DOI: 10.1002/anie.201001086

Germacyclic Compounds

Synthesis and Characterization of Two of the Three Isomers of a Germanium-Substituted Bicyclo[2.2.0]hexane Diradicaloid: Stretching the Ge–Ge Bond**

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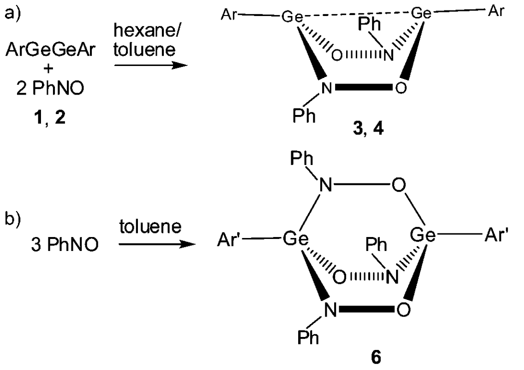
We recently showed that treatment of the digermyne Ar′GeGeAr′ (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-*i*Pr_2)$_2$) (**1**) with 1 equivalent of nitrosotoluene ONC_6H_4-2-CH_3 afforded an unsymmetric oxo/imido bridged stable singlet diradicaloid Ar′Ge(μ-O)(μ-NC_6H_4-2-CH_3)GeAr′.[1] This species was the newest member of a broad class of stable singlet diradicaloids featuring four-membered ring core structures.[2] It was distinguished by the fact that it featured oxygen as part of a stable diradicaloid. We wished to explore the chemistry of these species by the synthesis of further derivatives with use of different nitrosoarenes as well as germanium substituents. In sharp contrast to the earlier result, we now show that the reactions of **1** or 3,5-*i*Pr_2-Ar*GeGeAr*-3,5-*i*Pr_2 (3,5-*i*Pr_2-Ar* = C_6H-2,6-(C_6H_2-2,4,6-*i*Pr_3)$_2$-3,5-*i*Pr_2) (**2**) with the parent nitrosobezene PhNO, afford the polycyclic species Ar′Ge(η^1,η^1:μ_2-PhNO)$_2$GeAr′ (**3**), 3,5-*i*Pr_2-Ar*Ge(η^1,η^1:μ_2-PhNO)$_2$GeAr*-3,5-*i*Pr_2 (**4**), and Ar′Ge(η^1,η^1:μ_2-PhNO)$_3$-GeAr′ (**6**; Scheme 1). The compounds **3** and **4** feature different Ge–Ge bond distances and represent two of the three possible conformational isomeric structures of the bicylic diradicaloid system. The weakness of the Ge–Ge bond in **3** (or **4**) is underlined by the fact that it reacts further with PhNO to give **6**.

The reaction of **1** or **2** with 2 equivalents of PhNO rapidly resulted in a color change of the solution from red to purple-red. UV/Vis spectroscopy in hexane indicated mixtures of the inorganic bicyclo[2.2.0]hexane (λ_{max}: **3** 458 nm, **4** 472 nm) (Scheme 1 a) and ArGe(μ-O)(μ-NPh)GeAr (λ_{max}: Ar = Ar′ 542 nm, Ar = 3,5-*i*Pr_2-Ar* 546 nm) based on the similarity of the λ_{max} to that from the reaction of **1** with nitrosotoluene (λ_{max} = 554 nm).[1] Recrystallization afforded orange crystals of **3** or **4**. Reaction of **1** or **2** with 1 equivalent of PhNO gave **3** or **4** in reduced yields. Both **3** and **4** were characterized by spectroscopy and X-ray crystallography.[3]



1, 3 Ar = Ar′ = C_6H_3-2,6-(C_6H_3-2,6-*i*Pr_2)$_2$
2, 4 Ar = 3,5-*i*Pr_2-Ar* = C_6H-2,6-(C_6H_2-2,4,6-*i*Pr_3)$_2$-3,5-*i*Pr_2

Scheme 1. Synthetic routes to **3**, **4**, and **6**.

X-ray crystallographic data for **3** and **4** (Figure 1) showed that they have bicyclic structures in which the germaniums are four-coordinated and linked by two η^1,η^1:μ_2-PhNO bridges as well as a Ge–Ge single bond. The Ge–Ge bond (2.4731(7) Å) in **3** is longer than a normal Ge–Ge single bond (ca. 2.42 Å).[4c] The two GeNOGe rings, each of which is almost planar, display a fold angle of 110° with respect to each other. The bridgehead germaniums have extremely distorted tetrahedral coordination in which the C1, Ge1, Ge2, and C31 atoms are arranged almost linearly (C1-Ge1-Ge2 174.80(12)°, C31-Ge2-Ge1 171.88(12)°, C1-Ge2-Ge1-C43 –25.12(11)°) in contrast to the much more strongly bent skeletons of bicyclo-[2.2.0]hexane and silicon or tin analogues (Scheme 2).[5] The Ge–N (avg. 1.87 Å) and Ge–O bonds (avg. 1.82 Å) are in the normal range for Ge–N[6] and Ge–O[7] single bonds, as are the N–O (avg. 1.45 Å)[8] single bonds of the linking PhNO moieties. The structure of **4** (Figure 1, bottom) resembles that of **3** with similar Ge–N (avg.1.89 Å), Ge–O (avg. 1.83 Å) and N–O (avg. 1.44 Å) bond lengths. However, **4** has a significantly longer Ge–Ge bond (2.5403(3) Å) and slightly wider C–Ge–Ge angles (avg. 177.3(1)°) than **3**. In addition, the structures of **3** and **4** differ in the orientation of phenyl substituents as shown in Figure 2, where in **3** one Ph group is

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[**] We thank the Department of Energy Office of Basic Energy Sciences (DE-FG02-07ER46475), a Grant-in-Aid for Creative Scientific Research on a Priority Area Nanotechnology Support Project, and the Next-Generation Computing Project (Nanoscience Program) from the MEXT of Japan. We are grateful to a reviewer for useful suggestions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201001086.

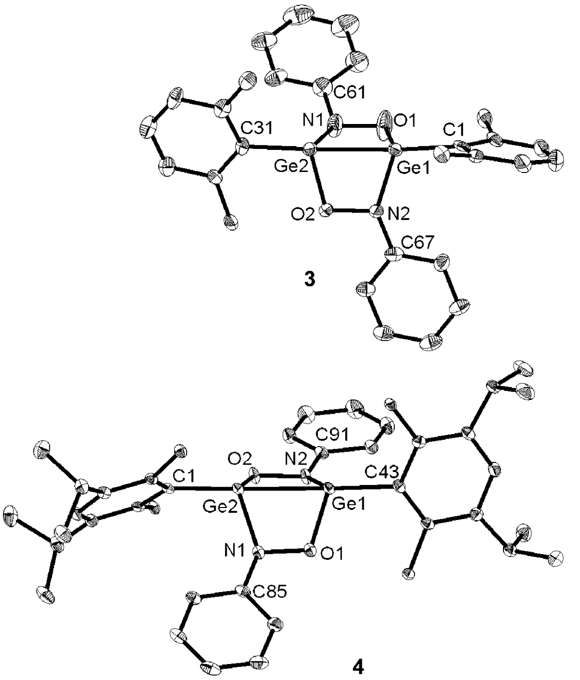
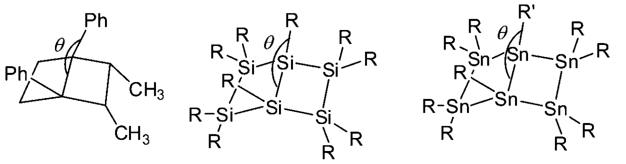
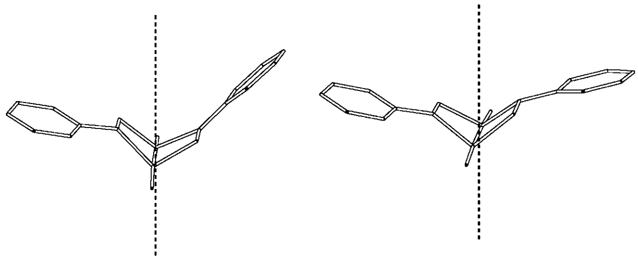


Figure 1. Thermal ellipsoid (50%) plots of **3** and **4**. H atoms and flanking aryl rings (except *ipso* carbon atoms) are not shown. Selected bond lengths [Å] and bond angles [deg]: **3** Ge1–Ge2 2.4731(7), C1–Ge1 1.933(4), Ge1–N2 1.861(4), Ge1–O1 1.818(3), Ge2–C31 1.944(4), Ge2–O2 1.815(3), Ge2–N1 1.883(4), O1–N1 1.449(5), O2–N2 1.459(4); C1-Ge1-Ge2 174.80(12), C1-Ge1-O1 108.00(16), C1-Ge1-N2 110.48(16), N2-Ge1-O1 103.7(2), Ge1-Ge2-O2 74.99(9), Ge1-Ge2-N1 73.48(11), C31-Ge2-Ge1 171.88(12). **4** Ge1–Ge2 2.5403(3), C1–Ge1 1.9474(17), Ge1–N1 1.8947(16), Ge1–O2 1.8236(13), Ge2–C43 1.9588(17), Ge2–O1 1.8371(13), Ge2–N2 1.8871(15), O1–N1 1.4366(19), O2–N2 1.4372(18); C1-Ge1-Ge2 177.60(5), C1-Ge1-O2 108.78(6), C1-Ge1-N1 107.71(7), N1-Ge1-O2 102.45(6), Ge2-Ge1-O2 73.35(4), Ge2-Ge1-N1 72.62(5), C43-Ge2-Ge1 177.05(5).



$\theta = 128.6°$[5a] $\theta = 124.3°$, R = *i*Pr[5b] $\theta = 123.0°$, R = 2,6-$Et_2C_6H_3$, R' = *n*Bu[5c]

Scheme 2. Selected Group 14 element bicyclo[2.2.0]hexane derivatives.



(*R*,*R*)-**3**
e,*a*

(*R*,*R*)-**4**
e,*e*

Figure 2. Drawings of the cores of (*R*,*R*)-**3** and (*R*,*R*)-**4**.

axial and the other is equatorial whereas in **4** both Ph groups are in equatorial positions.

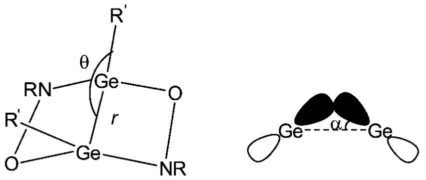
DFT calculations were performed for the model compound MeGe(η^1,η^1:μ_2-HNO)$_2$GeMe (**5**),[9] in which the aryl substituents are replaced by H or Me groups. Selected computational and experimental structural data for **5a–c**, **3**, and **4** are shown in Table 1. **5** was found to have three local minima on the potential energy surface that correspond to different orientations of the N hydrogens (**5a–c**, Figure 3). The most stable, **5c**, has two equatorial H atoms (*e*,*e*). The next in order of stability, **5b**, has one equatorial and one axial hydrogen (*e*,*a*), whereas the least stable, **5a**, has two axial hydrogens (*a*,*a*). Structures **5b** and **5c** correspond to **3** and **4**, respectively, and the calculated Ge–Ge distances for **5b** (2.440 Å) and **5c** (2.545 Å) are in remarkably good agreement with the observed 2.4731(7) Å in **3** and the 2.5403(3) Å in **4**. The data suggest that the reasons for different Ge–Ge distances are due primarily to the different molecular conformations (which could be induced by packing forces) rather than steric effects. Calculations at a lower level of theory (B3PW91//ECP < Ge > (3-21G)) on real molecules **3** and **4** also afford different Ge–Ge bond lengths (see Supporting Information). The calculated occupancies of the Ge–Ge bonding and antibonding orbitals is consistent with increasing diradicaloid character as the Ge–Ge bond is stretched (Table 1).

The calculated orbitals (HOMO−1, Figure 4) of **5a–c** offer a possible explanation for the changed Ge–Ge bond lengths. In **5c**, the π^* orbitals (of NO) are orientated in such a way that they can interact with the antibonding orbital of the Ge–Ge bond. This leads to multi-center bonding along the O-Ge-N ridges (Figure 4, **5c**), which is antibonding with respect to the Ge–Ge vector, hence lengthening the Ge–Ge bond. In **5a** (*a*,*a* isomer), the above mentioned interaction becomes unfavorable (Figure 4, **5a**) and hence a shorter Ge–Ge bond and a narrower C-Ge-Ge angle are expected. The N–O bond lengths in **5a** are slightly longer than those in the *e*,*e* isomer **5c** (1.471 Å versus 1.424 Å), consistent with the bonding picture. **5b** (*a*,*e* isomer) has structural parameters that lie between that of **5a** and **5c**. The NBO (natural bond orbital) analysis (Table 1) shows **5c**, which contains the most stretched Ge–Ge bond, has least population and the largest bending angle α (56.4°) of the Ge–Ge bonding orbital.

A number of long-bond isomers[10] for an inorganic-[1.1.1.]propellane derivative (analogues of **A**; Scheme 3)[2,11] of Si or Sn and four-membered ring inorganic bicyclo-[1.1.0]butane derivatives (analogues of **B**) involving CPBP[2,12] in which the bond stretching is the result of different substituent properties, are known. However, the observation of different stretched bond lengths in **3** and **4** represents the first instance of this phenomenon for larger rings or cages such as **C** for bicyclo[2.2.0] hexane in Scheme 3 and the first experimental evidence for its basis in conformational changes.

The strained Ge environments in **3** and **4** suggest enhanced chemical reactivity, which is supported by the reaction of **1** with 3 equivalents of PhNO or by the reaction of **3** with 1 equivalent of PhNO to give **6**. X-ray crystallography (Figure 5) showed that three molecules of PhNO are now

Table 1: X-ray structural parameters for **3** and **4**, and calculated results for **5a–c**.



Compd.	Position of R[a]	r [Å]	N–O [Å] (av)	N–Ge [Å] (av)	θ [deg] (av)[b]	ΔH [kJ mol^{-1}]		NBO Analysis	
							population of Ge–Ge σ-bond	population of Ge–Ge σ* bond	angular deviation [deg][c]
3	*a*, *e*	2.473	1.454	1.872	173.3	–	–	–	–
4	*e*, *e*	2.540	1.437	1.891	177.3	–	–	–	–
5a	*a*, *a*	2.382	1.471	1.896	161.5	0	1.82	0.12	39.7
5b	*a*, *e*	2.440	1.453	1.896	167.2	−6.7	1.77	0.20	45.1
5c	*e*, *e*	2.545	1.424	1.894	175.5	−13.4	1.67	0.33	56.4

[a] *a* = axial, *e* = equatorial. [b] θ = Ge-Ge-C angle (see table header). [c] See table header for angular deviation α.

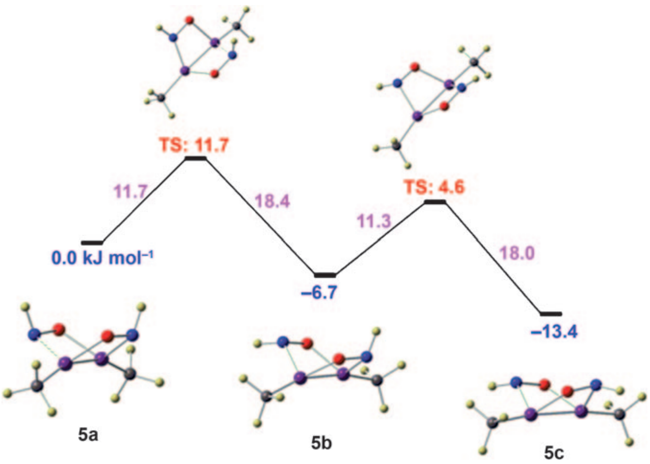
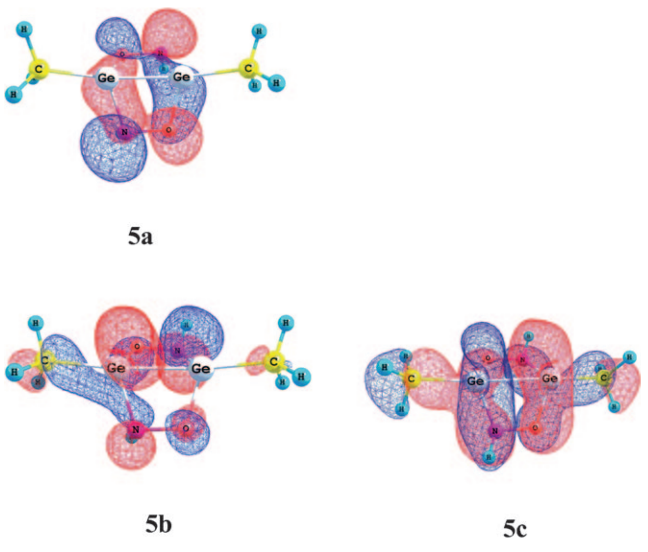


Figure 3. Energy diagram for isomeric transformations of the model species **5a–c**.

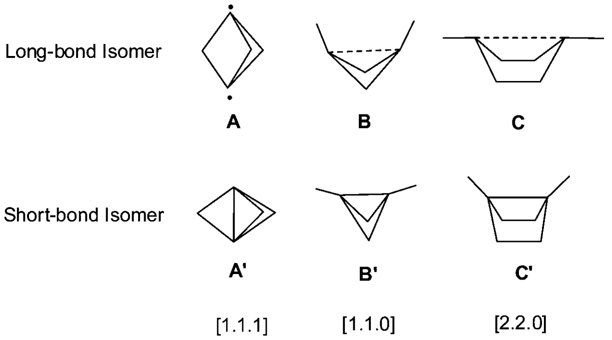


5a

5b

5c

Figure 4. Representation of the HOMO−1 of **5a–c**.



Scheme 3. Long- and short-bond isomers of [1.1.1], [1.1.0], and [2.2.0] hydrocarbons.

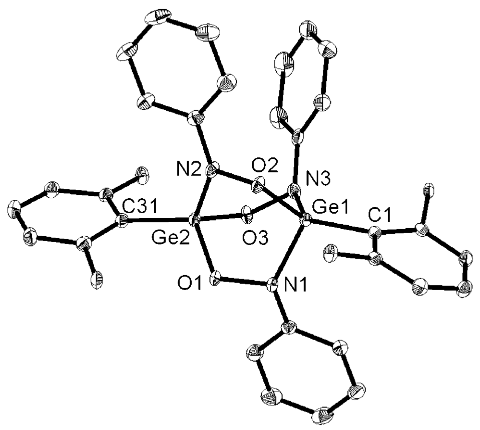
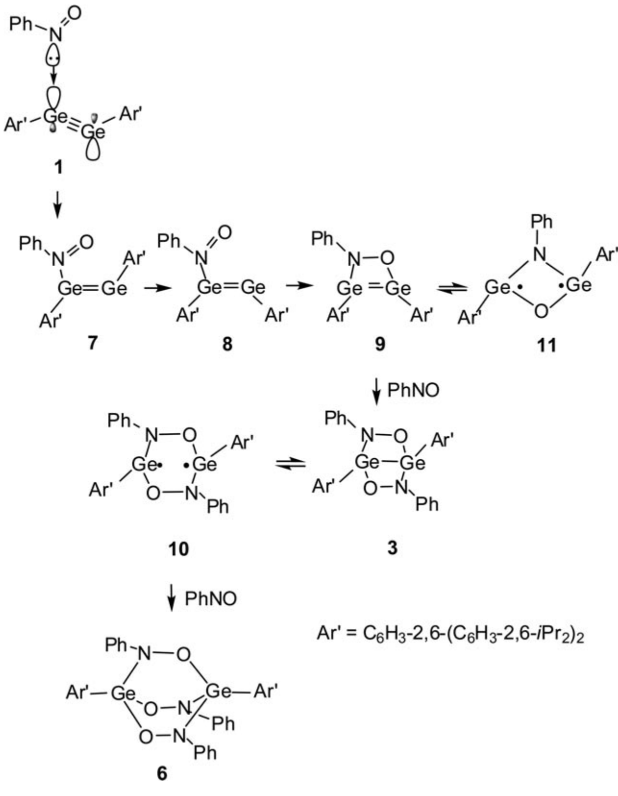


Figure 5. Thermal ellipsoid (50%) plot of **6**. H atoms and flanking aryl rings (except *ipso* carbon atoms) are not shown. Selected bond lengths [Å] and bond angles [deg] for **6**: C1–Ge1 1.9265(17), Ge1–N1 1.8569(15), Ge1–N3 1.8601(15), Ge1–O2 1.8071(12), Ge2–O1 1.7938(12), Ge2–N2 1.8399(15), Ge2–O3 1.8083(12), O1–N1 1.4531(18), O2–N2 1.4519(19), O3–N3 1.4640(19), Ge1⋯Ge2 2.9979(15); C1-Ge1-N3 124.2(1), C1-Ge1-O2 118.1(1), C1-Ge1-N1 107.0(1).

included in the product to form a trinitrosobenzene-1,4-digermabicyclo[2.2.2]octane structure, which features a Ge–Ge separation of ca. 3.0 Å consistent with the absence of a

Ge–Ge bond. One germanium (Ge1) binds two N atoms (N1, N3) and one oxygen (O2) while the other germanium (Ge2) binds to one nitrogen (N2) and two oxygens (O1, O3).

A proposed reaction pathway for the formation of **3**, **4**, and **6** is presented in Scheme 4. The initial step is the interaction of the frontier orbitals of the digermyne **1** with those of PhNO, which gives an intermediate **7** in which PhNO is σ-bonded through N to one germanium atom in the C(*ipso*)GeGeC(*ipso*) plane. The intramolecular donor–acceptor interaction leads to the [2+2] cycloaddition species **9**. The purple color of the reaction solution implies a possible equilibrium between **9** and the singlet diradicaloid Ar′Ge(μ-O)(μ-NPh)GeAr′ (**11**).[1] Addition of a further equivalent of PhNO tends to form **3**. **6** can be reasonably explained by the formation of the diradical intermediate **10**[13] resulting from the cleavage of the strained central Ge–Ge bond in **3**, followed by an effective trapping reaction with 1 equivalent of PhNO. An equilibrium between **3** and the hypothetical singlet diradicaloid **10** in solution is anticipated.



Scheme 4. Possible mechanism for the formation of **3**, **4**, and **6**.

In summary, we have described reactions of digermynes with PhNO, which led to the formation of three compounds **3**, **4**, and **6** that provide novel coordination modes of a nitrosoarene to metals.[8] The reaction products are quite different from the previously reported reaction of the digermyne **1** with the nitrosotoluene ON-C_6H_4-2-CH_3, in which the N=O double bond was cleaved to form a singlet diradicaloid Ar′Ge(μ-O)(μ-NC_6H_4-2-CH_3)GeAr′.[6] The different Ge–Ge bond lengths in **3** and **4** are mainly a result of conformational changes and calculations show that a third isomer with a shorter Ge–Ge bond is possible. The weakness of the Ge–Ge bonds was confirmed by the further reaction of **3** with PhNO to give **6**.

Received: February 22, 2010
Published online: May 20, 2010

Keywords: alkyne analogues · bicyclohexanes · digermyne · germanium · nitrosobenzene

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[3] Crystal data for **3**, **4**, and **6** at 90(2) K with $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å). **3**·C_7H_8·0.5 C_6H_{14}: $C_{82}H_{99}Ge_2N_2O_2$, $M = 1289.81$, monoclinic, space group $P2_1/c$, $Z = 4$, $\mu = 0.894$ mm^{-1}, $a = 23.004(5)$, $b = 12.260(3)$, $c = 25.495(5)$ Å, $\beta = 99.229(3)°$, $V = 7097(3)$ Å^3, $R1 = 0.0651$ for 10566 ($I > 2\sigma(I)$) reflections, $wR2 = 0.1459$ (all data). **4**·C_6H_{14}: $C_{102}H_{146}Ge_2N_2O_2$, $M = 1577.44$, triclinic, space group $P\bar{1}$, $Z = 2$, $\mu = 0.714$ mm^{-1}, $a = 14.5812(11)$, $b = 14.8893(11)$, $c = 22.0668(17)$ Å, $\alpha = 94.719(1)$, $\beta = 108.827(1)$, $\gamma = 90.363(1)°$, $V = 4516.3(6)$ Å^3, $R1 = 0.0375$ for 15918 ($I > 2\sigma(I)$) reflections, $wR2 = 0.0917$ (all data). **6**·2 C_7H_8: $C_{92}H_{105}Ge_2O_3N_3$, $M = 1445.97$, monoclinic, space group $P21/c$, $Z = 4$, $\mu = 0.835$ mm^{-1}, $a = 12.4138(5)$, $b = 13.4407(5)$, $c = 46.3247(17)$ Å, $\beta = 96.089(1)$, $V = 7685.7(5)$ Å^3, $R1 = 0.0347$ for 14370 ($I > 2\sigma(I)$) reflections, $wR2 = 0.0869$ (all data). CCDC 749783 (**3**), 749782 (**4**), and 749781 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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