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A Germanium(II) Hydride as an Effective Reagent for Hydrogermylation Reactions

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Abstract: Herein we report on the reactivity of the stable germanium(II) hydride LGeH (L = CH{(CMe)(2,6-iPr$_2$C$_6$H$_3$N)}$_2$) (**2**), which contains a low-valent germanium atom. **2** is prepared from the corresponding germanium(II) chloride LGeCl (**1**) using $H_3Al\cdot NMe_3$ or K[HB(iBu)$_3$] in toluene. The reaction of **2** with carbon dioxide in toluene at room temperature affords a germanium(II) ester of formic acid, LGe−O−C(O)H (**3**), which is formed by insertion of the carbon dioxide into the germylene hydrogen bond. **2** also reacts with alkynes at room temperature to give the first germanium(II)-substituted alkenes (**4**, **5**, and **6**). These two reaction types have in common the fact that the hydrogen and germylene from LGeH are transferred to an unsaturated bond: the carbon−oxygen double bond (C=O) in the former case and the carbon−carbon triple bond (C≡C) in the latter. Moreover, the reaction of **2** with elemental sulfur in toluene at room temperature leads to the germanium dithiocarboxylic acid analogue LGe(S)SH (**7**). Compound **7** is formed by the unprecedented insertion of elemental sulfur into the germylene hydrogen bond and oxidative addition of elemental sulfur to the germanium(II) atom. This leads to the formal conversion of the GeH hydride to a SH proton. Compounds **3**−**7** were investigated by microanalysis, multinuclear NMR spectroscopy, and single-crystal X-ray structural analyses.

Introduction

Metal hydrides and their complexes are considered valuable synthons in chemistry. It has been demonstrated that main-group and transition-metal hydrides are important intermediates in industrial processes and also function as catalysts.[1] In recent years, the chemistry of stable heteroleptic metal hydrides has attracted much attention because of their versatile reactivity.[2] In comparison with that of main-group hydrides, the chemistry of transition-metal hydrides is well-documented.[3] Organometallic hydrides of group 14 play an important role in various metathesis reactions, and therefore the reactivity of hydrides such as R_3SiH, R_3GeH, and R_3SnH are well-studied.[4] To date, there is no reported use of germanium(II) hydrides for hydrogenation reactions. The main reason for this imbalance is the synthetic difficulty and the stability of these low-valent group 14 hydrides. In 2001, our group reported the first four-coordinate monomeric germanium(II) hydride, which exists as an adduct with the Lewis acid BH_3.[5] In 2003, Power and co-workers[6] reported the first isomeric germanium(II) hydride with a bulky aryl ligand. Recently, we published the molecular structure of the unique, stable three-coordinate germanium(II) hydride LGeH (**2**) bearing the bulky β-diketiminate ligand L (L = CH{(CMe)(2,6-iPr$_2$C$_6$H$_3$N)}$_2$).[7] The corresponding carbon and silicon analogues have not yet been reported. The unusual species **2** led us to explore the reactivity pattern of the germylene hydrogen bond.

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(1) (a) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231–281. (b) McGrady, G. S.; Guilera, G. *Chem. Soc. Rev.* **2003**, *32*, 383–392. (c) Aldridge, S.; Downs, A. J. *Chem. Rev.* **2001**, *101*, 3305–3365. (d) Himmel, H.-J. *Dalton. Trans.* **2003**, 3639–3649. (e) Himmel, H.-J. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1551–1564. (f) Mitzel, N. W. *Angew. Chem.* **2003**, *115*, 3984–3986. (g) Mitzel, N. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 3856–3858. (h) Mueller, W. M.; Blackledge, J. P.; Libowitz, G. G. *Metal Hydrides*; Academic Press: London, 1968, pp 1−21. (i) Lefebvre, F.; Basset, J.-M. *Main Group Met. Chem.* **2002**, *25*, 15–32. (j) Zhao, J.; Goldman, A. S.; Hartwig, J. F. *Science* **2005**, *307*, 1080–1082.

(2) (a) Yu, Y.; Sadique, A. R.; Smith, J. M.; Dugan, T. R.; Cowley, R. E.; Brennessel, W. W.; Flaschenriem, C. J.; Bill, E.; Cundari, T. R.; Holland, P. L. *J. Am. Chem. Soc.* **2008**, *130*, 6624–6638. (b) Spielmann, J.; Harder, S. *Chem.—Eur. J.* **2007**, *13*, 8928–8938. (c) Butovskii, M. V.; Tok, O. L.; Wagner, F. R.; Kempe, R. *Angew. Chem.* **2008**, *120*, 6569–6572. (d) Butovskii, M. V.; Tok, O. L.; Wagner, F. R.; Kempe, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 6469–6472.

(3) (a) Sabo-Etienne, S.; Chaudret, B. *Chem. Rev.* **1998**, *98*, 2077–2092. (b) Hoskin, A. J.; Stephan, D. W. *Coord. Chem. Rev.* **2002**, *233−234*, 107–129. (c) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193–2242. (d) Hou, Z.; Nishiura, M.; Shima, T. *Eur. J. Inorg. Chem.* **2007**, 2535–2545.

(4) (a) Hiyama, T.; Kusumoto, T. *Comprehensive Organic Synthesis*; Pergamon: Oxford, U.K., 1991; Vol. 8, pp 763−792. (b) Beard, C. D.; Craig, J. C. *J. Am. Chem. Soc.* **1974**, *96*, 7950–7954. (c) Saegusa, T.; Ito, Y.; Kobayashi, S.; Hirota, K. *J. Am. Chem. Soc.* **1967**, *89*, 2240–2241. (d) Connor, J. A.; Rose, P. D.; Turner, R. M. *J. Organomet. Chem.* **1973**, *55*, 111–119. (e) Razuvaev, G. A. *J. Organomet. Chem.* **1980**, *200*, 243–259. (f) Manuel, G.; Bertrand, G.; Mazerolles, P. *J. Organomet. Chem.* **1978**, *146*, 7–16. (g) Bradley, G. F.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1974**, 264–269. (h) Adams, R. D.; Cotton, F. A.; Cullen, W. R.; Hunter, D. L.; Mihichuk, L. *Inorg. Chem.* **1975**, *14*, 1395–1399. (i) Blaukat, U.; Neumann, W. P. *J. Organomet. Chem.* **1973**, *63*, 27–39.

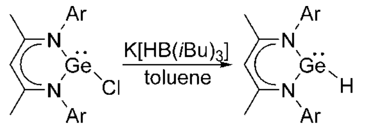
(5) Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 4806–4811.

(6) Richards, A. F.; Phillips, A. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 3204–3205.

(7) (a) Pineda, L. W.; Jancik, V.; Starke, K.; Oswald, R. B.; Roesky, H. W. *Angew. Chem.* **2006**, *118*, 2664–2667. (b) Pineda, L. W.; Jancik, V.; Starke, K.; Oswald, R. B.; Roesky, H. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 2602–2605.

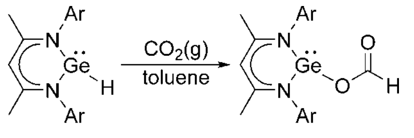
10.1021/ja808656t CCC: $40.75

Scheme 1. Preparation of **2**



1 Ar = 2,6-*i*$Pr_2C_6H_3$ **2**

Scheme 2. Preparation of **3**



2 Ar = 2,6-*i*$Pr_2C_6H_3$ **3**

Herein, we report the first reactions of LGeH with carbon dioxide and alkynes. To our surprise, the formal oxidation state (II) at the germanium atom persists during the transfer of the hydrogen and the germanium moiety from **2** to the corresponding carbon−oxygen double bond and to the carbon−carbon triple bond. Moreover, we report for the first time an insertion of elemental sulfur into the germanium(II) hydrogen bond with simultaneous oxidation of the germanium(II). This results in the formation of a germanium dithiocarboxylic acid analogue, LGe(S)SH (**7**). However, to the best of our knowledge, there are no known precedents even for hydrogenation reactions using germanium(IV) hydride and carbon dioxide or elemental sulfur. In the literature there are some reports on the hydrogenation of alkynes, but they involve mostly reactions operating in the presence of a catalyst and using Ge(IV) derivatives.[8] Although dithiocarboxylic acids and their derivatives are well-known in literature,[9] the corresponding analogues of silicon are very rare.[10] Carbon dioxide is a readily accessible atmospheric gas that could in principle be a useful synthon for organic compounds.[11] The kinetic and thermodynamic stabilities of carbon dioxide and elemental sulfur present significant challenges in designing efficient chemical transformations based on these two potential feedstocks.

Results and Discussion

Germylene Hydride Starting Material. In our previous communication we reported the synthesis of the germanium(II) hydride **2** from the reaction of the corresponding germanium(II) chloride, LGeCl (**1**),[12] with 1 equiv of $AlH_3 \cdot NMe_3$ in toluene.[7] Preparation of **2** using $AlH_3 \cdot NMe_3$ resulted in the formation of the expected product contaminated with small amounts of the starting material **1**. This slightly impure LGeH led to products containing chlorine when it was used in hydrogermylation reactions. Therefore, the method of preparation had to be improved. Treatment of **1** with potassium triisobutylborohydride (K[HB(*i*Bu)$_3$]) in toluene at −10 °C afforded the germanium(II) hydride **2** in high yield (82%) (Scheme 1). The crude reaction product was recrystallized from *n*-hexane and obtained as pure red crystals that were investigated by ^1H NMR spectroscopy.

Reaction with Carbon Dioxide. Reactions of the metal hydrides with carbon dioxide to generate the metal formates are quite well known for transition-metal hydrides and alkali-metal hydrides.[13] For group 14 metal hydrides, there are only a few reports on the hydrogenation of carbon dioxide using silicon(IV) hydride[14] and tin(IV) hydride.[15] The reaction of carbon dioxide and silicon(IV) hydride requires a transition-metal catalyst. To the best of our knowledge, there are no reports on the hydrogenation of carbon dioxide using low-valent group 14 metal hydrides. Herein, we report on the synthesis of a germylene ester of formic acid, LGe−O−C(O)H (**3**), in quantitative yield by the reaction of **2** with carbon dioxide at room temperature without any catalyst (Scheme 2).

3 is a yellow solid that is soluble in benzene, THF, *n*-hexane, and *n*-pentane and shows no decomposition on exposure to air. The compound was thoroughly characterized by multinuclear NMR spectroscopy, IR spectroscopy, electron impact mass spectrometry (EI-MS), elemental analysis, and X-ray structural analysis. The ^1H NMR spectrum of **3** exhibits an upfield-shifted singlet ($\delta = 8.64$ ppm), which can be assigned to the C*H* proton. Moreover, the ^1H NMR spectrum shows a singlet ($\delta = 5.06$ ppm) for the γ-C*H* proton and two septets ($\delta = 3.53$ and 3.08 ppm) corresponding to the two different C*H* protons of the *i*Pr moieties. The complete absence of the resonance at $\delta = 8.08$ ppm arising from the hydride proton in LGeH **2** clearly indicates the formation of **3**. The IR spectrum shows two bands at 2854 and 1690 cm^{-1}, which are assigned to the C−H and C═O stretching frequencies.

Colorless crystals of **3** can be obtained after storage of a saturated *n*-hexane solution at −32 °C for 1 day. **3** crystallizes in the triclinic space group $P\bar{1}$ with one monomer in the asymmetric unit. The coordination polyhedron around the germanium atom features a distorted tetrahedral geometry with a stereochemically active lone pair (Figure 1).

Reactions with Compounds Containing C≡C Triple Bond. The hydrogenation of unsaturated hydrocarbon compounds with Ge(IV)−H reagents give a variety of acyclic and cyclic carbon-functional germanium compounds.[16] Because of the variable polarity of the Ge−H bond, various catalysts have been used in hydrogermane reactions to initiate different pathways.[17] Herein, we report hydrogermylation reactions of alkynes using germanium(II) hydride without any catalyst.

The germanium(II) hydride **2** reacts with the alkynes $HC{\equiv}CCO_2Et$, $MeO_2CC{\equiv}CCO_2Me$, and *t*$BuO_2CC{\equiv}CCO_2$*t*Bu at room temperature to form the germanium(II)-substituted alkenes **4**, **5**, and **6**.

4 is obtained by the 1,2-addition of the germylene hydride **2** to the alkyne ethyl propiolate, and the result is the transfer of the hydrogen atom and germylene across the carbon−carbon triple bond (Scheme 3) rather than the elimination of H_2 as a result of the differently polarized Ge−H and C−H bonds.

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[8] Satgé, J.; Rivière, P. *J. Organomet. Chem.* **1969**, *16*, 71–82.

[9] Kano, N.; Kawashima, T. *Top. Curr. Chem.* **2005**, *251*, 141–180.

[10] So, C.-W.; Roesky, H. W.; Oswald, R. B.; Pal, A.; Jones, P. G. *Dalton Trans.* **2007**, 5241–5244.

[11] Arakawa, H.; et al. *Chem. Rev.* **2001**, *101*, 953–996.

[12] Ding, Y.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 1190–1194.

[13] (a) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129–168. (b) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259–272. (c) Yi, C. S.; Liu, N. *Organometallics* **1995**, *14*, 2616–2617. (d) Gibson, D. G. *Chem. Rev.* **1996**, *96*, 2063–2095. (e) McLoughlin, M. A.; Keder, N. L.; Harrison, W. T. A.; Flesher, R. J.; Mayer, H. A.; Kaska, W. C. *Inorg. Chem.* **1999**, *38*, 3223–3227.

[14] (a) Jansen, A.; Görls, H.; Pitter, S. *Organometallics* **2000**, *19*, 135–138. (b) Deglmann, P.; Ember, E.; Hofmann, P.; Pitter, S.; Walter, O. *Chem.—Eur. J.* **2007**, *13*, 2864–2879.

[15] Albertin, G.; Antoniutti, S.; Castro, J.; García-Fontán, S.; Zanardo, G. *Organometallics* **2007**, *26*, 2918–2930.

[16] Lesbre, M.; Mazerolles, P.; Satgé, J. *The Organic Compounds of Germanium*; John Wiley and Sons: London, 1971.

[17] Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1972**, *40*, 97–105.

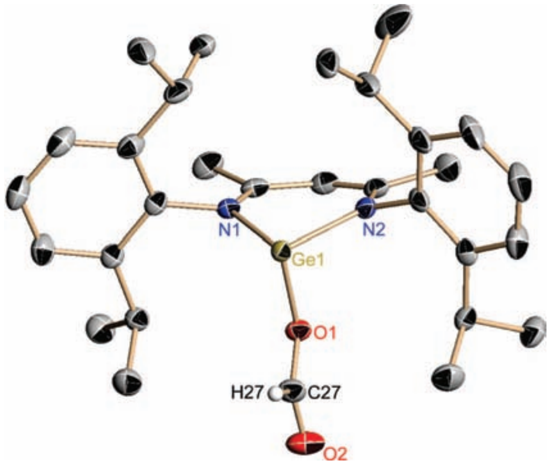


Figure 1. Anisotropic displacement parameters of **3**, depicted at the 50% probability level. All the hydrogen atoms except that for the C(O)H group have been omitted for clarity. Two of the *i*Pr groups are disordered. Selected bond lengths (Å) and angles (deg): Ge1−O1, 1.9339(18); O1−C27, 1.304(3); C27−O2, 1.204(3); Ge1−N1, 1.969(2); Ge1−N2, 1.968(2); Ge1−O1−C27, 120.07(17); O1−C27−O2, 125.1(3); N2−Ge1−N2, 91.34(9).

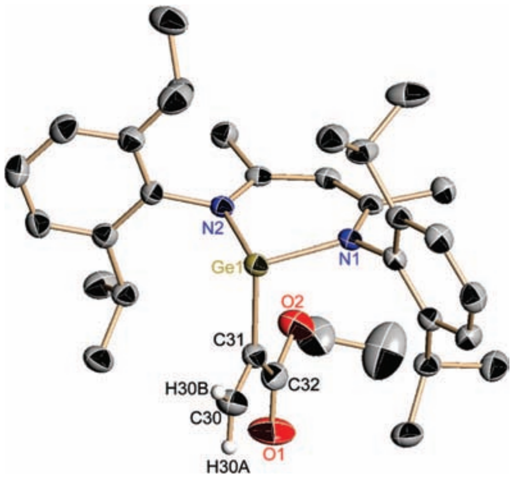
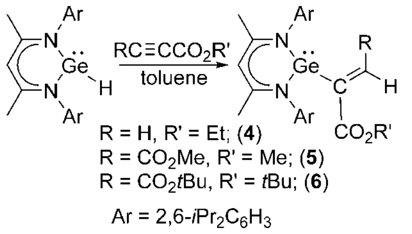


Figure 2. Anisotropic displacement parameters of **4**, depicted at the 50% probability level. All the hydrogen atoms except those for the CH_2 group have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1−C31, 2.033(3); C30−C31, 1.324(4); C31−C32, 1.491(4); C32−O1, 1.200(4); C32−O2, 1.337(4); Ge1−N1, 2.002(2); Ge1−N2, 1.994(2); Ge1−C31−C32, 130.5(2); C31−C32−O1, 126.6(3); C31−C32−O2, 111.2(2); N1−Ge1−N2, 91.65(9).

Scheme 3. Preparation of **4**, **5**, and **6**



4 is a red solid that is soluble in benzene, THF, *n*-hexane, and *n*-pentane and shows no decomposition on exposure to air. **4** was characterized by multinuclear NMR and IR spectroscopy, EI-MS, elemental analysis, and X-ray structural analysis (Figure 2). The ^{1}H NMR spectrum of **4** exhibits two broad resonances ($\delta = 6.25$ and 5.85 ppm), which correspond to the two alkenyl protons. Moreover, the ^{1}H NMR spectrum shows quartet and triplet resonances ($\delta = 4.07$ and 0.87 ppm, respectively) corresponding to the two different types of C*H* protons of the ethyl moieties. The IR spectrum exhibits bands at 3379 and 1723 cm^{-1}, which are assigned to the C−H and C═O stretching frequencies.

Compound **4** crystallizes in the monoclinic space group $P2_1/c$, with one monomer in the asymmetric unit. Single crystals were obtained from a saturated *n*-hexane solution at −32 °C after 2 days (Table 1). The coordination polyhedron around the germanium atom features a distorted tetrahedral geometry with a stereochemically active lone pair.

Furthermore, we were interested in the selectivity of the addition across the carbon−carbon triple bond. Therefore, we selected the disubstituted alkynes dimethyl acetylenedicarboxylate and di-*tert*-butyl acetylenedicarboxylate. **2** reacts with these dialkyl acetylenedicarboxylates, ($RO_2CC{\equiv}CCO_2R$, R = Me, *t*Bu) in toluene at room temperature to form only the corresponding isomers **5** and **6** with the (*E*)-germylene-substituted alkene. This was confirmed by ^{1}H NMR in solution. The ^{1}H NMR spectra show singlet resonances at $\delta = 6.64$ and 6.65 ppm, respectively, corresponding to the alkenyl protons of the germylene-substituted alkenes **5** and **6**, respectively. In addition, these compounds exhibit resonances at 4.89 and 4.96 ppm, respectively, for the γ-C*H* proton.

5 is red and **6** is yellow in the solid state. These compounds are soluble in benzene, THF, *n*-hexane, and *n*-pentane and show no decomposition on exposure to air.

5 crystallizes in the monoclinic space group $P2_1/n$, with one monomer in the asymmetric unit. Single crystals were obtained from a saturated *n*-hexane solution at −32 °C after 1 day (Figure 3). In the solid state as well, the (*E*)-isomer is the only one that was observed.

6 crystallizes in the monoclinic space group $P2_1/n$, with one monomer in the asymmetric unit. Single crystals were obtained from a saturated *n*-hexane solution at −32 °C after 2 days (see Figure S1 in the Supporting Information).

Reactions with Elemental Sulfur. The insertion of elemental sulfur into the metal hydride bond and oxidative addition to a low-valent metal center in the presence of transition-metal catalysts are quite well known.[18] In contrast, no reactions where germanium hydrides were used for the formation of germanium thiols by insertion of elemental sulfur have been reported. However, there are some reports on the preparation of germanium thiols using other routes.[19] There are some additional reports of the synthesis of silane thiols by insertion of elemental sulfur into Si−H bonds.[20] The oxidative addition of elemental sulfur to germanium(II) is known.[21] Herein, we report the simultaneous insertion of elemental sulfur into the germylene hydrogen bond and addition of elemental sulfur

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(18) (a) Mautz, J.; Huttner, G. *Eur. J. Inorg. Chem.* **2008**, 1423–1434. (b) Hossain, M. M.; Lin, H.-M.; Shyu, S.-G. *Organometallics* **2007**, *26*, 685–691. (c) Zhang, Z.-X.; Li, Y.-R.; Liu, R.-T.; Chen, Z.-X.; Weng, L.-H.; Zhou, X.-G. *Polyhedron* **2007**, *26*, 4986–4992. (d) Bacchi, A.; Baratta, W.; Calderazzo, F.; Marchetti, F.; Pelizzi, G. *Inorg. Chem.* **2002**, *41*, 3894–3900. (e) Burford, N.; Losier, P.; Mason, S.; Bakshi, P. K.; Cameron, T. S. *Inorg. Chem.* **1994**, *33*, 5613–5614.

(19) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1999**, *121*, 8811–8824.

(20) Becker, B.; Wojnowski, W. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 565–582.

(21) (a) Kuchta, M. C.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1351–1352. (b) Akkari, A.; Byrne, J. J.; Saur, I.; Rima, G.; Gornitzka, H; Barrau, J. *J. Organomet. Chem.* **2001**, *622*, 190–198.

Table 1. Crystallographic Data at $T = 100$ K for the Structural Analyses of Compounds **3**−**7**

	3	**4**	**5**	**6**	**7**
empirical formula	$C_{30}H_{42}GeN_2O_2$	$C_{34}H_{48}GeN_2O_2$	$C_{35}H_{48}GeN_2O_4$	$C_{41}H_{60}GeN_2O_4$	$C_{29}H_{42}GeN_2S_2 \cdot C_7H_8$
molecular weight	535.25	589.33	633.34	717.50	647.49
color	colorless	pale yellow	yellow	yellow	colorless
CCDC no.	706621	706622	706623	706624	667925
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (pm)	874.49(12)	1199.17(19)	1201.06(19)	1157.88(19)	1274.26(10)
b (pm)	1170.58(16)	2041.71(32)	1501.0(2)	1755.9(3)	1565.50(12)
c (pm)	1497.0(2)	1379.73(22)	1963.5(3)	1977.8(3)	1809.31(14)
α (deg)	98.446(2)	90	90	90	90
β (deg)	96.896(2)	106.896(3)	103.980(2)	103.221(2)	106.3350(10)
γ (deg)	109.595(2)	90	90	90	90
V (nm^3)	1.4042(3)	3.2323(8)	3.4349(9)	3.9145(11)	3.4636(5)
Z	2	4	4	4	4
ρ_{calc} (Mg m^{-3})	1.266	1.211	1.225	1.217	1.242
μ (mm^{-1})	1.119	0.978	0.929	0.823	1.031
F(000)	568	1256	1344	1536	1376
crystal size (mm)	0.1 × 0.1 × 0.05	0.3 × 0.2 × 0.1	0.2 × 0.2 × 0.1	0.2 × 0.1 × 0.05	0.2 × 0.2 × 0.1
θ range (deg)	1.40−26.02	2.52−25.03	2.21−26.37	1.57−26.37	1.75−27.90
reflections collected	26322	29205	55980	63793	65843
independent reflections	5494	5716	7008	8000	8257
data/restraints/parameters	5494/6/369	5716/0/363	7008/0/391	8000/0/449	8275/0/379
$R1$ [$I > 2\sigma(I)$]	0.0342	0.0401	0.0264	0.0279	0.0236
$wR2$ (all data)	0.0876	0.1094	0.0668	0.0689	0.0634
GOF	1.136	1.068	1.023	1.047	1.045
residual density max./min. (e Å^{-3})	0.680/−0.449	0.777/−0.481	0.320/−0.344	0.297/−0.330	0.521/−0.331

to the germylene atom at room temperature without any catalyst. The resulting compound is a germanium dithiocarboxylic acid analogue, which contains a Ge(S)SH moiety. To the best of our knowledge, there are only five other crystal structures deposited in the Cambridge Structural Database[22] with a Ge−S−H unit and only one derivative that contains a bridging Ge(S)SH moiety, which has the composition [Dmp(Dep)Ge(μ-S)(μ-SH)Ru(PPh$_3$)]OTf.[23] Therefore, compound **7** is the first example of a dithiocarboxylic acid analogue with a heavier group 14 element and a terminal SH bond.

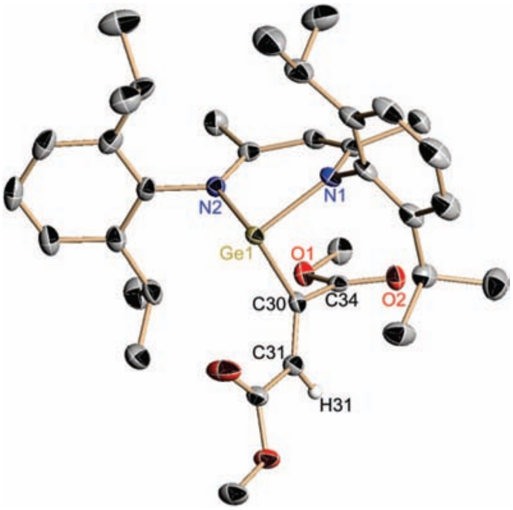
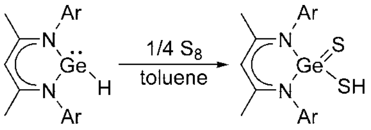


Figure 3. Anisotropic displacement parameters of **5**, depicted at the 50% probability level. All the hydrogen atoms except that for the CH group have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1−C30, 2.1093(14); C30−C31, 1.340(2); C30−C34, 1.4920(19); C34−O1, 1.3415(17); C34−O2, 1.2131(18); Ge1−N1, 2.0060(12); Ge1−N2, 2.0190(12); Ge1−C30−C31, 122.99(11); Ge1−C30−C34, 123.07(10); C30−C34−O1, 112.53(12); C30−C34−O2, 124.28(13); N1−Ge1−N2, 90.78(5).

Scheme 4. Preparation of **7**



2 Ar = 2,6-iPr$_2$C$_6$H$_3$ **7**

The reaction of **2** in the presence of 2 equiv of elemental sulfur at room temperature in toluene for 0.5 h leads to the white compound **7** in moderate yield (60%) (Scheme 4).

7 is a colorless solid that is soluble in benzene, THF, n-hexane, and n-pentane and shows no decomposition on exposure to dry air. **7** was characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, EI-MS, elemental analysis, and X-ray structural analysis. The ^{1}H NMR spectrum of **7** showed a low-frequency singlet ($\delta = -0.1$ ppm), which can be assigned to the SH proton by comparison with the Al−SH analogue.[24] The IR spectrum exhibited a weak band at 2590 cm^{-1}, whose wavenumber is less than the literature value of the wavenumber for H$_2$S(g) (2615 cm^{-1}).[25]

Maintaining a toluene solution of **7** for 2 days at −32 °C resulted in colorless single crystals suitable for X-ray structural analysis (see Table 1). **7** crystallizes in the monoclinic space group $P2_1/n$, with one molecule of **7** and one toluene solvent molecule in the asymmetric unit. **7** exists as a monomer in the solid state (Figure 4). There are no intermolecular hydrogen bonds observed in the crystal lattice. The coordination polyhedron around the germanium atom comprises two nitrogen atoms

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(22) *Cambridge Structural Database*, release 5.29; Cambridge Crystallographic Data Centre: Cambridge, U.K., 2007.

(23) Matsumoto, T.; Nakaya, Y.; Tatsumi, K. *Organometallics* **2006**, *25*, 4835–4845.

(24) Jancik, V.; Peng, Y.; Roesky, H. W.; Li, J.; Neculai, D.; Neculai, A. M.; Herbst-Irmer, R. *J. Am. Chem. Soc.* **2003**, *125*, 1452–1453.

(25) (a) Allen, H. C.; Blaine, L. R.; Plyler, E. K.; Cross, P. C. *J. Chem. Phys.* **1956**, *24*, 35–38. (b) Allen, H. C.; Plyler, E. K. *J. Chem. Phys.* **1956**, *25*, 1132–1136.

from the supporting ligand, one mercapto group, and one sulfur atom, featuring a distorted tetrahedral geometry. The Ge−N bond lengths are 1.9110(10) and 1.9157(10) Å, and the N−Ge−N angle is 95.79(4)°. A comparison shows that the Ge−N bond lengths in **1**−**6** are quite different than those in **7** as a result of the different oxidation states of the germanium atoms.

No evidence was found for any tautomeric equilibrium of **7**, and consequently, the two Ge−S bond lengths are very different: 2.0641(4) and 2.2421(4) Å. The shorter one (Ge1−S2) shows a good agreement with the Ge═S bond lengths[26] in [{HC(CMeNAr)$_2$}Ge(S)X] (X = Cl, F)[27] (2.053(6) and 2.050(9) Å, respectively) and can therefore be assigned to a formal double bond. Also, the Ge1−S1 bond length is comparable with that previously reported for the Ge−SH moiety.[28]

The formation of **7** requires the oxidation of germanium(II) to germanium(IV). Therefore, the synthesis of **7** also involves an unprecedented oxidative addition−insertion of elemental sulfur into the Ge(II)−H bond, which leads to the formal conversion of the GeH hydride to a SH proton. We assume that the first step of the reaction necessitates the intermediate LGe(II)SH, which can result from an insertion of sulfur into the germanium(II) hydride bond. The next step is the oxidative addition of elemental sulfur to LGe(II)SH, which leads to a concomitant LGe(S)SH formation. Alternatively, it may be possible that the oxidative addition of elemental sulfur to LGe(II)H might occur first, with the formation of LGe(S)H. The insertion of sulfur into the Ge−H bond would then lead to an oxidation of the hydride to a proton under reduction of the sulfur to sulfide. The existence of the recently isolated molecule LGe(II)OH[29] supports as a first step the insertion of sulfur rather than the oxidation of germanium. Surprisingly, there is no known precedent for a reaction of a group 14 element in which simultaneously an addition and insertion of sulfur is observed. We were not able to isolate any intermediate of this reaction.

Conclusion

In summary, we have demonstrated the reactivity of the first isolable three-coordinate germanium(II) hydride toward unsaturated molecules. The reaction of the germanium(II) hydride **2** with carbon dioxide resulted in the formation of a germanium(II) ester of formic acid (**3**), which represents a prototype of a new class of compounds of group 14 elements. For example, a low-valent stable carbon analogue of composition RC−O−C(O)H has not been reported to date. A RC−O−C(O)H species should be extremely unstable and rearrange to the corresponding 1,2-dicarbonyl compound, RC(O)−C(O)H. The reaction of **2** with alkynes resulted in the formation of germanium(II)-substituted alkenes **4**, **5**, and **6**. The germanium(II)-substituted alkenes have a lone pair on the germanium center and a carbon−carbon double bond, both of which are prone to react further. The unique property of these two reactions is the simultaneous transfer of the hydrogen and germylene from **2**. The reaction of **2** with elemental sulfur resulted in the formation of a germanium dithiocarboxylic acid analogue **7**, which represents a new precursor for many metal complexes. The stability of compounds **3**−**7** at room temperature favors their further functionalization as metal complexes and metal catalysts.

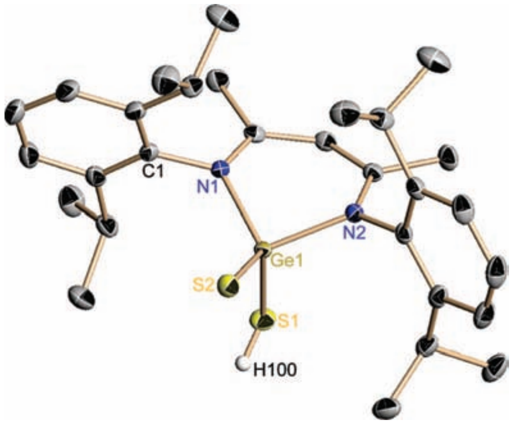

Figure 4. Anisotropic displacement parameters of **7**, depicted at the 50% probability level. The toluene molecule and all the hydrogen atoms except that for the SH group have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1−S1, 2.2422(4); Ge1−S2, 2.0641(4); Ge1−N1, 1.9157(10); Ge1−N2, 1.9111(10); S1−Ge1−S2, 119.485(16); S1−Ge1−N1, 100.66(3); S2−Ge1−N2, 116.10(3).

Experimental Section

All the manipulations were performed under a dry, oxygen-free atmosphere of N_2 using standard Schlenk techniques or inside an MBraun MB 150-GI glovebox maintained at or below 1 ppm of O_2 and H_2O. All the solvents were distilled from Na/benzophenone prior to use. The starting material **1** was prepared using literature procedures.[12] Carbon dioxide gas was purchased from Air Products and dried by passage over a P_4O_{10} column. Other chemicals were purchased commercially and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 MHz instrument and referenced to the deuterated solvent in each case. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Infrared spectral data were recorded on a PerkinElmer PE-1430 instrument. EI-MS was performed on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi B 540 melting point instrument and were not corrected.

Synthesis of [{HC(CMeNAr)$_2$}GeH] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (2). A solution of K[HB(*i*Bu)$_3$] in THF (2.00 mL, 1 M in THF) was slowly added drop by drop to a stirred solution of **1** (1.050 g, 2 mmol) in toluene (30 mL) at −10 °C. The reaction mixture was warmed to room temperature and then stirred for additional 3 h. After removal of all the volatiles, the residue was extracted with *n*-hexane (30 mL), concentrated to ∼10 mL, and stored in a −30 °C freezer. Red crystals of **2** were formed after 1 day. Yield: 0.80 g (88%). Mp: 170 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 8.08 (s, 1H, Ge–*H*), 7.10−7.15 (m, 6H, Ar−*H*), 4.86 (s, 1H, γ-C*H*), 3.59 (sept, 2H, C*H*(CH$_3$)$_2$), 3.37 (sept, 2H, C*H*(CH$_3$)$_2$), 1.60 (s, 6H, C*H*$_3$), 1.35 (d, 6H, CH(C*H*$_3$)$_2$), 1.22 (d, 6H, CH(C*H*$_3$)$_2$), 1.19 (d, 12H, CH(C*H*$_3$)$_2$).[7]

Synthesis of [{HC(CMeNAr)$_2$}GeOC(O)H] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (3). In a 100 mL Schlenk flask, a solution of **2** (0.490 g, 1.00 mmol) in 20 mL of toluene was treated with dry carbon dioxide gas at room temperature. After the addition of carbon dioxide with stirring, the reaction mixture slowly changed color from red to yellow, and stirring was continued for 15 min. After removal of all the volatiles, the residue was extracted with *n*-hexane (20 mL), concentrated to ∼10 mL, and stored in a −30 °C freezer. Yellow crystals of **3** suitable for X-ray diffraction analysis were formed after 1 day. Yield: 0.48 g (90%). Mp: 183 °C. ^{1}H NMR (500 MHz, C_6D_6): δ

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(26) (a) Veith, M.; Becker, S.; Huch, V. *Angew. Chem.* **1989**, *101*, 1287–1288. (b) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1237–1238.

(27) Ding, Y.; Ma, Q.; Usón, I.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2002**, *124*, 8542–8543.

(28) Matsumoto, T.; Tatsumi, K. *Chem. Lett.* **2001**, *30*, 964–965.

(29) (a) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Neculai, D.; Neculai, A. M. *Angew. Chem.* **2004**, *116*, 1443–1445. (b) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Neculai, D.; Neculai, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1419–1421.

8.64 (s, 1H, C*H*), 7.05−7.19 (m, 6H, Ar−*H*), 5.06 (s, 1H, γ-C*H*), 3.53 (sept, 2H, C*H*(CH$_3$)$_2$), 3.08 (sept, 2H, C*H*(CH$_3$)$_2$), 1.54 (s, 6H, C*H*$_3$), 1.28 (d, 6H, CH(C*H*$_3$)$_2$), 1.20 (d, 6H, CH(C*H*$_3$)$_2$), 1.14 (d, 6H, CH(C*H*$_3$)$_2$), 1.12 (d, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.77 MHz, C$_6$D$_6$): δ 165.31 (*C*N), 164.91 (H*C*), 146.44, 143.50, 139.88, 124.27, 123.53 (Ar−*C*), 99.87 (γ-*C*), 29.38 (*C*H(CH$_3$)$_2$), 28.58 (*C*H(CH$_3$)$_2$), 27.89 (CH(*C*H$_3$)$_2$), 27.17 (CH(*C*H$_3$)$_2$), 24.63 (CH(*C*H$_3$)$_2$), 24.56 (CH(*C*H$_3$)$_2$), 23.32 (*C*H$_3$). IR (Nujol, KBr) $\tilde{\nu}$ (cm^{-1}): 2815 (C−H), 1689 (C═O). EI-MS (70 eV) *m*/*z* (%): 536 (20) [M]$^+$, 491 (100) [M − HCO$_2$]$^+$. Anal. Calcd for $C_{30}H_{42}GeN_2O_2$ (535.25): C, 67.31; H, 7.91; N, 5.23. Found: C, 66.87; H, 8.85; N, 5.21.

Synthesis of [{HC(CMeNAr)$_2$}GeC(CO$_2$Et)CH$_2$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (4). A solution of ethyl propionate (0.100 g, 1.00 mmol) in 5 mL of toluene was added drop by drop by cannula to a solution of **2** (0.490 g, 1.00 mmol) in 15 mL of toluene at room temperature. After 0.5 h under constant stirring at ambient temperature, the red solution turned deep-red. All the volatiles were removed under vacuum, and the remaining residue was extracted with *n*-hexane (15 mL), concentrated to ∼5 mL, and stored in a −30 °C freezer. Red crystals of **4** suitable for X-ray diffraction analysis were formed after 2 days. Yield: 0.50 g (85%). Mp: 170 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.09−7.16 (m, 6H, Ar−*H*), 6.20 (d, 1H,), 5.82 (d, 1H,), 4.89 (s, 1H, γ-C*H*), 4.07 (q, 2H, C*H*$_2$), 3.65 (sept, 2H, C*H*(CH$_3$)$_2$), 3.48 (sept, 2H, C*H*(CH$_3$)$_2$), 1.59 (s, 6H, C*H*$_3$), 1.31 (d, 6H, CH(C*H*$_3$)$_2$), 1.27 (d, 6H, CH(C*H*$_3$)$_2$), 1.18 (d, 6H, CH(C*H*$_3$)$_2$), 1.15 (d, 6H, CH(C*H*$_3$)$_2$), 0.87 (t, 3H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (125.75 MHz, C$_6$D$_6$): δ 165.81 (*C*N), 144.90, 143.28, 143.21, 126.69, 124.45, 124.37 (Ar−*C*), 97.94 (γ-*C*), 29.02 (*C*HMe$_2$), 27.68 (*C*HMe$_2$), 27.11 (CH*Me*$_2$), 24.89 (CH*Me*$_2$), 24.72 (CH*Me*$_2$), 23.96 (CH*Me*$_2$), 23.95 (*Me*), 16.24 (Sn−*C*H$_3$). IR (Nujol, KBr) $\tilde{\nu}$ (cm^{-1}): 2725, 2674 (C−H), 1723 (C═O). EI-MS *m*/*z* (%): 590 (100) [M]$^+$. Anal. Calcd for $C_{34}H_{48}GeN_2O_2$ (589.40): C, 69.29; H, 8.21; N, 4.75. Found: C, 68.25; H, 9.83; N, 4.53.

Synthesis of [{HC(CMeNAr)$_2$}GeC(CO$_2$Me)CHCO$_2$Me] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (5). A solution of dimethyl acetylenedicarboxylate (0.145 g, 1.00 mmol) in 5 mL of toluene was added drop by drop by cannula to a solution of **2** (0.490 g, 1.00 mmol) in 15 mL of toluene at room temperature. After 15 min under constant stirring at ambient temperature, the red solution turned deep-red. All the volatiles were removed under vacuum, and the remaining residue was extracted with *n*-hexane (15 mL), concentrated to ∼5 mL, and stored in a −30 °C freezer. Red crystals of **5** suitable for X-ray diffraction analysis were formed after 1 day. Yield: 0.510 g (80%). Mp: 162 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.05−7.15 (m, 6H, Ar−*H*), 6.64 (s, 1H, C*H*), 4.89 (s, 1H, γ-C*H*), 3.90 (sept, 2H, C*H*(CH$_3$)$_2$), 3.43 (s, 3H, C*H*$_3$), 3.33 (sept, 2H, C*H*(CH$_3$)$_2$), 3.16 (s, 3H, C*H*$_3$), 1.59 (s, 6H, C*H*$_3$), 1.32 (d, 6H, CH(C*H*$_3$)$_2$), 1.24 (q, 12H, CH(C*H*$_3$)$_2$), 1.12 (d, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.75 MHz, C$_6$D$_6$): δ 175.52, 167.25 (*C*N), 147.33, 143.99, 141.76, 131.20, 125.13, 124.30, (Ar−*C*), 100.67 (γ-*C*), 51.46, 50.64, 28.96 (*C*HMe$_2$), 27.41 (*C*HMe$_2$), 26.52 (CH*Me*$_2$), 25.43 (CH*Me*$_2$), 24.83 (CH*Me*$_2$), 24.64 (CH*Me*$_2$), 24.10 (*Me*). IR (Nujol, KBr) $\tilde{\nu}$ (cm^{-1}): 1688 (C═O), 1720 (C═O). EI-MS *m*/*z* (%): 634 (100) [M$^+$]. Anal. Calcd for $C_{37}H_{52}GeN_2O_4$ (633.41): C, 66.37; H, 7.64; N, 4.42. Found: C, 66.21; H, 7.64; N, 4.38.

Synthesis of [{HC(CMeNAr)$_2$}GeC(CO$_2$tBu)CHCO$_2$tBu] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (6). A solution of di-*tert*-butyl acetylenedicarboxylate (0.230 g, 1.00 mmol) in 5 mL of toluene was added drop by drop by cannula to a solution of **2** (0.490 g, 1.00 mmol) in 15 mL of toluene at room temperature. After 45 min under constant stirring at ambient temperature, the red solution turned yellow. All the volatiles were removed under vacuum, and the remaining residue was extracted with *n*-hexane (15 mL), concentrated to ∼5 mL, and stored in a −30 °C freezer. Red crystals of **6** suitable for X-ray diffraction analysis were formed after 2 days. Yield: 0.630 g (88%). Mp: 168 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.04−7.15 (m, 6H, Ar−*H*), 6.65 (s, 1H, C*H*), 4.96 (s, 1H, γ-C*H*), 3.77 (sept, 2H, C*H*(CH$_3$)$_2$), 3.38 (sept, 2H, C*H*(CH$_3$)$_2$), 1.67 (s, 6H, C*H*$_3$), 1.41 (s, 9H, C(C*H*$_3$)$_3$), 1.34 (d, 6H, CH(C*H*$_3$)$_2$), 1.32 (d, 6H, CH(C*H*$_3$)$_2$), 1.28 (d, 6H, CH(C*H*$_3$)$_2$) 1.18 (s, 9H, C(C*H*$_3$)$_3$), 1.15 (d, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.75 MHz, C$_6$D$_6$): δ 174.82, 173.15, 166.84, 166.58 (*C*N), 147.32, 144.07, 141.93, 135.15, 125.10, 124.23 (Ar−*C*), 100.38 (γ-*C*), 80.60, 79.24, 28.91 (*C*HMe$_2$), 28.41 (*C*HMe$_2$), 28.02 (CH*Me*$_2$), 27.24 (CH*Me*$_2$), 26.73 (CH*Me*$_2$), 25.32 (CH*Me*$_2$), 25.28 (*Me*), 24.78, 24.16. IR (Nujol, KBr) $\tilde{\nu}$ (cm^{-1}): 1687 (C═O), 1710 (C═O). EI-MS *m*/*z* (%): 718 (100) [M$^+$]. Anal. Calcd for $C_{37}H_{52}GeN_2O_4$ (717.57): C, 68.63; H, 8.43; N, 3.90. Found: C, 68.83; H, 8.26; N, 3.88.

Synthesis of [{HC(CMeNAr)$_2$}Ge(S)SH] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) (7). A solution of **2** (1.47 g, 3.00 mmol) in toluene (30 mL) was slowly added to a suspension of elemental sulfur (0.192 g, 6.00 mmol) in toluene (15 mL) by cannula at room temperature. After 0.5 h under constant stirring at ambient temperature, the red solution turned slightly yellow. All the volatiles were removed under vacuum, and the remaining residue was extracted with toluene (15 mL). The solvent was removed in vacuo to yield **7** as a slightly yellow powder. Yield: 0.980 g (60%). Mp: 220 °C (decomp). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 6.99−7.14 (m, 6H, Ar−*H*), 4.83 (s, 1H, γ-C*H*), 3.56 (sept, 2H, C*H*(CH$_3$)$_2$), 3.33 (sept, 2H, C*H*(CH$_3$)$_2$), 1.72 (s, 6H, C*H*$_3$), 1.65 (d, 6H, CH(C*H*$_3$)$_2$), 1.49 (d, 12H, CH(C*H*$_3$)$_2$), 1.13 (d, 6H, CH(C*H*$_3$)$_2$), −0.094 (s, 1H, S*H*). ^{13}C{^{1}H} NMR (125.76 MHz, C$_6$D$_6$): δ 169.52 (*C*N), 161.48, 145.85, 128.68, 124.91 (Ar−*C*), 99.24 (γ-*C*), 29.20 (*C*H(CH$_3$)$_2$), 28.58 (CH(*C*H$_3$)$_2$), 25.77 (CH(*C*H$_3$)$_2$), 20.74 (*C*H$_3$). IR (Nujol, KBr) $\tilde{\nu}$ (cm^{-1}): 2590 (S−H). EI-MS (70 eV) *m*/*z* (%): 522 (40) [M − SH]$^+$, 506 (100) [M − SH − Me]$^+$. Anal. Calcd for $C_{29}H_{42}GeN_2S_2$ (552.25): C, 62.71; H, 7.62; N, 5.04. Found: C, 61.26; H, 7.70; N, 4.89.

Crystallographic details for compounds 3−7. Data for the structures of **3**−**6** were collected from shock-cooled crystals on an INCOATEC instrument equipped with a Bruker Apex II detector mounted on a D8 goniometer at 100 K (Mo Kα radiation, $\lambda = 0.71073$ Å).[30] The data set for **7** was collected on a Bruker TXS-Mo rotating anode equipped with INCOATEC Helios mirror optics (Mo Kα radiation, $\lambda = 0.71073$ Å). The integration was performed with SAINT version 7.46A (**3**−**6**) or 7.23A (**7**),[31] which was followed by an empirical absorption correction with SADABS 2004/1 (**7**) or 2008/1 (**3**−**6**).[32] The structures were solved by direct methods (SHELXS)[33] and refined with SHELXL[34] against F^2. All of the non-hydrogen atoms were refined with anisotropic displacement parameters. The position of the sulfur-bonded hydrogen atom H100 of **7** was taken from the difference map and refined freely. Hydrogen atoms bonded to sp^2 (sp^3) carbon atoms were assigned ideal positions and refined using a riding model with U_{iso} constrained to 1.2 (1.5) times the U_{eq} value of the parent carbon atom.

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Supporting Information Available: X-ray data for **3**−**7** (CIF), Figure S1 showing the molecular structure of **6**, and complete ref 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) (a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615–619. (b) Kottke, T.; Lagow, R. J.; Stalke, D. *J. Appl. Crystallogr.* **1996**, *29*, 465–468. (c) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171–178.

(31) *SAINT*, version 7.46A; Bruker AXS Inc.: Madison, WI, 2005.

(32) Sheldrick, G. M. *SADABS*, version 2008/1; University of Göttingen: Göttingen, Germany, 2007.

(33) Sheldrick, G. M. *SHELXS*, version 6.10; Bruker AXS Inc.: Madison, WI, 2000.

(34) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–120.