A Germanium(II) Hydroxide

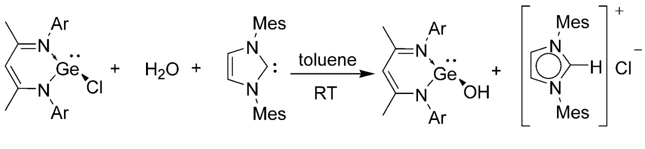
Preparation and Structure of the First Germanium(II) Hydroxide: The Congener of an Unknown Low-Valent Carbon Analogue**

Leslie W. Pineda, Vojtech Jancik, Herbert W. Roesky, Dante Neculai, and Ana M. Neculai*

Dedicated to Professor Pedro Aymonino
on the occasion of his 75th birthday

In 1984 it was noted that the picture of the structural chemistry of hydroxides is far from complete,[1] and 20 years later this is still the case. In recent years, we have been interested in organometallic hydroxides. We reported on the preparation and structural characterization of unusual compounds such as $[\mathrm{LAl(OH)_2}]$[2] ($\mathrm{L = HC\{(CMe)(2,6\text{-}\mathit{i}Pr_2C_6H_3N)\}_2}$), $[\mathrm{(Me_3Si)_3CSnO(OH)}]_3$,[3] and $[\mathrm{(CpZr)_6(\mu_4\text{-}O)(\mu\text{-}O)_4(\mu\text{-}OH)_8}]$,[4] and a series of experiments concerning the so-called water effect in organometallic chemistry.[5] Interestingly, only a few examples of well-characterized germanium(IV) hydroxides are known: $\mathrm{Ph_3GeOH}$, $\mathrm{(C_{10}H_7)_3GeOH}$, $\mathrm{(C_6H_{11})_3GeOH}$,[6] $\mathrm{2\,\mathit{t}Bu_2Ge(OH)_2\cdot(\mathit{t}Bu_2GeOH)_2O\cdot H_2O}$,[7] and $\mathrm{[Fc(\mathit{t}Bu)(OH)Ge]_2O}$ $[\mathrm{Fc = CpFe(\eta^5\text{-}C_5H_4)}]$,[8] and no such compounds based on germanium(II) have been reported. The most common route to organogermanium hydroxides is through the hydrolysis of organohalogermanes, but they can be only isolated when the supporting ligand is bulky enough.[9]

Here we report on the hydrolysis of the stable germanium(II) chloride $[\mathrm{HC\{(CMe)(2,6\text{-}\mathit{i}Pr_2C_6H_3N)\}_2GeCl}]$ (**1**),[10] with a slight excess of water and one equivalent of 1,3-dimesitylimidazol-2-ylidene[11] (**2**; $\mathrm{Mes = 2,4,6\text{-}Me_3C_6H_2}$) in toluene at room temperature, which led to the formation of $[\mathrm{HC\{(CMe)(2,6\text{-}\mathit{i}Pr_2C_6H_3N)\}_2GeOH}]$ (**3**) in good yield (Scheme 1). In contrast, conventional hydrolysis of **1** in the presence of an amine or in liquid ammonia was unsuccessful



1 **2** **3** **4**

Scheme 1. $\mathrm{Ar = 2,6\text{-}\mathit{i}Pr_2C_6H_3}$, $\mathrm{Mes = 2,4,6\text{-}Me_3C_6H_2}$.

---

[*] Dipl.-Chem. L. W. Pineda, Dipl.-Chem. V. Jancik,
Prof. Dr. H. W. Roesky, Dr. D. Neculai, Dr. A. M. Neculai
Institut für Anorganische Chemie
Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)
Fax: (+49) 551-39-3373
E-mail: hroesky@gwdg.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. L.W.P thanks the Deutscher Akademischer Austauschdienst (DAAD) for a predoctoral fellowship.

DOI: 10.1002/ange.200353205

due to the formation of several side products. Moreover, the separation of **3** from the amine·HCl adduct was not possible. Addition of HCl to the N-heterocyclic carbene **2** is clearly a key step in this reaction. The easy formation of **4** and its low solubility allow the separation of **3** from **4**.

Compound **3** is a yellow solid that is soluble in pentane, THF, dichloromethane, benzene, and diethyl ether, but insoluble in hexane. It was characterized by IR, ^{1}H, and ^{13}C NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray single-crystal analysis. In the IR spectrum a sharp absorption around 3571 cm^{-1} can be attributed to the O–H stretching frequency. Theoretical calculations on $Ge(OH)_2$ showed that two vibrational frequencies could be expected at 3675 and 3735 cm^{-1}.[12] These values are in good agreement with that of **3** when it is taken into account that some symmetry constraints are involved. In addition, the monoanionic ligand in **3** might affect the vibrational frequency by means of its steric demand and bonding mode. The ^{1}H NMR spectrum shows the expected pattern for the β-diketiminato ligand[10] and a resonance for the hydroxide proton at high field ($\delta = 1.54$ ppm), which is in accordance with the chemical shift observed for the OH group in $t\mathrm{Bu}_2\mathrm{Ge(OH)}_2$ ($\delta = 1.49$ ppm).[13] Surprisingly, the resonance for the corresponding group of $(\mathrm{FcN})_3\mathrm{GeOH}$ ($\mathrm{FcN} = \mathrm{CpFe}\{\eta^5\text{-}\mathrm{C_5H_3(CH_2NMe_2)}\text{-}2\}$) was found at $\delta = 8.98$ ppm.[14] The most intense peak in the EI mass spectrum appeared at $m/z = 403$ $[M{-}\mathrm{Me}{-}\mathrm{Ge}{-}\mathrm{OH}]^+$, and the signal at $m/z = 508$ (25 %) was assigned to the molecular ion $[M]^+$.

Single crystals of **3**[15] suitable for X-ray structural analysis were grown by maintaining the reaction mixture in toluene/hexane (2.5:1) at −20 °C for three weeks. Complex **3** crystallizes in the monoclinic space group *C*12/*c*1, with two half dimers in the asymmetric unit. In **3** a germanium atom is attached to two nitrogen atoms from the backbone of the chelating ligand and a hydroxyl group, and a lone pair presumably occupies the fourth coordination site, an assumption that is supported by the presence of an intermolecular interaction between the H atom of the OH group, which was located and refined, and another germanium atom (O–H···Ge 3.064(26) Å). The coordination geometry about germanium is derived from a distorted tetrahedron (Figure 1). The Ge–N bond lengths and N-Ge-N angle are 2.008(1) Å and 89.5(1)°, respectively. These data can be compared with the slightly shorter Ge–N bond lengths in **1** (1.988(2) and 1.997(3) Å) and [LGeF] (1.977(19) and 1.978(18) Å; $\mathrm{L} = \mathrm{HC}\{(\mathrm{CMe})(2{,}6\text{-}i\mathrm{Pr_2C_6H_3N})\}_2$).[16] Conversely, the Ge–N bond lengths are slightly longer in $[\mathrm{HB(3{,}5\text{-}Me_2pz)_3Ge}]\mathrm{I}$,[17] (av 2.03(2) Å; pz = pyrazole ring) and [LGeMe] (2.008(2) and 2.038(2) Å).[16]

A noteworthy feature of compound **3** is the GeOH moiety (Ge–O 1.828(1), O–H 0.795(7) Å); the Ge–O bond length is in good agreement with those predicted for $Ge(OH)_2$ (av 1.804 Å).[12] Moreover, the O–H distance of **3** is somewhat shorter than that of water (0.96 Å). Interestingly, and as might be expected, shorter Ge–OH bond lengths are found in germanium(IV) compounds due to the smaller radius of $\mathrm{Ge^{IV}}$ relative to $\mathrm{Ge^{II}}$ (e.g., Ge–O 1.781(4) and 1.779(2) Å in $t\mathrm{Bu_2Ge(OH)_2}$,[13] and 1.779(5) Å in $(\mathrm{FcN})_3\mathrm{GeOH}$).[14]

In summary, compound **3** is the first example of the hitherto unknown germanium(II) hydroxides. A low-coordinate carbon analogue of composition RC(OH) has so far not been reported. An RC(OH) species should be extremely unstable and rearrange to the corresponding aldehyde.

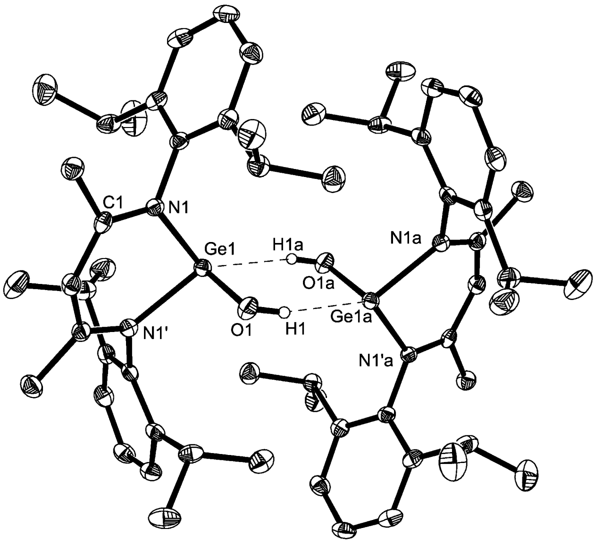


Figure 1. Thermal-ellipsoid plot of **3** at the 50% probability level. H atoms, except for the OH group, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge1–O 1.828(1), Ge1–N1 2.008(1), Ge1–N1′ 2.008(1); O1-Ge1-N1 93.9(6), O1-Ge1-N1′ 94.8(6), N1-Ge1-N1′ 89.5(1).

Experimental Section

All manipulations were performed under a dry and oxygen-free atmosphere (N_2 or Ar) by using Schlenk-line and glove-box techniques.

3: 1 (1.28 g, 2.43 mmol) and **2** (0.74 g, 2.43 mmol) were dissolved in toluene (20 mL) at room temperature, then water (87.5 μL, 2.0 mmol) was slowly added, and the mixture was stirred. A white precipitate immediately formed. The reaction mixture was stirred for about 15 min, then the white precipitate was separated by filtration in vacuo. The remaining colorless solution was evaporated, and the resulting yellow solid of **3** was rinsed with hexane (2 × 10 mL) and dried in vacuo. Yield: 1.04 g (84 %); m.p. 140 °C; IR (KBr): $\tilde{\nu} = 3571$, 2964, 2867, 1623, 1554, 1383, 1320, 1174, 1100, 1018, 918, 853, 795, 758, 588, 521, 366 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 7.15$ (m, 6 H, 2,6-$i\mathrm{Pr_2C_6H_3}$), 4.91 (s, 1 H, γ-CH), 3.60–3.80 (sept, 2 H, $(\mathrm{CH_3})_2$), 3.20–3.40 (sept, 2 H, $(\mathrm{CH_3})_2$), 1.60 (s, 6 H, $\mathrm{CH_3}$), 1.54 (s, 1 H, OH), 1.33 (d, 6 H, $\mathrm{CH(CH_3)_2}$), 1.29 (d, 6 H, $\mathrm{CH(CH_3)_2}$), 1.21 (d, 6 H, $\mathrm{CH(CH_3)_2}$), 1.12 ppm (d, 6 H, $\mathrm{CH(CH_3)_2}$); ^{13}C NMR (50.327 MHz, THF): $\delta = 163.31$ (NC), 146.37 (NC), 143.62 (ArC), 141.00 (ArC), 124.87 (ArC), 124.06 (ArC), 96.98 (γ-C), 29.16 ($\mathrm{CH(CH_3)_2}$), 28.02 ($\mathrm{CH(CH_3)_2}$), 26.69 ($\mathrm{CH(CH_3)_2}$), 24.73 ($\mathrm{CH(CH_3)_2}$), 24.57 ($\mathrm{CH(CH_3)_2}$), 24.08 ($\mathrm{CH(CH_3)_2}$), 23.25 ppm ($\mathrm{NC(CH_3)}$); MS (EI): *m*/*z* (%): 508 (25) $[M]^+$, 403 (100) $[M{-}\mathrm{Me}{-}\mathrm{Ge}{-}\mathrm{OH}]^+$; elemental analysis (%) calcd for $C_{29}H_{42}GeN_2O$ (507.24): C 68.67, H 8.35, N 5.52; found: C 69.20, H 8.48, N 5.52.

Received: October 31, 2003 [Z53205]

Keywords: carbenes · germanium · hydrolysis · hydroxides

---

[1] a) A. F. Wells, *Structural Inorganic Chemistry*, Clarendon, Oxford, **1984**, p. 627; b) A. F. Holleman, E. Wiberg, *Lehrbuch*

der Anorganischen Chemie, Walter de Gruyter, Berlin, **1995**, p. 960; c) N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Butterworth-Heinemann, Oxford, **1997**, pp. 382–383.

[2] G. Bai, Y. Peng, H. W. Roesky, J. Li, H.-G. Schmidt, M. Noltemeyer, *Angew. Chem.* **2003**, *115*, 1164–1167; *Angew. Chem. Int. Ed.* **2003**, *42*, 1132–1135.

[3] J. Janssen, J. Magull, H. W. Roesky, *Angew. Chem.* **2002**, *114*, 1425–1427; *Angew. Chem. Int. Ed.* **2002**, *41*, 1365–1367.

[4] G. Bai, H. W. Roesky, J. Li, T. Labahn, F. Cimpoesu, J. Magull, *Organometallics* **2003**, *22*, 3034–3038.

[5] H. W. Roesky, M. G. Walawalkar, R. Murugavel, *Acc. Chem. Res.* **2001**, *34*, 201–211, and references therein.

[6] M. Lesbre, P. Mazerolles, J. Satgé, *The Organic Compounds of Germanium*, Wiley, London, **1971**, p. 403.

[7] J. Beckmann, K. Jurkschart, M. Schürmann, *Eur. J. Inorg. Chem.* **2000**, 939–941.

[8] Y. Zhang, F. Cervantes-Lee, K. H. Pannell, *Organometallics* **2003**, *22*, 510–515.

[9] P. Rivière, M. Rivière-Baudet, J. Satgé in *Comprehensive Organometallic Chemistry*, *Vol. 2* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1982**, pp. 405–503.

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

[11] a) A. J. Arduengo III, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534; b) D. Bourissou, O. Guerrt, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.

[12] J. R. T. Johnson, I. Panas, *Chem. Phys.* **1999**, *249*, 273–303.

[13] H. Puff, S. Franken, W. Schuh, W. Schwab, *J. Organomet. Chem.* **1983**, *254*, 33–41.

[14] A. Fischer, K. Jacob, F. T. Edelmann, *Z. Anorg. Allg. Chem.* **2003**, *629*, 963–967.

[15] Crystal data for **3**: $C_{29}H_{42}GeN_2O$, $M_r = 507.24$, monoclinic, space group $C12/c1$, $a = 24.765(3)$, $b = 15.155(2)$, $c = 14.700(2)$ Å, $\beta = 94.56(2)°$, $V = 5499.6(12)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.251\ \mathrm{g\,cm^{-3}}$, $F(000) = 2160$, $\lambda = 1.54178$ Å, $T = 100(2)$ K, $\mu(\mathrm{Cu}_{K\alpha}) = 1.66\ \mathrm{mm^{-1}}$. Data were collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector. Intensity measurements were performed on a rapidly cooled crystal (dimensions $0.20 \times 0.10 \times 0.10$ mm) in the range $3.42 \leq 2\theta \leq 59.60°$. Of the 3752 measured reflections, 3635 were independent. The structure was solved by direct methods (SHELXS-97)[18] and refined for all data by full-matrix least-squares methods on F^2. The hydrogen atoms of C–H bonds were placed in idealized positions. The final refinements converged at $R1 = 0.0247$ for $I > 2\sigma(I)$ and $wR2 = 0.0650$ for all data. The final difference Fourier synthesis gave min./max. residual electron density of $-0.338/0.318\ \mathrm{e\,Å^{-3}}$. CCDC 222748 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[16] Y. Ding, H. Hao, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, *Organometallics* **2001**, *20*, 4806–4811. For comparison, see also a) Y. Ding, Q. Ma, H. W. Roesky, R. Herbst-Irmer, I. Usón, M. Noltemeyer, H.-G. Schmidt, *Organometallics* **2002**, *21*, 5216–5220; b) M. Stender, A. D. Phillips, P. P. Power, *Inorg. Chem.* **2001**, *40*, 5314–5315.

[17] D. L. Reger, P. S. Coan, *Inorg. Chem.* **1996**, *35*, 258–260.

[18] G. M. Sheldrick, SHELXS-97, Program for crystal structure refinement, University of Göttingen, Göttingen, Germany, **1997**.