1972 *Organometallics* **2007,** *26,* 1972−1980

Preparation and Coordination Chemistry of Bidentate Benzimidazoline-2-germylenes

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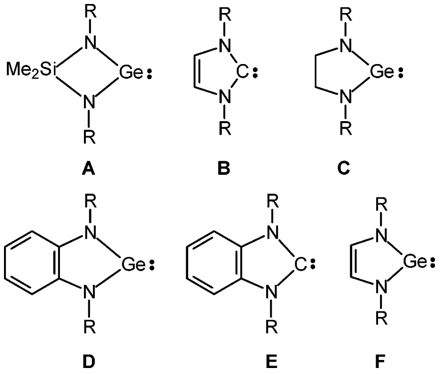
Bridged bis(benzimidazoline-2-germylene)s have been prepared in good yield by the reaction of $N,N',N,''N'''$-tetralithiated tetraamines with $GeCl_2 \cdot 1,4$-dioxane or by the direct transamination reaction between tetraamines and $Ge[N(SiMe_3)_2]_2$. Four bis(benzimidazoline-2-germylene)s with different bridging groups between the benzimidazoline-2-germylene groups have been shown by X-ray diffraction analysis to exhibit different types of weak intermolecular interactions, but no significant Ge···Ge interaction was observed in the solid state. One of the bisgermylenes disproportionates in solution at ambient temperature to yield a Ge(IV) spiro compound and elemental germanium. The bisgermylenes can act as chelate ligands replacing norbornadiene in $[Mo(nbd)(CO)_4]$ with formation of complexes of the type $[Mo(\eta^2\text{-bisgermylene})(CO)_4]$, which have been investigated by ^1H NMR and vibrational spectroscopy and X-ray diffraction analysis.

Introduction

When comparing the reasonable stability of $GeCl_2$ to the very transient CCl_2, it is not surprising that diamides of Ge(II) have been described[1] long before the first reports on stable carbenes appeared.[2] The subsequent report[3] of the first heterocyclic germylene (NHGe), **A** (Scheme 1), predates Arduengo's description of the first N-heterocyclic carbene (NHC),[4] **B**, by almost 10 years. Later, the first NHGe's derived from saturated imidazoles **C** were reported.[5] The molecular structure of the first benzannulated NHGe, **D**, was described[6] in 1989 again some 10 years before its carbene analogue **E** was prepared.[7] Finally, NHGe analogues of Arduengo's carbene **F** were first described in 1992.[8] Meanwhile cationic NHGe's[9] and ring-functionalized NHGe's exhibiting betaine reactivity[10] have been prepared.

Scheme 1. N-Heterocyclic Carbenes and Germylenes



It is generally accepted that the π-interaction in NHGes between germanium and the ring nitrogen atoms is weaker than in NHCs. However, The N→Ge←N π-donor interaction becomes stronger when the NHGe coordinates to a metal center.[11] A number of such metal complexes bearing different NHGe ligands[8a,12] and noncyclic germylenes[13] are known today.

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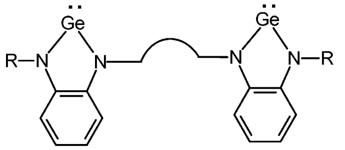
Scheme 2



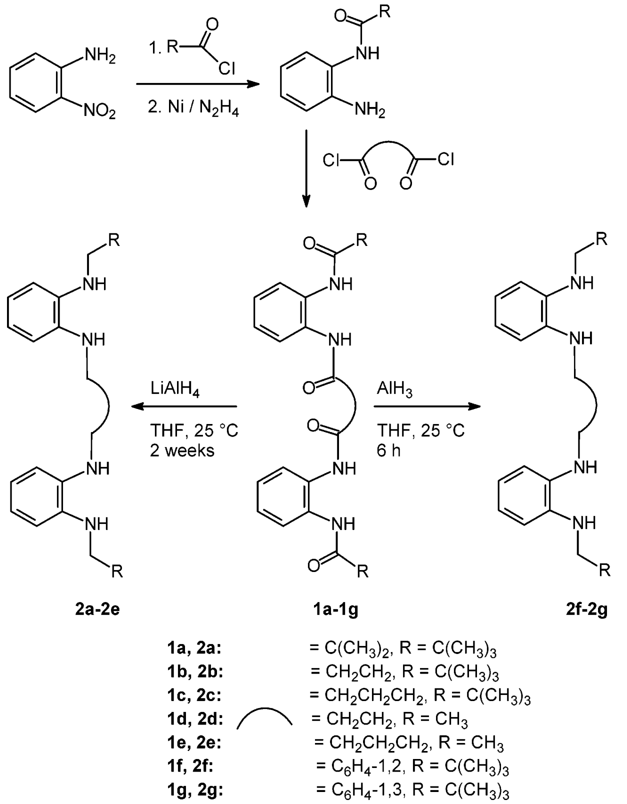
G

Polydentate NHC ligands[14] with two imidazolin-2-ylidene[15] or benzimidazolin-2-ylidene[16] donor groups that are capable of forming chelate complexes including tridentate derivatives with pincer topology[17] are known together with some tris(imidazolin-2-ylidenes)[18] and a cyclic tetra(benzimidazolin-2-ylidene)[19] ligand. Knowledge about bisgermylenes is limited to some cyclic[20] or noncyclic[21] derivatives, none of which can act as a chelate ligand. We describe in this contribution the preparation and coordination chemistry of the first bisgermylene derivatives of type **G** (Scheme 2) containing two benzannulated NHGe units that can coordinate to transition metals in a chelating fashion.

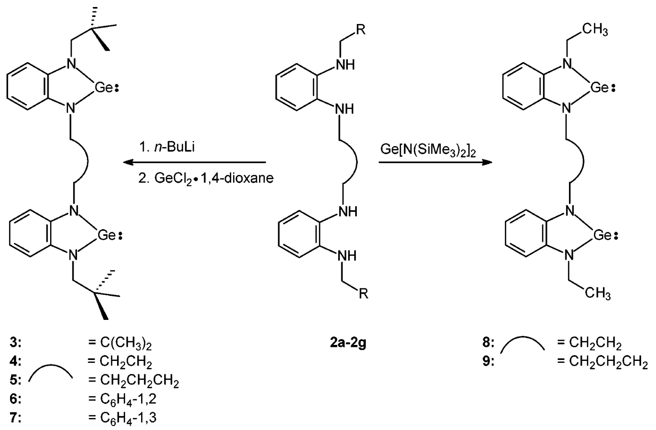
Results and Discussion

The N-heterocyclic bisgermylenes of type **G** were obtained from the tetraamines **2a**−**2g**, which were prepared by reduction of the carbonyl groups in the corresponding tetraamides **1a**−**1g** (Scheme 3). The tetraamides were prepared by acylation of *ortho*-phenyleneaminoamides with differently bridged α,*ω*-di(carboxylic acid chlorides) in the presence of Et_3N. The bridging unit present in the tetraamides determined which reducing agent had to be used in the subsequent reaction. The carbonyl groups in the tetraamides **1a**−**1e** with an alkyl backbone were reduced with $LiAlH_4$ in THF at ambient temperature. Reduction of the carbonyl groups in the phenylene-bridged tetraamides **1f**, **1g** was achieved with AlH_3 in THF at ambient temperature. The $LiAlH_4$ reduction (yield 65−84%) proceeds in slightly better yield than the AlH_3 reduction (yield 62−66%).

Scheme 3. Preparation of the Tetraamines 2a−2g



Scheme 4. Preparation of the Bisgermylenes 3−9



The bisgermylenes **3**−**9** were obtained from the tetraamines **2a**−**2g** by two different methods. Bisgermylenes **3**−**7**, with the sterically demanding N−CH_2−*t*-Bu groups, were prepared by the metalation of the tetraamines **2a**−**2c**, **2f**, or **2g** using first *n*-BuLi followed by reaction of the resulting organolithiums with $GeCl_2 \cdot 1,4$-dioxane at −78 °C (Scheme 4).[11b] Bisgermylenes **8** and **9** with *N*-ethyl groups were isolated after the diret transamination reaction between the tetraamine **2d** or **2e** and $Ge[N(SiMe_3)_2]_2$ (Scheme 4).[1a,8c,12d,22] All bisgermylenes were isolated in good yield (50−80%). They can be purified by recrystallization from *n*-hexane or toluene to give red, orange, or pale yellow air and moisture-sensitive crystalline solids.

^1H NMR signals for the protons of the CH_2 groups attached to the nitrogen atoms are shifted downfield upon NHGe formation from δ 2.66−3.24 ppm for the free amines to δ 3.71−4.07 ppm for the bisgermylenes with the exception of the resonance for the benzylic protons in tetraamines **2f**,**2g**, which

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Table 1. Crystallographic Data for 4, 5, 6, 8, 10, and 11

parameter	**4**	**5**	**6**	**8**	**10**	**11**
formula	$C_{26}H_{38}N_4Ge_2$	$C_{27}H_{40}N_4Ge_2$	$C_{30}H_{38}N_4Ge_2$	$C_{20}H_{26}N_4Ge_2$	$C_{27}H_{40}N_4Ge$	$C_{31}H_{40}N_4Ge_2MoO_4$
cryst size [mm]	0.47 × 0.08 × 0.06	0.27 × 0.07 × 0.03	0.14 × 0.10 × 0.08	0.36 × 0.05 × 0.03	0.16 × 0.12 × 0.04	0.15 × 0.05 × 0.03
M_r	551.78	565.81	599.82	467.63	493.22	773.79
a [Å]	5.8909(15)	22.904(8)	16.9549(2)	7.3257(3)	12.562(2)	10.4872(13)
b [Å]	6.2233(15)	19.022(7)	5.78920(10)	16.5928(8)	15.564(2)	12.482(2)
c [Å]	18.540(5)	7.464(3)	28.8671(4)	33.0186(15)	13.464(2)	13.893(2)
α [deg]	98.641(4)	90	90	90	90	102.470(3)
β [deg]	92.131(4)	103.719(6)	97.7960(10)	90	99.296(2)	108.320(3)
γ [deg]	99.696(5)	90	90	90	90	98.591(3)
V [Å^3]	661.0(3)	3159(2)	2807.27(7)	4013.5(3)	2597.6(6)	1638.7(4)
Z	1	4	4	8	4	2
space group	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$
ρ_{calcd} [g cm^{-3}]	1.386	1.190	1.419	1.548	1.261	1.568
μ [mm^{-1}]	2.294 (Mo Kα)	1.921 (Mo Kα)	2.820 (Cu Kα)	3.765 (Cu Kα)	1.200 (Mo Kα)	2.240 (Mo Kα)
2θ range [deg]	2.2−60.0	4.2−47.0	5.3−140.2	3.0−130.0	4.0−60.1	3.2−55.0
no. of data collected	7455	9730	15 699	22 436	29 370	16 213
no. of unique data, R_{int}	3737, 0.0314	2332, 0.0764	5057, 0.0455	6821, 0.0888	7552, 0.0493	7523, 0.0537
no. of obsd data [$I \geq 2\sigma(I)$]	3222	1684	3764	3963	5689	5724
R (all data)	0.0490	0.0932	0.0449	0.0908	0.0691	0.0706
R_w (all data)	0.0964	0.1831	0.0625	0.0824	0.1106	0.1026
no. of variables	148	153	331	483	297	387
peak/hole [e Å^{-3}]	0.968/−0.555	1.142/−0.409	0.344/−0.332	0.737/−0.487	0.911/−0.421	0.769/−0.701

are shifted from δ 4.11−4.36 ppm to δ 4.82−4.98 ppm in the bisgermylenes **6** and **7**. A similar trend was observed in the ^{13}C NMR spectra, where the resonance for the *ipso*-carbon atoms in the free tetraamines ($\delta \approx 138$ ppm) is shifted to lower field upon NHGe formation ($\delta \approx 143$ ppm). These values are in good agreement with the corresponding values reported for the monodentate *N,N*′-di(neopentyl)benzimidazoline-2-germylene.[11f] MS spectra for all bisgermylenes exhibited peaks for the molecular ions ($[M]^+$, correct isotope distribution) and for typical fragmentation products ($[M - t\text{-Bu}]^+$).

The molecular structures of the bisgermylenes **4**−**6** and **8** were determined by X-ray diffraction (Table 1). Bisgermylene **4** was crystallized from a concentrated toluene solution. The molecule resides on a crystallographic inversion center (midpoint of the C11−C11* bond). Bisgermylene **4** crystallizes as a monomer (Figure 1) with no significant interactions in the solid state. The germylene units adopt an *anti* arrangement toward each other, and the alkyl bridge exhibits an all-*trans* conformation.

Crystals of the bisgermylene **5** were obtained from a hexane solution at ambient temperature. The molecule resides on a 2-fold axis that passes through atom C9. The two heterocycles in **5** adopt a *cis* orientation toward each other (Figure 2, top). The germylene moieties and the alkyl bridge with an all-*trans* conformation are arranged in one plane, as was observed for **4**. The intermolecular Ge···Ge separation measures 3.577(2) Å and is shorter than twice the van der Waals radius of the germanium atom (4.3 Å).[23] If this is taken as a weak intermolecular interaction, it leads to indefinite chains of bisgermylenes **5** linked by Ge···Ge contacts (Figure 2, bottom). However, the short intermolecular Ge···Ge separation in the solid state could also be attributed to crystal-packing forces.

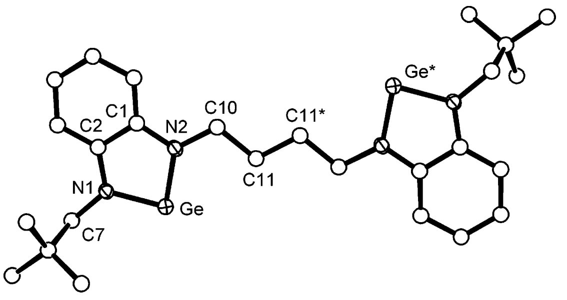

Figure 1. Molecular structure of bisgermylene **4**. Selected bond lengths (Å) and angles (deg): Ge−N1 1.866(2), Ge−N2 1.866(2), N1−C2 1.387(3), N1−C7 1.463(3), N2−C1 1.384(3), N2−C10 1.459(3), C1−C2 1.417(3), C10−C11 1.519(3), C11−C11* 1.519(4); N1−Ge−N2 85.06(8), Ge−N1−C2 114.05(14), Ge−N1−C7 123.81(14), C2−N1−C7 121.9(2), Ge−N2−C1 113.78(14), Ge−N2−C10 127.86(15), C1−N2−C10 118.35(2).

Crystals of the phenylene-bridged bisgermylene **6** were obtained by recrystallization from toluene. The crystal structure analysis (Figure 3) indicates an interaction of the empty p-orbital at the germanium atoms with the π-system of the benzene ring of a parallel oriented adjacent molecule. This interaction again leads to a polymeric arrangement of the bisgermylene molecules in the crystal lattice. The distances between the germanium atoms and the carbon atoms of the benzene ring fall in the range 3.199(3)−4.036(2) Å. A similar interaction has been described previously for the analogous *N,N*′-di(neopentyl)benzimidazoline-2-stannylene,[24] but it is absent for *N,N*′-di(neopentyl)benzimidazoline-2-ylidene[11f] and -silylene.[25]

Crystals of the bisgermylene **8** were obtained from a concentrated hexane solution at ambient temperature. The asymmetric unit contains two molecules of **8**. Compound **8**, with the sterically less demanding *N*-ethyl groups, crystallized as a bimolecular aggregate with intermolecular Ge···N contacts. The intermolecular Ge···N separations of 3.533(2) and 3.532(2) Å are indicative of weak donor−acceptor interactions (Figure 4). Previously, similar but much stronger and shorter Sn···N contacts (2.514(2) Å) were observed for benzimidazoline-2-stannylenes.[26]

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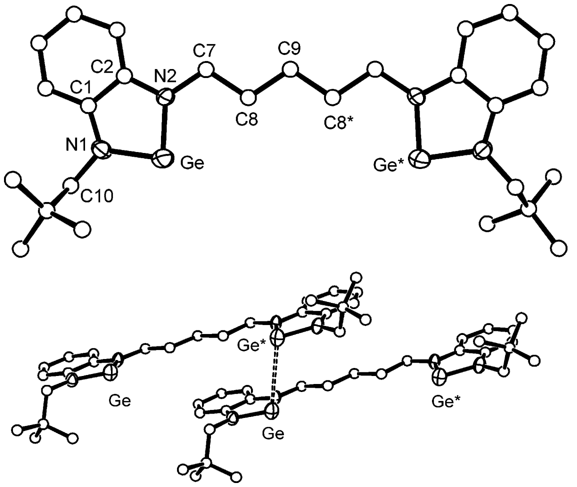


Figure 2. Molecular structure of bisgermylene **5** (top) and intermolecular interaction of two bisgermylene molecules leading to indefinite chains in the crystal lattice (bottom). Selected bond lengths (Å) and angles (deg): Ge−N1 1.875(6), Ge−N2 1.857(5), N1−C1 1.376(8), N1−C10 1.466(8), N2−C2 1.396(8), N2−C7 1.483(8), C1−C2 1.420(9), C7−C8 1.521(9), C8−C9 1.516(8); N1−Ge−N2 84.7(2), Ge−N1−C1 114.7(4), Ge−N1−C10 122.7(5), C1−N1−C10 122.4(6), Ge−N2−C2 114.1(4), Ge−N2−C7 126.9(4), C2−N2−C7 119.1(5).

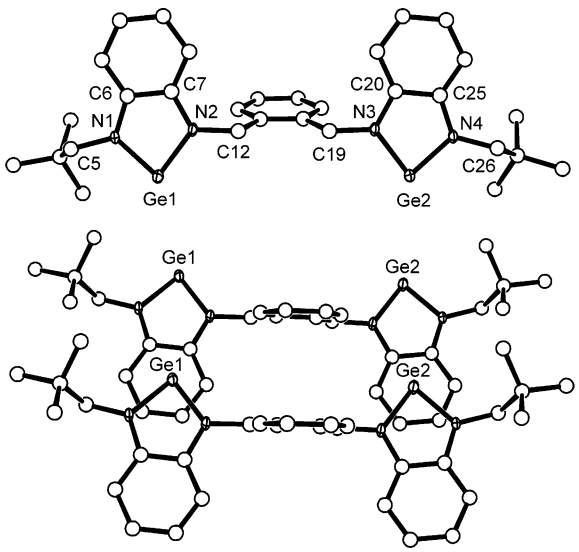


Figure 3. Molecular structure of bisgermylene **6** (top) and intermolecular interaction of the bisgermylenes in the crystal lattice (bottom). Selected bond lengths (Å) and angles (deg): Ge1−N1 1.871(2), Ge1−N2 1.857(2), Ge2−N3 1.862(2), Ge2−N4 1.860(2), N1−C5 1.460(3), N1−C6 1.381(3), N2−C7 1.389(3), N2−C12 1.454(3), N3−C19 1.451(3), N3−C20 1.388(3), N4−C25 1.382(3), N4−C26 1.464(3), C6−C7 1.422(3), C20−C25 1.414(3); N1−Ge1−N2 85.03(9), N3−Ge2−N4 84.55(9), Ge1−N1−C5 122.8(2), Ge1−N1−C6 114.0(2), C5−N1−C6 122.3(2), Ge1−N2−C7 114.1(2), Ge1−N2−C12 124.7(2), C7−N2−C12 120.4(2), Ge2−N3−C19 124.7(2), Ge2−N3−C20 114.3(2), C19−N3−C20 121.0(2), Ge2−N4−C25 114.7(2), Ge2−N4−C26 123.2(2), C25−N4−C26 122.0(2).

Bond distances and angles within the NHGe moieties of the bisgermylenes **4**−**6** and **8** are identical within experimental error with those reported for the parent mono-NHGe molecules **D** and **F** (R = $CH_2-C(CH_3)_3$, Scheme 1).[11f] The weak intermolecular contacts in **5**, **6**, and **8** do not lead to a significant change in the bond parameters of the NHGe units.

Shortly after the preparation of the first NHGe's of type and **D**[6] and **F**[8c] (Scheme 1) it was noticed that such germylenes disproportionate upon heating to yield spiro compounds with a central $Ge^{IV}N_4$ core. Computational methods were used to study the mechanism of the formation of these derivatives from germylene **F**.[8c] In analogy with these observations, we noticed that prolonged (2 weeks) standing of a hexane solution of bisgermylene **3** leads at ambient temperature to formation of the spiro compound **10** and elemental germanium (Scheme 5). The formation of a spiro compound like **10** at room temperature was not observed with any other bisgermylene described in this contribution.

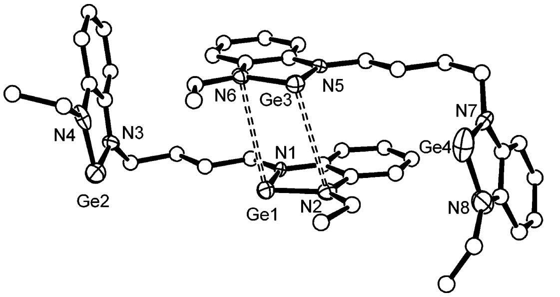
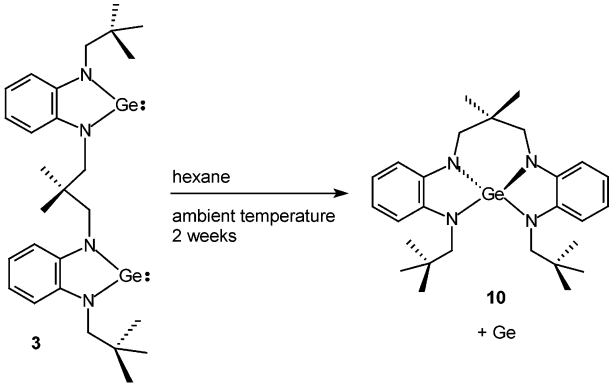


Figure 4. Molecular structure of the dimeric bisgermylene **8**. Selected bond lengths (Å) and angles (deg): Ge1−N1 1.864(5), Ge1−N2 1.865(5), Ge2−N3 1.862(6), Ge2−N4 1.838(6), Ge3−N5 1.871(5), Ge3−N6 1.871(5), Ge4−N7 1.837(5), Ge4−N8 1.882(7); N1−Ge1−N2 84.3(2), N3−Ge2−N4 84.5(3), N5−Ge3−N6 84.1(2), N7−Ge4−N8 83.8(3).

Scheme 5. Disproportionization of Bisgermylene 3



Compound **10** crystallized from a hexane solution. The X-ray diffraction analysis showed a Ge^{IV} atom that is surrounded in a strongly distorted tetrahedral fashion by four nitrogen atoms (Figure 5). The N−Ge−N angles within the five-membered chelate rings are smallest (90.44(8)° and 90.41(8)°), with a larger angle found for the six-membered chelate ring (N2−Ge−N4 103.67(8)°) involving the bridging group. The Ge−N bond distances are generally shorter than those in the bisgermylenes **4**−**6** and **8** and correspond well to the expected values for $Ge^{IV}-N$ bonds.

The resonance signals for the methylene protons in **10** appear in the ^1H NMR spectrum as four doublets in the range from 2.88 to 3.56 ppm. They exhibit ^2J coupling constants typical for geminal diastereotopic protons (14.5 Hz, $N-CH_2-CMe_2$ and 12.7 Hz, $N-CH_2-CMe_3$). Formation of the spiro compound leads to a rigid skeleton that does not allow rotation about C−C bonds involving the methylene groups. Consequently, the methylene protons become chemically inequivalent and diastereotopic. The ^{13}C NMR spectrum of **10** shows upfield shifts for the *ipso*-carbon atoms of the aromatic rings (δ 139.7 and 138.9 ppm) compared to the bisgermylene **3** (δ 143.3 and 143.2 ppm), and the resonances are close to those for the parent tetraamine **2a** (δ 138.4 and 137.5 ppm).

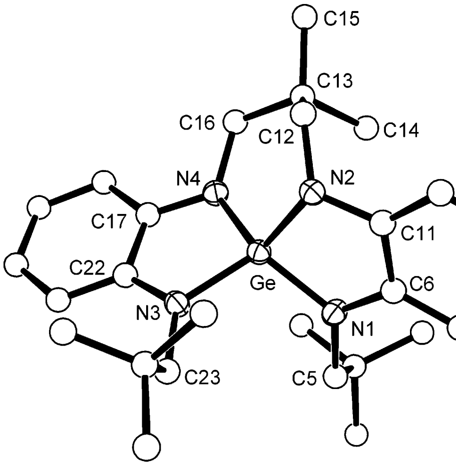
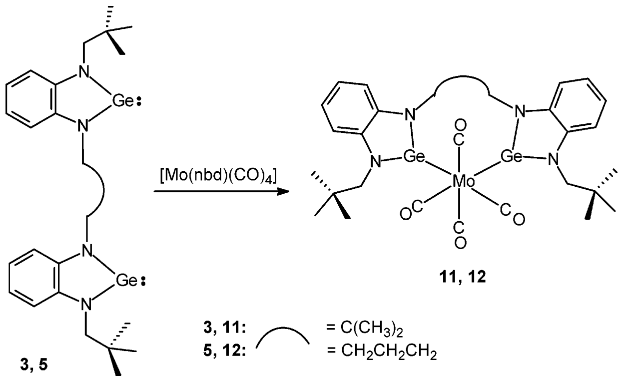


Figure 5. Molecular structure of the spiro compound **10**. Selected bond lengths (Å) and angles (deg): Ge−N1 1.825(2), Ge−N2 1.819(2), Ge−N3 1.814(2), Ge−N4 1.812(2), N1−C5 1.461(3), N1−C6 1.405(3), N2−C11 1.403(3), N2−C12 1.467(3), N3−C22 1.404(3), N3−C23 1.461(3), N4−C16 1.463(3), N4−C17 1.401(3), C6−C11 1.419(3), C17−C22 1.427(3); N1−Ge−N2 90.44(8), N1−Ge−N3 108.97(8), N1−Ge−N4 135.19(8), N2−Ge−N3 135.37(8), N2−Ge−N4 103.67(8), N3−Ge−N4 90.41(8).

Scheme 6. Preparation of the Bisgermylene Chelate Complexes 11 and 12



The linkage of two NHGe units with a flexible alkyl chain makes the resulting bisgermylenes **3**−**9** flexible enough to coordinate to a metal center in a chelating fashion. The bisgermylenes **3** and **5** were therefore used for the preparation of the chelate complexes **11** and **12** (Scheme 6). The biscarbene analogue of ligand **3** has previously been shown to form a chelate complex with the Mo(CO)$_4$ complex fragment.[16b] Bisgermylenes **3** and **5** react with [Mo(nbd)(CO)$_4$] (nbd = norbornadiene) in THF under formation of the bright yellow, air-sensitive complexes **11** and **12** in 80−90% yield. X-ray quality crystals of **11** were obtained by cooling of a saturated toluene solution.

The X-ray structure analysis (Figure 6) shows complex **11** to contain a molybdenum atom coordinated by four CO ligands and the two NHGe units of a bisgermylene in a slightly distorted octahedral fashion. The Mo−Ge bond lengths (Mo−Ge1 2.5204(6), Mo−Ge2 2.5189(6) Å) fall in the range observed in the trisgermylene complex *fac*-[Mo(ImGe)$_3$(CO)$_3$] (ImGe = *N*,*N*′-di(*tert*-butyl)imidazoline-2-germylene) (2.535 Å)[12f] and are also comparable to Mo−Ge^{IV} bond lengths.[27] A significant amount of Mo→Ge π-backbonding could explain the observation that the Mo−(NHGe) (Ge^{II}) separation in **11** is similar to the Mo−Ge^{IV} bond lengths (*vide infra*).

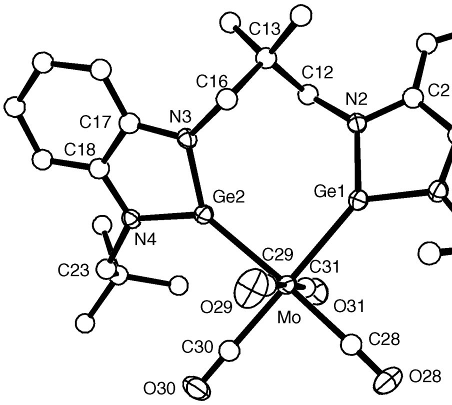


Figure 6. Molecular structure of complex **11**. Selected bond lengths (Å) and angles (deg): Mo−Ge1 2.5204(6), Mo−Ge2 2.5189(6), Mo−C28 1.997(4), Mo−C29 2.047(4), Mo−C30 1.998(4), Mo−C31 2.030(5), Ge1−N1 1.827(3), Ge1−N2 1.824(3), Ge2−N3 1.824(3), Ge2−N4 1.823(3), N1−C1 1.398(5), N1−C7 1.468(5), N2−C2 1.403(5), N2−C12 1.455(5), N3−C16 1.468(5), N3−C17 1.389(5), N4−C18 1.395(5), N4−C23 1.466(5); Ge1−Mo−Ge2 90.69(2), Ge1−Mo−C28 91.57(12), Ge1−Mo−C29 89.37(11), Ge1−Mo−C30 179.04(11), Ge1−Mo−C31 92.26(12), Ge2−Mo−C28 177.37(12), Ge2−Mo−C29 92.98(12), Ge2−Mo−C30 88.47(12), Ge2−Mo−C31 88.07(11), C28−Mo−C29 88.4(2), C28−Mo−C30 89.3(2), C28−Mo−C31 90.50(2), C29−Mo−C30 91.1(2), C29−Mo−C31 178.1(2), C30−Mo−C31 87.3(2), N1−Ge1−N2 87.93(14), N3−Ge2−N4 87.73(14).

The NHGe planes deviate only slightly from the Mo/Ge1/Ge2/C28/C30 plane, which causes the two NHGe units to be arranged essentially coplanar. The orientation of the germylene units allows for a π-interaction between d-orbitals of the molybdenum atom and the empty p-orbital at the germylenes. The average Ge−N bond lengths in the free bisgermylenes measure 1.863 Å (**4**−**6**, **8**, total of 16 Ge−N bonds), which is a value similar to the Ge−N distances found in the monodentate *N*,*N*′-di(neopentyl)benzimidazoline-2-germylene (1.861(3) and 1.866(3) Å)[11f] and *N*,*N*′-bis(trimethylsilyl)benzimidazoline-2-germylene (1.861(8) and 1.866(9) Å).[6] In accord with theoretical predictions,[11c] the Ge−N distances shrink significantly upon coordination of the bisgermylene to the molybdenum atom (range 1.823(3)−1.827(3) Å). In addition and again in accordance with theoretical predictions for germylenes,[11c] complex formation causes the N−Ge−N angles in **11** (87.93(14)° and 87.73(14)°) to expand relative to the free bisgermylenes (range 83.8(3)−85.06(8)°).

The angle Ge−Mo−Ge in **11** measures 90.69(2)°, whereas the corresponding C−Mo−C angle in the complex with the analogous biscarbene ligand is significantly larger, 95.11(14)°.[16b] The bond distances Mo−CO$_{cis}$ (1.997(4) and 1.998(4) Å) are significantly shorter than the Mo−CO$_{trans}$ bond distances (2.047(4) and 2.030(5) Å). The difference between the Mo−CO$_{cis}$ and Mo−CO$_{trans}$ bond distances is smaller in **11** (≈0.04 Å) than in the analogous biscarbene complex (≈0.07 Å), indicating that the bisgermylene ligand is a weaker σ-donor (or a better π-acceptor) than the biscarbene ligand.

The ^{1}H NMR spectrum of **11**, measured at 280 K, shows two broad multiplets for the methylene protons between δ 3.34 and 3.91 ppm (Figure 7). At elevated temperature (355 K) coalescence of the signals leads to two singlets for the CH_2−*t*-Bu and CH_2−C(Me$_2$)−CH_2 protons. The resonance signals of methylene protons become resolved at low temperature (240 K) and appear as four sharp doublets (δ 3.95, 3.82, 3.73,

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[27] Holloway, C. E.; Melnik, M. *Main Group Met. Chem.* **2002**, *25*, 331.

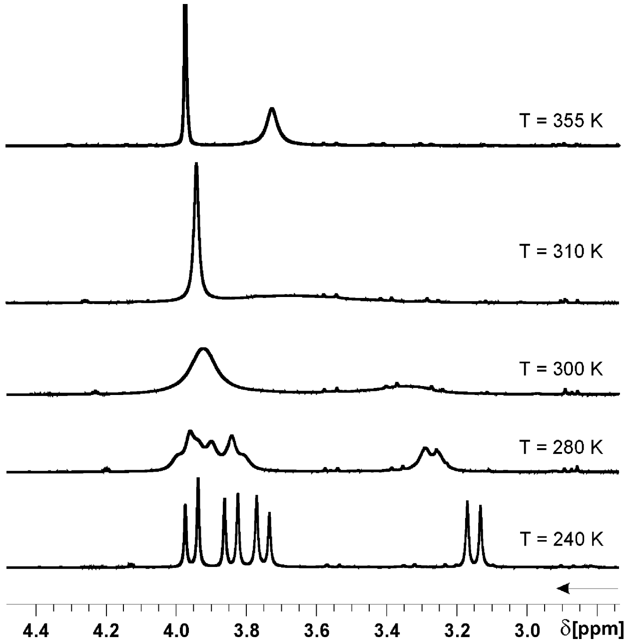

Figure 7. Variable-temperature ^{1}H NMR spectra of **11** (in toluene-d_8).

and 3.12 ppm) with geminal coupling constants $^2J_{HH} = 14.6$ and 15.6 Hz, a behavior that is similar to that found for compound **10** (Figure 7). The ^{1}H NMR spectrum of **12** at ambient temperature shows for the $N-CH_2$ protons a singlet ($N-CH_2-t$-Bu) and a triplet ($N-CH_2CH_2CH_2$) owing to the nonrigid bridge between the NHGe units in this complex.

The Raman spectrum of **11** shows three lines in the region of the ν_{CO} stretching modes ($2A_1+B_1$). The B_2 stretching vibration, which is nonactive in the Raman spectrum, was observed in the IR spectrum. The wave numbers for the ν_{CO} frequencies in the IR spectrum are significantly higher for **11** (2031 (A_1), 1942 (A_1), 1929 (B_1), and 1908 (B_2) cm^{-1}) than in the analogous biscarbene complex (2002, 1889, 1857, and 1799 cm^{-1}), which we take as another indication of the weaker σ-donor (or a better π-acceptor) properties of the bisgermylene compared to the biscarbene ligand. Seven instead of three ν_{CO} absorptions were observed in the Raman spectrum of crystalline **12**. This suggests that more than one conformer of **12** with the nonrigid ligand backbone is present in the solid state. The IR spectra of **11** and **12** are very similar.

Conclusion

We have prepared the first bisgermylenes, **3**−**9**, containing two N-heterocyclic germylene (NHGe) donor groups. These ligands are capable of forming chelate complexes with transition metals. A significant shortening of the Ge−N bond lengths and a widening of the N−Ge−N bond angle was observed upon coordination of the bisgermylene **3** onto the $Mo(CO)_4$ complex fragment. Bisgermylene **3** acts as a weaker σ-donor (or a better π-acceptor) than the analogous biscarbene ligand. The synthetic concept for the preparation of the bisgermylene ligands is also suitable for the preparation of bisstannylenes, and corresponding investigations are currently in progress.

Experimental Section

General Comments. All manipulations were carried out under an argon atmosphere with standard Schlenk or glovebox techniques. Solvents were dried over sodium/benzophenone under argon and were freshly distilled prior to use. Compound $GeCl_2 \cdot 1,4$-dioxane was purchased (Aldrich), and $Ge[N(SiMe_3)_2]_2$ was prepared as described previously.[22] Toluene-d_8 and THF-d_8 were dried over Na/K alloy. ^{1}H and ^{13}C NMR spectra were measured on Bruker AC-200 or AV-400 spectrometers at 200 or 400 MHz for ^{1}H and 100.6 or 50.3 MHz for ^{13}C. IR spectra were recorded on a Bruker Vector 22 FTIR spectrometer. The Raman spectra were measured on a Labram Jobin Yvon HR-800 spectrometer using the 632.8 nm line of a He−Ne laser.

General Procedure for the Synthesis of the Tetraamides 1a−1g. The tetraamides **1a**−**1g** were synthesized starting from commercially available *o*-nitroaniline. In a first reaction step the amine function was acylated with either acetyl chloride or pivalyl chloride followed by reduction of the nitro group. Two equivalents of the obtained primary *o*-aminoamides were then coupled with different α,ω-di(carboxylic acid chlorides). To achive this, a carboxylic acid chloride (5.0 mmol) was slowly added to the solution of an *o*-aminoamide (10.4 mmol) and Et_3N (1.6 mL, 11.0 mmol) in THF (60 mL) at −78 °C. The mixture was allowed to warm 25 °C under stirring for 8 h. The solvent was removed *in vacuo*, and a water/acetone mixture (8:1, v/v) was added to the solid residue. The resulting suspension was stirred for 30 min. Filtration gave a white residue, which was washed twice with the water/acetone mixture. The resulting white residue was dried *in vacuo*.

2,2-Dimethyl-N^1,N^3-bis(2-pivalamidophenyl)malonamide (1a). Yield: 82%. ^{1}H NMR (200 MHz, DMSO-d_6): δ 9.23, 9.11 (s, 2H, NH−C=O), 7.63 (m, 2H, Ar−H), 7.40 (m, 2H, Ar−H), 7.20 (m, 4H, Ar−H), 1.60 (s, 6H, $C(CH_3)_2$), 1.17 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 177.2, 171.6 (N−C=O), 131.1, 130.9 (Ar−C_{ipso}), 129.4, 128.6, 125.3, 113.8 (Ar−C_{meta} and Ar−C_{ortho}), 51.1 ($C(CH_3)_2$), 38.8 ($C(CH_3)_3$), 27.2 ($C(CH_3)_3$), 23.5 ($C(CH_3)_2$).

N^1,N^4-Bis(2-pivalamidophenyl)succinamide (1b). Yield: 70%. ^{1}H NMR (200 MHz, DMSO-d_6): δ 9.84, 8.85 (s, 4H, NH−C=O), 7.86−7.54 (m, 2H, Ar−H), 7.32−7.14 (m, 6H, Ar−H), 2.73 (m, 4H, $N-C(O)-CH_2$), 1.16 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 176.1, 171.0 (N−C=O), 131.3, 130.2 (Ar−C_{ipso}), 125.4, 125.2 (Ar−C_{meta}), 124.7 (br, Ar−C_{ortho}), 38.9 ($C(CH_3)_3$), 30.5 ($C(O)-CH_2$), 27.1 $C(CH_3)_3$. MS (MALDI): *m/z* 489 $[M + Na]^+$, 467 $[M + H]^+$.

N^1,N^5-Bis(2-pivalamidophenyl)glutaramide (1c). Yield: 80%. ^{1}H NMR (200 MHz, DMSO-d_6): δ 9.09, 8.97 (s, 4H, NH−C=O), 7.58−7.53 (m, 2H, Ar−H), 7.32−7.14 (m, 6H, Ar−H), 2.46 (m, 4H, $N-C(O)-CH_2$), 1.97 (m, 2H, $N-C(O)-CH_2-CH_2$), 1.20 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 176.1, 171.6 (N−C=O), 131.4, 130.3 (Ar−C_{ipso}), 125.5, 125.2 (Ar−C_{meta}), 124.9, 124.7 (Ar−C_{ortho}), 38.9 ($C(CH_3)_3$), 35.0 ($N-C(O)-CH_2$), 27.2 ($C(CH_3)_3$), 21.5 (($N-C(O)-CH_2-CH_2$). MS (MALDI): *m/z* 503 $[M + Na]^+$, 481 $[M + H]^+$.

N^1,N^4-Bis(2-acetamidophenyl)succinamide (1d). Yield: 35%. ^{1}H NMR (200 MHz, DMSO-d_6): δ 9.56, 9.27 (s, 4H, NH−C=O), 7.64−7.62 (m, 2H, Ar−H), 7.51−7.47 (m, 2H, Ar−H) 7.14−7.09 (m, 4H, Ar−H), 2.71 (s, 4H, $N-C(O)-CH_2$), 2.03 (s, 6H, $N-C(O)-CH_3$). MS (MALDI): *m/z* 405 $[M + Na]^+$, 393 $[M + H]^+$. The solubility of compound **1d** was not sufficient to record a ^{13}C NMR spectrum.

N^1,N^5-Bis(2-acetamidophenyl)glutaramide (1e). Yield: 55%. ^{1}H NMR (200 MHz, DMSO-d_6): δ 9.34 (s, 4H, NH−C=O), 7.56−7.59 (m, 4H, Ar−H), 7.14−7.09 (m, 4H, Ar−H), 2.43 (s, 4H, $N-C(O)-CH_2-CH_2$), 2.04 (s, 6H, $N-C(O)-CH_3$), 1.97 (m, 2H, $N-C(O)-CH_2-CH_2$). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 171.1, 168.6 (N−C=O), 130.5, 130.3 (Ar−C_{ipso}), 124.9, 124.5 (br, Ar−C_{meta} and Ar−C_{ortho}, not resolved), 35.2 ($N-C(O)-CH_2-CH_2$), 23.6 ($N-C(O)-CH_3$), 21.0 ($N-C(O)-CH_2-CH_2$). MS (MALDI): *m/z* 419 $[M + Na]^+$, 397 $[M + H]^+$.

***N*^{1},*N*^{2}-Bis(2-pivalamidophenyl)phthalamide (1f).** Yield: 47%. ^{1}H NMR (200 MHz, DMSO-d_6): δ 10.32, 8.98 (s, 4H, NH−C=O), 7.91−7.12 (m, 12H, Ar−H), 1.16 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 176.4, 167.3 (N−C=O), 136.0, 134.4, 131.8, 130.2, 127.8, 125.6, 125.4, 125.2, 124.7 (Ar−C), 38.9 (*C*(CH$_3$)$_3$), 27.1 (C(*C*H$_3$)$_3$).

***N*^{1},*N*^{3}-Bis(2-pivalamidophenyl)isophthalamide (1g).** Yield: 91%. ^{1}H NMR (200 MHz, DMSO-d_6): δ 10.26, 9.03 (s, 4H, NH−C=O), 8.55 (s, 1H, N−C(O)−C$_6$H$_4$), 8.18 (m, 2H, N−C(O)−C$_6$H$_4$), 7.74 (m, 1H, NC(O)C$_6$H$_4$), 7.56−7.51 (m, 4H, (O=CN)$_2$C$_6$H$_4$), 7.32−7.24 (m, 4H, (O=CN)$_2$C$_6$H$_4$), 1.17 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (50.3 MHz, DMSO-d_6): δ 176.7, 161.2 (N−C=O), 148.3, 140.4, 131.5, 131.6, 126.3, 125.7, 125.3, 125.2 (Ar−C), 38.8 (*C*(CH$_3$)$_3$), 26.9 (C(*C*H$_3$)$_3$).

General Procedure for the Synthesis of the Tetraamines 2a−2e. One of the tetraamides **1a**−**1e** (2.09 mmol) was added to a well-stirred suspension of LiAlH$_4$ (0.75 g, 19.7 mmol) in THF (100 mL) at 0 °C. After stirring for 2 weeks the remaining LiAlH$_4$ was carefully hydrolyzed with degassed water at 0 °C and the tetraamine was extracted into Et$_2$O (5 times, 20 mL each). The combined organic fractions were dried over MgSO$_4$. Evaporation of the solvents produced solids or oils of the tetraamines. Further purification was achieved by column chromatography (Al$_2$O$_3$, 4% H$_2$O, eluent Et$_2$O/hexane, 1:6, v/v). Removal of the solvents gave the air-sensitive tetraamines as colorless solids.

***N,N′*-Bis(2-neopentylaminophenyl)-2,2-dimethylpropane-1,3-diamine (2a).** Yield: 75%. ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.95−6.78 (m, 8H, Ar−H, 3.59 (s, 4H, NH), 3.18 (s, 4H, NCH$_2$), 2.94 (s, 4H, NCH$_2$), 1.29 (s, 6H, C(CH$_3$)$_2$), 1.12 (s, 18H, C(CH$_3$)$_3$). ^{13}C MR (50.3 MHz, CDCl$_3$): δ 138.4, 137.5 (Ar−C$_{ipso}$), 119.5, 118.8 (Ar−C$_{meta}$), 112.6, 111.9 (Ar−C$_{ortho}$), 56.0 (NCH$_2$), 53.4 (NCH$_2$), 34.7 (*C*(CH$_3$)$_2$), 31.2 (*C*(CH$_3$)$_3$), 27.4 (C(*C*H$_3$)$_3$), 24.1 (C(*C*H$_3$)$_2$). MS (EI, 70 eV) *m/z* (%): 424 (100) [M]$^+$.

***N,N′*-Bis(2-neopentylaminophenyl)butane-1,4-diamine (2b).** Yield: 84%. ^{1}H NMR (200 MHz, toluene-d_8): δ 6.97−6.88 (m, 4H, Ar−H), 6.70−6.60 (m, 4H, Ar−H), 3.09 (s br, 4H, NH), 2.79 (m, 4H, NC*H*$_2$−CH$_2$), 2.67 (s, 4H, NC*H*$_2$−C(CH$_3$)$_3$), 1.42 (m, 4H, NCH$_2$C*H*$_2$), 0.91 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (50.3 MHz, toluene-d_8): δ 138.8, 138.2 (Ar−C$_{ipso}$), 120.0, 119.7 (Ar−C$_{meta}$), 112.8, 112.7 (Ar−C$_{ortho}$), 56.5 (N*C*H$_2$−C(CH$_3$)$_3$), 44.7 (N*C*H$_2$−CH$_2$), 31.5 (*C*(CH$_3$)$_3$), 27.9 (NCH$_2$−*C*H$_2$), 27.8 (C(*C*H$_3$)$_3$). MS (EI, 70 eV) *m/z* (%): 410 (100) [M]$^+$.

***N,N′*-Bis(2-neopentylaminophenyl)pentane-1,5-diamine (2c).** Yield: 81%. ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.93−6.78 (m, 8H, Ar−H), 3.37 (s, 4H, NH), 3.23 (t, $^3J_{HH}$ = 6.9 Hz, 4H, NC*H*$_2$CH$_2$), 2.95 (s, 4H, NC*H*$_2$-C(CH$_3$)$_3$), 1.85 (m, 4H, NCH$_2$−C*H*$_2$), 1.71 (m, 2H, NCH$_2$−CH$_2$−C*H*$_2$), 1.15 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ 138.1, 137.7 (Ar−C$_{ipso}$), 119.1, 119.3 (Ar−C$_{meta}$), 112.1, 112.0 (Ar−C$_{ortho}$), 56.4 (N*C*H$_2$−C(CH$_3$)$_3$), 44.5 (NC*H*$_2$−CH$_2$), 31.6 (*C*(CH$_3$)$_3$), 29.7 (NCH$_2$−*C*H$_2$), 27.9 (C(*C*H$_3$)$_3$), 25.1 (NCH$_2$−CH$_2$−*C*H$_2$). MS (EI, 70 eV) *m/z* (%): 424 (100) [M]$^+$.

***N,N′*-Bis(2-ethylaminophenyl)butane-1,4-diamine (2d).** Yield: 65%. ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.85−6.81 (m, 4H, Ar−H), 6.75−6.69 (m, 4H, Ar−H), 3.67 (s, 4H, NH), 3.19 (m, 4H, NC*H*$_2$−CH$_2$), 3.17 (q, $^3J_{HH}$ = 7.2 Hz, 4H, NC*H*$_2$−CH$_3$), 1.86 (m, 6H, NCH$_2$−C*H*$_2$), 1.31 (t, $^3J_{HH}$ 0 = 7.2 Hz, 6H, CH$_2$−C*H*$_3$). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ 137.1, 136.7 (Ar−C$_{ipso}$), 119.4, 119.1 (Ar−C$_{meta}$), 112.0, 111.6 (Ar−C$_{ortho}$), 44.2 (N*C*H$_2$CH$_2$), 39.0 (N*C*H$_2$CH$_3$), 27.3 (NCH$_2$*C*H$_2$), 14.8 (NCH$_2$*C*H$_3$). MS (EI, 70 eV) *m/z* (%): 326 (100) [M]$^+$.

***N,N′*-Bis(2-ethylaminophenyl)pentane-1,5-diamine (2e).** Yield: 71%. ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.87−6.81 (m, 4H, Ar−H), 6.77−6.70 (m, 4H, Ar−H), 3.29 (s, 4H, NH), 3.24−3.13 (m, 8H, NCH$_2$), 1.79 (m, 4H, NCH$_2$−C*H*$_2$), 1.62 (m, 2H, NCH$_2$−CH$_2$−C*H*$_2$), 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH$_2$−C*H*$_3$). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ 137.2 (br, Ar−C$_{ipso}$), 118.9, 118.8 (Ar−C$_{meta}$), 111.4, 111.2 (Ar−C$_{ortho}$), 44.2 (N*C*H$_2$−CH$_2$), 38.7 (N*C*H$_2$−CH$_3$), 29.4 (NCH$_2$−*C*H$_2$), 24.4 (NCH$_2$CH$_2$−*C*H$_2$), 14.9 (NCH$_2$−*C*H$_3$). MS (EI, 70 eV) *m/z* (%): 340 (100) [M]$^+$.

General Procedure for the Synthesis of the Tetraamines 2f and 2g. A dried Schlenk flask was charged with THF (100 mL) and LiAlH$_4$ (1.51 g, 40 mmol). The suspension was cooled to −5 °C, and concentrated sulfuric acid (1.96 g, 20 mmol) was added (***CAUTION***: exothermic reaction and hydrogen evolution!). The suspension was stirred at room temperature for 1 h. Subsequently one of the solid tetraamides **1f** or **1g** (1.77 mmol) was slowly added to the aluminum hydride suspension. The reaction mixture was stirred overnight and cautiously hydrolyzed with degassed water. The tetraamines were isolated as described for **1a**−**1e**.

***N,N′*-Bis(2-neopentylaminophenyl)-1,2-di(methylenamino)-benzene (2f).** Yield: 66%. ^{1}H NMR (200 MHz, toluene-d_8): δ 7.24−6.64 (m, 12H, Ar−H), 4.11 (s, 4H, NC*H*$_2$−C$_6$H$_4$), 3.34 (s br, 4H, NH), 2.66 (s, 4H, NC*H*$_2$−C(CH$_3$)$_3$), 0.84 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (50.3 MHz, toluene-d_8): δ 139.0, 138.0, 137.7 (Ar−C$_{ipso}$), 129.0, 127.7 (Ar−C$_{ortho}$ and Ar−C$_{meta}$ for NCH$_2$−C$_6$H$_4$), 120.6, 119.5 (Ar−C$_{meta}$ for (NH)$_2$C$_6$H$_4$), 113.7, 112.6 (Ar−C$_{ortho}$ for (NH)$_2$C$_6$H$_4$), 56.5 (N*C*H$_2$−C(CH$_3$)$_3$), 47.0 (N*C*H$_2$−C$_6$H$_4$), 31.5 (*C*(CH$_3$)$_3$), 27.7 (C(*C*H$_3$)$_3$). MS (EI, 70 eV) *m/z* (%): 458 (48.8) [M]$^+$.

***N,N′*-Bis(2-neopentylaminophenyl)-1,3-di(methylenamino)-benzene (2g).** Yield: 62%. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.47 (s, 1H, NCH$_2$−C$_6$*H*$_4$), 7.37 (m, 3H, NCH$_2$−C$_6$*H*$_4$), 6.87−6.69 (m, 8H, (NH)$_2$C$_6$*H*$_4$), 4.36 (s, 4H, NC*H*$_2$−C$_6$H$_4$), 3.51 (s br, 4H, NH), 2.90 (s, 4H, NC*H*$_2$−C(CH$_3$)$_3$), 1.06 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ 140.0, 138.2, 137.2 (Ar−C$_{ipso}$), 128.8, 126.8, 126.3 (NCH$_2$−C$_6$H$_4$), 119.6, 118.9 (Ar−C$_{meta}$ for (NH)$_2$C$_6$H$_4$), 112.4, 111.9 (Ar−C$_{ortho}$ for (NH)$_2$C$_6$H$_4$), 56.2 (N*C*H$_2$−C(CH$_3$)$_3$), 48.8 (N*C*H$_2$−C$_6$H$_4$), 31.4 (*C*(CH$_3$)$_3$), 27.8 (C(*C*H$_3$)$_3$). MS (EI, 70 eV) *m/z* (%): 458 (100) [M]$^+$.

General Procedure for the Synthesis of the Bisgermylenes 3−7. A suitable tetraamine (0.236 mmol) in THF (5 mL) was lithiated at −78 °C with *n*-BuLi in hexane (0.95 mmol, 0.62 mL of a 1.6 M solution). After stirring for 1 h at −78 °C a solution of GeCl$_2$·1,4-dioxane (119 mg, 0.51 mmol) in THF (4 mL) was added dropwise, and the mixture was allowed to warm to room temperature. The solvents were removed *in vacuo*, and the bisgermylene was extracted into hexane (for **3**, **5**, and **7**) or toluene (for **4** and **6**). Removal of the solvent produced a crude product, which was recrystallized from hexane (**3**, **5**, and **7**) or toluene (for **4** and **6**).

1,3-Bis(*N*-neopentylbenzimidazoline-2-germylene)-2,2-dimethylpropane (3). Yield: 50% of a beige solid. ^{1}H NMR (200 MHz, toluene-d_8): δ 7.02−6.96 (m, 8H, Ar−H), 3.97 (s, 4H, NCH$_2$), 3.74 (s, 4H, NCH$_2$), 0.95 (s, 6H, C(CH$_3$)$_2$), 0.89 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (50.3 MHz, toluene-d_8): δ 143.3, 143.2 (Ar−C$_{ipso}$), 118.0, 117.9 (Ar−C$_{meta}$), 110.4, 110.3 (Ar−C$_{ortho}$), 56.7 (N*C*H$_2$−C(CH$_3$)$_3$), 54.5 (N*C*H$_2$−CH$_2$), 38.2 (*C*(CH$_3$)$_2$), 33.0 (*C*(CH$_3$)$_3$), 28.5 (C(*C*H$_3$)$_3$), 25.6 (C(*C*H$_3$)$_2$). MS (EI, 70 eV) *m/z* (%): 566 (100) [M]$^+$, 509 (46) [M − *t*-Bu]$^+$. Anal. Calcd: C, 57.31; H, 7.13; N, 9.90. Found: C, 57.74; H, 7.53; N, 9.87.

1,4-Bis(*N*-neopentylbenzimidazoline-2-germylene)butane (4). Yield: 74% of yellow crystals. ^{1}H NMR (200 MHz, toluene-d_8): δ 7.03−6.91 (m, 8H, ArH), 3.74 (m, 8H, NCH$_2$), 1.81 (m, 4H, NCH$_2$−C*H*$_2$), 0.86 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (50.3 MHz, toluene-d_8): δ 144.0, 142.1 (Ar−C$_{ipso}$), 118.5, 118.1 (Ar−C$_{meta}$), 110.4, 109.4 (Ar−C$_{ortho}$), 56.8 (N*C*H$_2$−C(CH$_3$)$_3$), 46.4 (N*C*H$_2$−CH$_2$), 33.0 (*C*(CH$_3$)$_3$), 29.7 (NCH$_2$*C*H$_2$), 28.5 (C(*C*H$_3$)$_3$). MS (EI, 70 eV) *m/z* (%): 552 (100) [M]$^+$, 495 (87) [M − *t*-Bu]$^+$. Anal. Calcd: C, 56.59; H, 6.94; N, 10.15. Found: C, 56.52; H, 6.83; N, 10.01.

1,5-Bis(*N*-neopentylbenzimidazoline-2-germylene)pentane (5). Yield: 80% of a bright orange solid. ^{1}H NMR (200 MHz, toluene-d_8): δ 7.04−6.91 (m, 8H, ArH), 3.75 (m, 8H, NCH$_2$), 1.74 (m, 4H, NCH$_2$−C*H*$_2$−CH$_2$), 1.31 (m, 2H, NCH$_2$−CH$_2$−C*H*$_2$), 0.89 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (50.3 MHz, toluene-*d*$_8$): δ 144.1, 142.1 (Ar−C$_{ipso}$), 118.5, 118.2 (Ar−C$_{meta}$), 110.5, 109.5 (Ar−C$_{ortho}$), 56.9 (NCH$_2$−C(CH$_3$)$_3$), 46.7 (N*C*H$_2$−CH$_2$), 33.1 (*C*(CH$_3$)$_3$), 31.5 (NCH$_2$−*C*H$_2$), 28.6 (C(*C*H$_3$)$_3$), 26.0 (NCH$_2$− CH$_2$−*C*H$_2$). MS (EI, 70 eV) *m*/*z* (%): 566 (100) [M]$^+$, 509 (28) [M − *t*-Bu]$^+$. Anal. Calcd: C, 57.31; H, 7.13; N, 9.90. Found: C, 56.16; H, 7.18; N, 9.75.

1,2-Bis(*N*-neopentyl-*N'*-methylenebenzimidazolin-2-germylene)benzene (6). Yield: 86% of a pale orange solid. ^{1}H NMR (200 MHz, toluene-*d*$_8$): δ 7.11−6.90 (m, 12H, Ar−H), 4.98 (s, 4H, NC*H*$_2$−C$_6$H$_4$), 3.71 (s, 4H, NCH$_2$−C(CH$_3$)$_3$), 0.87 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (50.3 MHz, toluene-*d*$_8$): δ 144.2, 142.3 (Ar−C$_{ipso}$ for N$_2$Ge−C$_6$H$_4$), 138.1 (Ar−C$_{ipso}$ for NCH$_2$−C$_6$H$_4$), 129.5, 128.3 (Ar−C$_{meta}$ and Ar−C$_{ortho}$ for NCH$_2$−C$_6$H$_4$), 118.8, 118.1 (Ar−C$_{meta}$ for N$_2$Ge−C$_6$H$_4$), 110.4, 110.2 (Ar−C$_{ortho}$ for N$_2$Ge−C$_6$H$_4$), 56.8 (N*C*H$_2$−C(CH$_3$)$_3$), 47.8 (N*C*H$_2$−C$_6$H$_4$), 33.0 (*C*(CH$_3$)$_3$), 28.5 (C(*C*H$_3$)$_3$). MS (EI, 70 eV) *m*/*z* (%): 600 (100) [M]$^+$, 543 (56) [M − *t*-Bu]$^+$. Anal. Calcd: C, 60.07; H, 6.39; N, 9.34. Found: C, 59.96; H, 6.39; N, 9.15.

1,3-Bis(*N*-neopentyl-*N'*-methylenebenzimidazoline-2-germylene)benzene (7). Yield: 80% of a pale orange solid. ^{1}H NMR (200 MHz, toluene-*d*$_8$): δ 7.14−7.00 (m, 12H, Ar−H), 4.82 (s, 4H, NC*H*$_2$−C$_6$H$_4$), 3.85 (s, 4H, NC*H*$_2$−C(CH$_3$)$_3$), 0.86 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (50.3 MHz, toluene-*d*$_8$): δ 144.2, 142.2 (Ar−C$_{ipso}$ for N$_2$Ge−C$_6$H$_4$), 140.6 (Ar−C$_{ipso}$ for NCH$_2$−C$_6$H$_4$), 129.2, 128.3, 127.3 (NCH$_2$−*C*$_6$H$_4$), 118.7, 118.1 (Ar−C$_{meta}$ for N$_2$Ge−C$_6$H$_4$), 110.5, 110.3 (Ar−C$_{ortho}$ for N$_2$Ge −C$_6$H$_4$), 56.8 (N*C*H$_2$−C(CH$_3$)$_3$), 50.3 (N*C*H$_2$−C$_6$H$_4$), 33.0 (*C*(CH$_3$)$_3$), 28.6 (C(*C*H$_3$)$_3$). MS (EI, 70 eV) *m*/*z* (%): 600 (86) [M]$^+$, 543 (91) [M − *t*-Bu]$^+$). Anal. Calcd: C, 60.07; H, 6.39; N, 9.34. Found: C, 60.01; H, 6.59; N, 9.33.

General Procedure for the Synthesis of the Bisgermylenes 8 and 9. A sample of di[bis(trimethylsilyl)amino]germanium(II), Ge[N(SiMe$_3$)$_2$]$_2$ (245 mg, 0.614 mmol), was added to a solution of tetraamine **2d** or **2e** (0.307 mmol) in THF (5 mL). The reaction mixture was stirred for 4 days at ambient temperature. Subsequently the solvent and volatile products were removed *in vacuo*. The red solid obtained was dissolved in hot hexane and filtered. Red crystals of the bisgermylenes **8** and **9** formed during cooling of the filtrate.

1,4-Bis(*N*-ethylbenzimidazoline-2-germylene)butane (8). Yield: 85% of red crystals. ^{1}H NMR (200 MHz, THF-*d*$_8$): δ 6.96 (m, 4H, Ar−H), 6.84 (m, 4H, Ar−H), 4.07 (m, 4H, NC*H*$_2$−CH$_2$), 4.02 (q, $^3J_{\mathrm{HH}} = 7.1$ Hz, 4H, C*H*$_2$−CH$_3$), 2.02 (m, 4H, NCH$_2$−C*H*$_2$), 1.55 (t, $^3J_{\mathrm{HH}} = 7.1$ Hz, 6H, CH$_2$−C*H*$_3$). ^{13}C NMR (50.3 MHz, THF-*d*$_8$): δ 143.1, 143.4 (Ar−C$_{ipso}$), 118.8, 118.7 (Ar−C$_{meta}$), 109.6, 109.4 (Ar−C$_{ortho}$), 46.8 (N*C*H$_2$−CH$_2$), 41.7 (N*C*H$_2$−CH$_3$), 30.4 (NCH$_2$−*C*H$_2$), 18.4 (CH$_2$−*C*H$_3$). MS (EI, 70 eV) *m*/*z* (%): 468 (100) [M]$^+$. Anal. Calcd: C, 51.37; H, 5.60; N, 11.98. Found: C, 50.55; H, 5.81; N, 11.87.

1,5-Bis(*N*-ethylbenzimidazoline-2-germylene)pentane (9). Yield: 80% of red crystals. ^{1}H NMR (400 MHz, 333 K, THF-*d*$_8$): δ 6.88 (m, 4H, Ar−H), 6.76 (m, 4H, Ar−H), 3.98 (m, 8H, NC*H*$_2$−CH$_2$−CH$_2$ and NC*H*$_2$−CH$_3$), 1.90 (m, 4H, NCH$_2$−C*H*$_2$−CH$_2$), 1.54 (m, 2H, NCH$_2$−CH$_2$−C*H*$_2$), 1.49 (t, $^3J_{\mathrm{HH}} = 7.1$ Hz, 6H, CH$_2$−C*H*$_3$).^{13}C NMR (100.6 MHz, 333 K, THF-*d*$_8$): δ 143.5 (s br, Ar−C$_{ipso}$), 118.8, 118.7 (Ar−C$_{meta}$), 109.6, 109.5 (Ar−C$_{ortho}$), 46.9 (N*C*H$_2$−CH$_2$−CH$_2$), 41.7 (N*C*H$_2$−CH$_3$), 32.2 (NCH$_2$−*C*H$_2$−CH$_2$), 26.4 (NCH$_2$−CH$_2$− *C*H$_2$), 18.5 (CH$_2$−*C*H$_3$). MS (EI, 70 eV) *m*/*z* (%): 482 (100) [M]$^+$. Anal. Calcd: C, 52.37; H, 5.86; N, 11.63. Found: C, 49.26; H, 5.49; N, 10.36. Satisfactory microanalytical data for **9** were difficult to obtain owing to the sensitivity of the compoud toward moisture and air.

Spiro Compound of Ge$^{\mathrm{IV}}$ (10). Compound **10** precipitated as colorless crystals from a hexane solution of the bisgermylene **3** over several weeks under concurrent formation of elemental germanium. The yield was not measured. ^{1}H NMR (200 MHz, toluene-*d*$_8$): δ 6.87−6.74 (m, 8H, Ar−H), 3.56 (d, $^2J_{\mathrm{HH}} = 14.5$ Hz, 2H, NCH$_2$−CMe$_2$), 3.39 (d, $^2J_{\mathrm{HH}} = 12.7$ Hz, 2H, NCH$_2$−CMe$_3$), 3.26 (d, $^2J_{\mathrm{HH}} = 12.7$ Hz, 2H, NCH$_2$−CMe$_3$), 2.88 (d, $^2J_{\mathrm{HH}} = 14.5$ Hz, 2H, NCH$_2$−CMe$_2$), 0.77 (s, 18H, C(CH$_3$)$_3$), 0.73 (s, 6H, C(CH$_3$)$_2$). ^{13}C NMR (50.3 MHz, toluene-*d*$_8$): δ 139.7, 138.9 (Ar−C$_{ipso}$), 118.7, 117.9 (Ar−C$_{meta}$), 111.6, 108.9 (Ar−C$_{ortho}$), 59.6 (NCH$_2$), 55.3 (NCH$_2$), 36.8 (*C*(CH$_3$)$_2$), 34.6 (*C*(CH$_3$)$_3$), 27.8 (C(*C*H$_3$)$_3$), 25.3 (C(*C*H$_3$)$_2$). MS (EI, 70 eV) *m*/*z* (%): 494 (100) [M]$^+$, 437 (45) [M − *t*-Bu]$^+$.

General Procedure for the Synthesis of the Complexes 11 and 12. Complex [Mo(nbd)(CO)$_4$] (nbd = norbornadiene) (35 mg, 0.117 mmol) was added to a solution of the bisgermylene **3** or **5** (0.106 mmol) in THF (4 mL). After stirring at ambient temperature for 1 day the solvent and liberated norbornadiene were removed *in vacuo*. An orange oil was obtained, which was washed with hexane to produce a yellow solid.

[1,3-Bis(*N*-neopentylbenzimidazoline-2-germylene)-2,2-dimethylpropane]tetracarbonylmolybdenum(0) (11). Yield: 83%. ^{1}H NMR (200 MHz, toluene-*d*$_8$): δ 7.01−6.85 (m, 8H, Ar−H), 3.91−3.34 (m, 8H, NCH$_2$, see discussion), 1.02 (s, 18H, C(CH$_3$)$_3$), 0.67 (s, 6H, C(CH$_3$)$_2$). ^{13}C NMR (50.3 MHz, toluene-*d*$_8$): δ 214.5 (CO$_{trans}$), 206.2 (CO$_{cis}$), 142.8, 142.6 (Ar−C$_{ipso}$), 118.5, 118.2 (Ar−C$_{meta}$), 110.6, 110.5 (Ar−C$_{ortho}$), 55.7 (NC*H*$_2$−C(CH$_3$)$_3$), 47.9 (NC*H*$_2$−C(CH$_3$)$_2$), 38.8 (*C*(CH$_3$)$_2$), 33.9 (*C*(CH$_3$)$_3$), 28.9 (C(*C*H$_3$)$_3$), 24.9 (C(*C*H$_3$)$_2$). IR (KBr, cm^{-1}): ν(CO) 2031, 1942, 1929, 1908. Raman spectrum (pure substrate, cm^{-1}): ν(CO) 2028, 1950, 1925. MS (EI, 70 eV) *m*/*z* (%): 774 (50) [M]$^+$, 718 (100) [M − 2CO]$^+$, 662 (93) [M − 4CO]$^+$.

[1,5-Bis(*N*-neopentylbenzimidazolin-2-germylene)-2,2-dimethylpentane]tetracarbonylmolybdenum(0) (12). Yield: 91%. ^{1}H NMR (200 MHz, toluene-*d*$_8$): δ 7.02−6.72 (m, 8H, Ar−H), 3.90 (s, 4H, NCH$_2$), 3.75 (t, $^3J_{\mathrm{HH}} = 6.3$ Hz, 4H, NC*H*$_2$−CH$_2$), 1.64 (m, 4H, NCH$_2$−C*H*$_2$), 1.23 (m, 2H, NCH$_2$−CH$_2$−C*H*$_2$), 0.95 (s, 18H, C(CH$_3$)$_3$). ^{13}C NMR (50.3 MHz, toluene-*d*$_8$): δ 212.8 (CO$_{trans)}$), 209.1 (CO$_{cis}$), 143.0, 141.5 (Ar−C$_{ipso}$), 118.4, (Ar−C$_{meta}$), 110.7, 109.0 (Ar−C$_{ortho}$), 55.4 (N*C*H$_2$−C(CH$_3$)$_3$), 43.8 (N*C*H$_2$−CH$_2$), 34.2 (*C*(CH$_3$)$_3$), 29.0 (C(*C*H$_3$)$_3$), 28.7 (NCH$_2$−*C*H$_2$), 22.3 (NCH$_2$−CH$_2$−*C*H$_2$). IR (KBr, cm^{-1}): ν(CO) 2030, 1933, 1926, 1911. Raman spectrum (pure substrate, cm^{-1}): ν(CO) 2034, 2030, 1952, 1946, 1928, 1923, 1915. MS (EI, 70 eV) *m*/*z* (%): 774 (49) [M]$^+$, 718 (100) [M − 2CO]$^+$, 662 (88) [M − 4CO]$^+$. Microanalytical data for complexes **11** and **12** could not be obtained owing to their sensitivity toward moisture and air.

X-ray Diffraction Studies. Diffraction data for **4**, **5**, **10**, and **11** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Diffraction data for the bisgermylenes **6** and **8** were obtained with a Bruker SMART 6000 CCD diffractometer equipped with a rotating anode using Cu Kα radiation (λ = 1.54184 Å) at 100(2) K. Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[28] program package. For further crystal and data collection details see Table 1. Structure solutions were found with the SHELXS-97[29] package using the heavy-atom method and were refined with SHELXL-97[30] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions. The asymmetric unit of **5** was initially believed to contain

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(28) *SMART*, Bruker AXS; 2000.

(29) Sheldrick, G. M. *SHELXS-97. Acta Crystallogr.* **1990**, *A46*, 467.

(30) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen, 1997.

a molecule of hexane. However, the hexane molecule appeared to be severely disordered, and the site occupancy was less than one. Therefore calculations were carried out omitting the solvent molecule, which explains the remaining electron density in the asymmetric unit.

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Supporting Information Available: X-ray crystallographic files for compounds **4**, **5**, **6**, **8**, **10**, and **11** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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