

# Lewis Base Character of Hydroxygermylenes for the Preparation of Heterobimetallic LGe(OH)M Systems (M = Fe, Mn, L = HC[(CMe)(NAr)]<sub>2</sub>, Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)

Leslie W. Pineda,<sup>†</sup> Vojtech Jancik,<sup>†</sup> Juan F. Colunga-Valladares,<sup>‡</sup> Herbert W. Roesky,<sup>\*,†</sup> Anja Hofmeister,<sup>†</sup> and Jörg Magull<sup>†</sup>

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany, and Institut für Organische und Biomolekulare Chemie der Universität Göttingen, Tammannstrasse 2, 37077 Göttingen, Germany

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**Summary:** LGeOH (**1**; L = HC[(CMe)(NAr)]<sub>2</sub>, Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) reacted with iron and manganese complexes to give LGe(OH)Fe(CO)<sub>4</sub> (**2**) and LGe(OH)Mn(Cp)(CO)<sub>2</sub> (**3**; Cp = cyclopentadienyl). Compounds **2** and **3** were characterized by IR, multinuclear NMR, EI-MS, and single-crystal X-ray diffraction.

## Introduction

The preparation of compounds with bonds between a transition metal and silicon, germanium, tin, or lead has provided a rich chemistry, including synthetic and structural aspects as well as catalytic applications.<sup>1</sup> Furthermore, the investigation of the reactivity of divalent heavier group 14 elements has prompted a constant interest, due to the wide range of reaction possibilities.<sup>2</sup> The presence of bulky ligands and complexation with transition metals have greatly increased the stability of otherwise unstable species. In this regard, a compound of the composition ArGeOH·W(CO)<sub>5</sub> was obtained by hydrolysis of ArGeNR<sub>2</sub>·W(CO)<sub>5</sub> (Ar = 2,6-bis((diethylamino)methyl)phenyl; R = *i*Pr).<sup>3</sup> In some cases such low-valent group 14 compounds, by virtue

\* To whom correspondence should be addressed. E-mail: hroesky@gwdg.de. Fax: (+49) 551-393373.

<sup>†</sup> Institut für Anorganische Chemie.

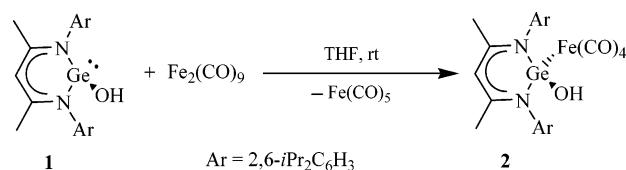
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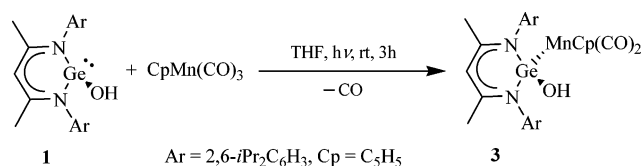
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## Scheme 1



## Scheme 2



of the electron lone pair, function as Lewis bases toward coordinatively unsaturated transition metals.<sup>4</sup> Recently, we reported the isolation and structural characterization of LGeOH (**1**; L = HC[(CMe)(NAr)]<sub>2</sub>, Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), which may either act as a donor or react at the OH functionality with transition metals.<sup>5</sup> The latter mode of reaction is reminiscent of a water-gas shift reaction.<sup>6</sup> Herein, we report the reaction of **1** with iron and manganese carbonyl complexes and their characterization by IR, mass spectrometry, multinuclear spectroscopy, and single-crystal X-ray structural analysis.

## Results and Discussion

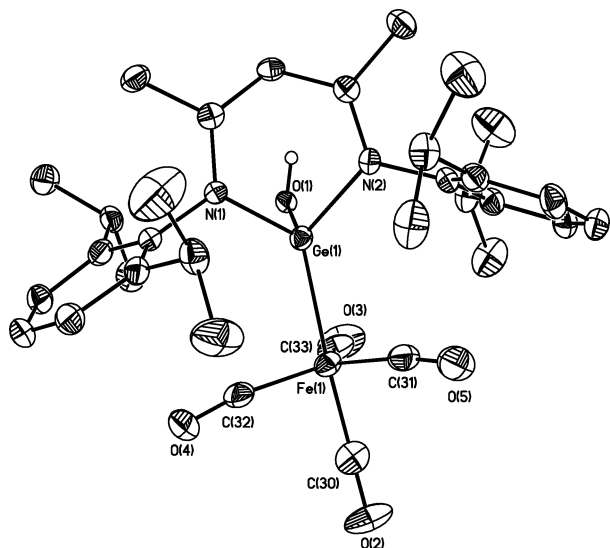
Compounds **2** and **3** were obtained by reaction of **1** with the respective transition-metal fragments. Compound **2** was isolated after separation of Fe(CO)<sub>5</sub>, also a product of the reaction of **1** and diiron nonacarbonyl, as a light brown powder (Scheme 1).

Compound **3** was prepared by the reaction of **1** with cyclopentadienylmanganese tricarbonyl with concomitant CO elimination during 3 h of UV irradiation in THF at ambient temperature (Scheme 2). Compounds **2** and **3** are air- and moisture-sensitive. **2** is soluble in THF, sparingly soluble in toluene, and insoluble in common organic solvents, whereas **3** is insoluble in the aforementioned solvents and in DMSO as well. **2** and **3** are thermally quite stable, and their mass spectra show the molecular ion peaks [*M*<sup>+</sup>] with proper isotopic patterns

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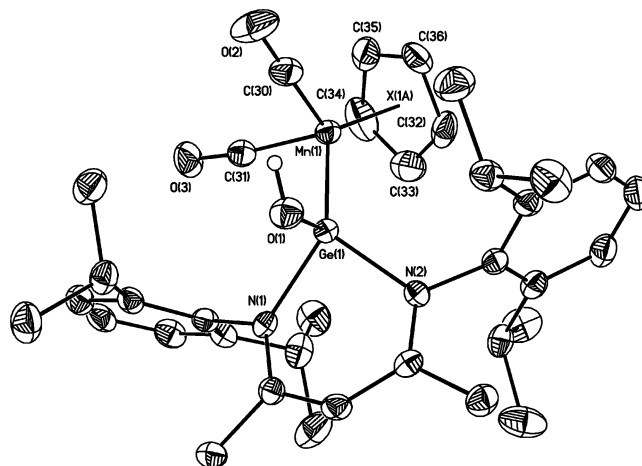
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**Figure 1.** Thermal ellipsoid plot of **2** with ellipsoids at the 50% probability level. H atoms, except for the OH group, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–O(1) = 1.840(2), Ge(1)–N(1) = 1.945(2), Ge(1)–N(2) = 1.948(2), Fe(1)–Ge(1) = 2.330(1), Fe(1)–C(30) = 1.772(3), Fe(1)–C(31) = 1.796(3), Fe(1)–C(32) = 1.795(4), Fe(1)–C(33) = 1.782(3); O(1)–Ge(1)–N(1) = 98.3(1), O(1)–Ge(1)–N(2) = 98.8(1), N(1)–Ge(1)–N(2) = 93.2(1), O(1)–Ge(1)–Fe(1) = 113.5(1), N(2)–Ge(1)–Fe(1) = 123.3(1), N(1)–Ge(1)–Fe(1) = 124.3(1), C(30)–Fe(1)–C(33) = 91.6(1), C(30)–Fe(1)–C(32) = 88.6(1), C(33)–Fe(1)–C(32) = 116.9(2), C(30)–Fe(1)–C(31) = 86.8(1), C(33)–Fe(1)–C(31) = 124.7(2), C(32)–Fe(1)–C(31) = 118.3(1), C(30)–Fe(1)–Ge(1) = 175.8(1), C(33)–Fe(1)–Ge(1) = 85.1(1), C(32)–Fe(1)–Ge(1) = 95.2(1), C(31)–Fe(1)–Ge(1) = 93.0(1).

(*m/z* 676 and 684, respectively), followed by stepwise elimination of CO. **3** displays a very sharp OH band in the IR spectrum ( $\tilde{\nu}$  3642  $\text{cm}^{-1}$ ). The corresponding absorption for **2** was found at lower wavenumber ( $\tilde{\nu}$  3599 (OH)  $\text{cm}^{-1}$ ). These values are in agreement with the OH frequency reported for  $\text{ArGeOH}\cdot\text{W}(\text{CO})_5$  ( $\tilde{\nu}$  3645  $\text{cm}^{-1}$ ; Ar = 2,6-bis((diethylamino)methyl)phenyl, R = *i*Pr).<sup>3</sup> Moreover, carbonyl absorptions for **2** and **3** were found at  $\tilde{\nu}$  2039, 1956, 1942  $\text{cm}^{-1}$  and at 1864, 1846  $\text{cm}^{-1}$ , respectively: these are in the expected range for terminal carbonyl groups.<sup>7</sup>

The  $^1\text{H}$  NMR spectrum of **2** in  $d_8$ -THF revealed a downfield ( $\delta$  4.24 ppm) resonance of the hydroxyl proton. The CO resonance in the  $^{13}\text{C}$  NMR spectrum was found at  $\delta$  214.8 ppm, a value comparable to that of  $\text{LGe}(\text{Cl})\text{Fe}(\text{CO})_4$  ( $\delta$  213.1 ppm).<sup>8</sup> Due to the poor solubility of **3**, analogous measurements could not be carried out. The molecular structures of **2** and **3** were determined by single-crystal X-ray analyses. **2** and **3**, respectively, were dissolved in hot toluene, and after the solution was cooled to ambient temperature, single crystals were obtained. **2** formed light brown crystals and **3** light orange-yellow crystals. Both compounds crystallize in the monoclinic space group  $P2_1/n$ . In **2**, a germanium atom binds to a monoanionic  $\beta$ -diketiminato ligand, to a hydroxyl group, and to an iron–carbonyl fragment, generating a four-coordinate germanium center, which adopts a distorted-tetrahedral geometry. Also, one can argue that germanium takes up the axial position of a distorted-trigonal-bipyramidal geometry at the  $\text{Fe}(\text{CO})_4$  fragment (Figure 1). The Ge–Fe bond length in **2** (2.330(1) Å) is comparable to



**Figure 2.** Thermal ellipsoid plot of **3** with ellipsoids at the 50% probability level. H atoms, except for the OH group, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–O(1) = 1.816(2), Ge(1)–N(2) = 1.970(2), Ge(1)–N(1) = 1.963(2), Mn(1)–Ge(1) = 2.345(1), O(2)–C(30) = 1.187(3), O(3)–C(31) = 1.165(4), Mn(1)–C(30) = 1.744(3), Mn(1)–C(31) = 1.772(3); O(1)–Ge(1)–N(2) = 93.7(1), O(1)–Ge(1)–N(1) = 93.4(1), N(1)–Ge(1)–N(2) = 91.1(1), O(1)–Ge(1)–Mn(1) = 119.0(1), N(1)–Ge(1)–Mn(1) = 123.5(1), N(2)–Ge(1)–Mn(1) = 127.4(1), C(30)–Mn(1)–Ge(1) = 87.6(1), C(31)–Mn(1)–Ge(1) = 95.0(1);  $X_{1A}$ –Mn(1) = 1.779(3),  $X_{1A}$ –Mn(1)–Ge(1) = 128.9(3),  $X_{1A}$ –Mn(1)–C(30) = 123.8(3),  $X_{1A}$ –Mn(1)–C(31) = 120.7(3).  $X_{1A}$  = centroid of the Cp ring.

that in  $[\{\eta^3\text{-}[(\mu\text{-}i\text{BuN})_2(\text{SiMeN}r\text{Bu})_2]\}\text{GeFe}(\text{CO})_4]$  (2.348(1) Å)<sup>9</sup> but is slightly longer in comparison with that in  $\text{L}'\text{Ge}(\text{Cl})\text{Fe}(\text{CO})_4$  (2.298(2) Å;  $\text{L}' = \text{HC}[(\text{CMe})(\text{NPh})]_2$ )<sup>8</sup> and is clearly shortened (2.240(2) Å) in  $[\text{Fe}(\text{CO})_4\{\text{Ge}(\text{OC}_6\text{H}_2i\text{Bu}_2\text{-}2,6\text{-Me-}4)_2\}]$ .<sup>10</sup> Moreover, a longer Ge–O bond length in **2** (1.840(2) Å) is observed compared with that in  $\text{LGeOH}$  (1.828(1) Å).<sup>5</sup> This is in contrast with the shortened Ge–O bond length found in  $\text{LGe}(\text{S})\text{OH}$  (1.751(2) Å;  $\text{L} = \text{HC}[(\text{CMe})(\text{NAr})]_2$ , Ar = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).<sup>11</sup>

In **3** both the germanium and the manganese atom reside in the center of a distorted-tetrahedral environment, where germanium is bonded to a  $\beta$ -diketiminato ligand, to a hydroxyl group, and to a manganese atom, while the coordination sphere around the manganese atom comprises two carbonyl groups and a cyclopentadienyl ligand (Figure 2). Previously reported germanium–manganese complexes such as  $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Mn}(\text{CO})_2]_3\text{Ge}$  and  $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Mn}(\text{CO})_2]_3\text{Ge}$  have Ge–Mn bond lengths between 2.236(1) and 2.573(1) Å and are in the same range as found in **3** (2.345(1) Å).<sup>12</sup> Further structural analysis of **3** shows that the Ge–O bond length (1.816(2) Å) is unchanged with respect to that in **2** and displays an OH orientation pointing toward the transition-metal center, in contrast to the case for **2**, where it is pointing toward the C<sub>3</sub>N<sub>2</sub>–Ge backbone.

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## Conclusion

The reactivity of the LGeOH compound with an electron lone pair and an OH moiety was demonstrated by the reaction with transition-metal fragments of manganese and iron, respectively.

## Experimental Section

**General Comments.** All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. The samples for spectral measurements were prepared in a drybox. The solvents were purified according to conventional procedures and were freshly distilled prior to use. Diiron nonacarbonyl was purchased from Aldrich and manganese cyclopentadienyltricarbonyl from Strem Chemicals, and both compounds were used as received. NMR spectra were recorded on a Bruker Avance 500 instrument, and the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported with reference to tetramethylsilane (TMS). Irradiation was carried out at ambient temperature using a low-pressure immersion lamp in a quartz reaction tube. IR spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer. Mass spectra were obtained on a Finnigan MAT 8230 spectrometer by EI techniques. Melting points were obtained in sealed capillaries on a Büchi B 540 instrument. CHN analyses were performed at the Analytical Laboratory of the Institut für Anorganische Chemie der Universität Göttingen, Göttingen, Germany.

**Preparation of LGe(OH)Fe(CO)<sub>4</sub> (2).** A flask was charged with **1** (1.99 g, 3.93 mmol) and Fe<sub>2</sub>(CO)<sub>9</sub> (1.42 g, 3.93 mmol) in THF (40 mL). The solution was stirred overnight at ambient temperature. The byproduct was removed by filtration over Celite, resulting in a clear pale brown filtrate. From the resulting solution the volatiles were removed, giving a pale brown solid. Recrystallization of the crude product was attained by gently heating a solution of toluene and **2** (20 mL) and keeping it at ambient temperature. **2** separates as pale brown crystals. Yield: 2.17 g (72%). Mp: 231 °C dec. IR (KBr pellet):  $\tilde{\nu}$  3599 s (OH), 2039 s, 1956 s, 1942 s (CO) cm<sup>-1</sup>.  $^1\text{H}$  NMR (500.13 MHz, *d*<sub>8</sub>-THF, 25 °C, TMS):  $\delta$  7.19–7.29 (m, 6H; *m*, *p* Ar *H*), 5.69 (s, 1H;  $\gamma$ -CH), 4.24 (s, 1H; OH), 3.67 (sept, 2H,  $^3J_{\text{H-H}} = 6.8$  Hz; CH(CH<sub>3</sub>)<sub>2</sub>), 3.07 (sept, 2H,  $^3J_{\text{H-H}} = 6.8$  Hz; CH(CH<sub>3</sub>)<sub>2</sub>), 1.93 (s, 6H; CH<sub>3</sub>), 1.34 (d, 6H,  $^3J_{\text{H-H}} = 6.8$  Hz; CH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (d, 6H,  $^3J_{\text{H-H}} = 6.8$  Hz; CH(CH<sub>3</sub>)<sub>2</sub>), 1.24 (d, 6H,  $^3J_{\text{H-H}} = 6.8$  Hz; CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 ppm (d, 6H,  $^3J_{\text{H-H}} = 6.8$  Hz; CH(CH<sub>3</sub>)<sub>2</sub>).  $^{13}\text{C}$  NMR (125.75 MHz, *d*<sub>8</sub>-THF, 25 °C, TMS):  $\delta$  214.8 (CO), 169.0 (CN), 147.1, 145.0, 140.0, 129.5, 125.8, 125.4 (*i*, *o*, *m*, *p* Ar), 101.6 ( $\gamma$ -CH), 29.9 (CH<sub>3</sub>), 28.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.4 ppm (CH(CH<sub>3</sub>)<sub>2</sub>). EI-MS (70 eV; *m/z* (%)): 676 (5) [*M*<sup>+</sup>], 592 (20) [*M*<sup>+</sup> - 3CO], 564 (70) [*M*<sup>+</sup> - 4CO], 491 (100) [*M*<sup>+</sup> - 4CO - Fe - OH]. Anal. Calcd for C<sub>33</sub>H<sub>42</sub>FeGeN<sub>2</sub>O<sub>5</sub> (675.13): C, 58.71; H, 6.27; N, 4.15. Found: C, 58.91; H, 6.20; N, 4.12.

**Preparation of LGe(OH)Mn(CO)<sub>2</sub>Cp (3).** Compound **1** (0.50 g, 0.98 mmol) and CpMn(CO)<sub>3</sub> (0.20 g, 0.98 mmol) were dissolved in THF (30 mL), and the mixture was irradiated for 3 h with UV light, during which time the initial yellow solution became orange.

Stirring was continued for 2 h; the solvent was removed in vacuo, and the resulting orange-yellow residue was rinsed with pentane (2 × 20 mL). Recrystallization of **3** was accomplished by gently heating a toluene solution. From the solution at ambient temperature orange-yellow crystals were obtained on standing overnight. Yield: 0.51 g (76%). Mp: 265 °C dec. IR (KBr pellet):  $\tilde{\nu}$  3642 s (OH), 1921 s, 1864 w, 1846 s (CO) cm<sup>-1</sup>. EI-MS (70 eV; *m/z* (%)): 684 (5) [*M*<sup>+</sup>], 610 (10) [*M*<sup>+</sup> - 2CO - OH], 491 (100) [*M*<sup>+</sup> - 2CO - Cp - Mn - OH]. Anal. Calcd for C<sub>36</sub>H<sub>47</sub>GeMnN<sub>2</sub>O<sub>3</sub> (684.22): C, 63.14; H, 6.92; N, 4.10. Found: C, 63.25; H, 6.95; N, 4.18.

**Molecular Structure Determination.** Data for **2** and **3** were collected on a Stoe IPDS II-array detector system instrument with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Intensity measurements were performed on a rapidly cooled crystal using  $\omega$  scans. The structures were solved by direct methods (SHELXS-97)<sup>13</sup> and refined with all data by full-matrix least squares on *F*<sup>2</sup>.<sup>14</sup> The hydrogen atoms of structures **2** and **3** of the OH groups were localized from the difference electron density maps and refined isotropically, whereas the hydrogen atoms of C-H bonds were placed in idealized positions and refined isotropically with a riding model. The non-hydrogen atoms were refined anisotropically. Crystal data for **2**: C<sub>33</sub>H<sub>42</sub>FeGeN<sub>2</sub>O<sub>5</sub>, *M*<sub>w</sub> = 675.13, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 16.004(1) Å, *b* = 9.874(1) Å, *c* = 20.379(1) Å,  $\beta = 96.42(1)^\circ$ , *V* = 3200(1) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}} = 1.401$  g cm<sup>-3</sup>, *F*(000) = 1408,  $\lambda = 0.71073$  Å, *T* = 133(2) K,  $\mu(\text{Mo K}\alpha) = 1.435$  mm<sup>-1</sup>. Of the 19 288 measured reflections, 5445 were independent (*R*(int) = 0.0614). The final refinements converged at *R*1 = 0.0501 for *I* > 2 $\sigma$ (*I*) and *wR*2 = 0.0643 for all data. The final difference Fourier synthesis gave a minimum/maximum residual electron density of +0.348/-0.254 e Å<sup>-3</sup>. Crystal data for **3**: C<sub>36</sub>H<sub>47</sub>GeMnN<sub>2</sub>O<sub>3</sub>, *M*<sub>w</sub> = 683.29, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 10.705(1) Å, *b* = 20.487(1) Å, *c* = 15.160(1) Å,  $\beta = 98.02(1)^\circ$ , *V* = 3292(1) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}} = 1.378$  g cm<sup>-3</sup>, *F*(000) = 1432,  $\lambda = 0.71073$  Å, *T* = 133(2) K,  $\mu(\text{Mo K}\alpha) = 1.334$  mm<sup>-1</sup>. Of the 31 533 measured reflections, 5672 were independent (*R*(int) = 0.0791). The final refinements converged at *R*1 = 0.0610 for *I* > 2 $\sigma$ (*I*) and *wR*2 = 0.0632 for all data. The final difference Fourier synthesis gave a minimum/maximum residual electron density of +0.406/-0.413 e Å<sup>-3</sup>.

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**Supporting Information Available:** X-ray data (CIF) for **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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