.9 (C_{ipso}); 182.1 (C_6H_5-*C*); 210.4 (CO). ^{29}Si NMR (59.63 MHz, THF-d_8): δ (ppm) 5.7 ($SiMe_3$). IR (KBr pellet): ν (cm^{-1}) 1894 (s) and 1941 (sh) (CO). Anal. Calcd for $C_{30}H_{46}Cl_2Ge_2N_4O_4Si_4W$: C, 34.68; H, 4.46; N, 5.39. Found: C, 34.62; H, 4.41; N, 5.22.

[{{Me$_3$SiNC(Ph)NSiMe$_3$}Ge(Cl)}$_2$Mo(CO)$_4$] (7). By using the same procedure as that described for **6**, (bicyclo[2.2.1]hepta-2,5-diene)tetracarbonylmolybdenum (0.16 g, 0.54 mmol) and **2a** (0.40 g, 1.08 mmol) gave **7** as pale yellow crystals. Yield: 0.12 g (24%). Mp: 140 °C dec. ^1H NMR (300.13 MHz, C_6D_6): δ (ppm) 0.13 (s, 36H, $SiMe_3$); 6.81−6.87 (m, 4H, C_6H_5); 6.89−6.92 (m, 3H, C_6H_5); 6.96−6.99 (m, 3H, C_6H_5). ^1H NMR (300.13 MHz, THF-d_8): δ (ppm) 0.10 (s, 36H, $SiMe_3$); 7.49−7.51 (m, 4H, C_6H_5); 7.52−7.54 (m, 3H, C_6H_5); 7.55−7.56 (m, 3H, C_6H_5). $^{13}C\{^1H\}$ NMR (75.47 MHz, THF-d_8): δ (ppm) −0.5 ($SiMe_3$); 126.7 (C_{ortho}); 128.5 (C_{meta}); 130.5 (C_{para}); 134.9 (C_{ipso}); 181.7 (C_6H_5-*C*); 210.2 (CO). ^{29}Si NMR (59.63 MHz, THF-d_8): δ (ppm) 5.6 ($SiMe_3$). MS *m*/*z* (%): $[M]^+ = 952$ (1); $[M - 2CO]^+ = 896$ (1); $[M - 3CO]^+ = 868$ (1); $[M - 4CO]^+ = 840$ (1); $[SiMe_3]^+ = 73$ (100). IR (KBr pellet) ν (cm^{-1}) 1903 (s) (CO). Anal. Calcd for $C_{30}H_{46}Cl_2Ge_2MoN_4O_4Si_4$: C, 37.88; H, 4.87; N, 5.89. Found: C, 38.34; H, 4.97; N, 5.71.

X-ray Structure Determinations. X-ray data (Table 1) were collected at low temperature (193(2) K) using an oil-coated shock-cooled crystal on a Bruker-AXS APEX II diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct phase determination (SHELXS-97)[30] and refined for all non-hydrogen atoms by full-matrix least-squares methods on F^2 and subjected to anisotropic refinement.[31]

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Supporting Information Available: CIF files for the structural determinations of compounds **2a**, **2c**, **3**, **4a**, **5**, **6**, **7**, and $[\{H(Me_3Si)NC(Ph)N(SiMe_3)H\}^+I^-]$. These materials are available free of charge via the Internet at http://pubs.acs.org.

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