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Facile Activation of Dihydrogen by an Unsaturated Heavier Main Group Compound

Geoffrey H. Spikes, James C. Fettinger, and Philip P. Power*

Department of Chemistry, University of California Davis, One Shields Avenue, Davis, California 95616

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The activation of dihydrogen by transition-metal complexes has been studied extensively for several decades.[1] In contrast, the reactions of H_2 with main group elements and their compounds have received much less attention.[2] Nonetheless, a number of studies have shown that vapor phase reactions of H_2 with heavier group 13 elements can occur (usually with photoactivation) and the products can be trapped in a frozen matrix.[3] We have reported the isolation of the heavier group 14 element alkyne analogue Ar′GeGeAr′ (**1**) (Ar′ = C_6H_3-2,6(C_6H_3-2,6-$Pr^i{}_2$)$_2$),[4] as well as related tin and lead species,[5,6] and have shown that the “digermyne” (**1**) reacts readily with unsaturated molecules such as alkynes and azides.[7] Calculations have also shown that the model species HGeGeH exhibits a highly exothermic heat of hydrogenation, $\Delta H^{\ominus}_R$ ca. -250 kJ mol^{-1}, to give H_2GeGeH_2, which in turn displays a $\Delta H^{\ominus}_R$ of hydrogenation of ca. -150 kJ mol^{-1} to afford H_3GeGeH_3.[8] We now report that **1** reacts directly with H_2 in hexane at room temperature and atmospheric pressure to yield a mixture of a “digermene”, a digermane, and a primary germane.

$$\begin{aligned} \mathrm{Ar'GeGeAr'}\ (\mathbf{1}) + 1\mathrm{H_2} \rightarrow\ & 60\%\ \mathrm{Ar'GeGeAr'}\ (\mathbf{1}) \\ & + 21\%\ \mathrm{Ar'HGeGeHAr'}\ (\mathbf{2}) \\ & + 10\%\ \mathrm{Ar'H_2GeGeH_2Ar'}\ (\mathbf{3}) \\ & + 9\%\ \mathrm{Ar'GeH_3}\ (\mathbf{4}) \end{aligned} \quad (1)$$

$$\begin{aligned} \mathrm{Ar'GeGeAr'}\ (\mathbf{1}) + 2\mathrm{H_2} \rightarrow\ & 2\%\ \mathrm{Ar'HGeGeHAr'}\ (\mathbf{2}) \\ & + 85\%\ \mathrm{Ar'H_2GeGeH_2Ar'}\ (\mathbf{3}) \\ & + 13\%\ \mathrm{Ar'GeH_3}\ (\mathbf{4}) \end{aligned} \quad (2)$$

$$\begin{aligned} \mathrm{Ar'GeGeAr'}\ (\mathbf{1}) + 3\mathrm{H_2} \rightarrow\ & 65\%\ \mathrm{Ar'H_2GeGeH_2Ar'}\ (\mathbf{3}) \\ & + 35\%\ \mathrm{Ar'GeH_3}\ (\mathbf{4}) \end{aligned} \quad (3)$$

The addition of 1, 2, or 3 equiv of H_2 to orange-red solutions of **1** in *n*-hexane afforded the products shown in eqs 1−3. Removal of the solvent under reduced pressure gave a mixture that was analyzed by ^{1}H NMR spectroscopy in C_6D_6. The presence of three products was indicated by three different Ge−H signals in the ^{1}H NMR spectrum at 3.21, 3.58, and 5.87 ppm. For the reaction with 2 equiv of H_2 (eq 2) the intensity ratio 89:10:1 was observed. Recrystallization from a minimum volume of hexane afforded colorless crystals of the digermane Ar′H_2GeGeH_2Ar′ (**3**) in high yield, which displayed a Ge−H resonance at 3.21 ppm, corresponding to the major product of the reaction.[9b] The resonance at 5.87 ppm was assigned to the orange “digermene” Ar′HGeGeHAr′ (**2**) whose synthesis has previously been reported by us but whose structure has now been redetermined.[9a,10] The third resonance at 3.58 ppm is due to the germane Ar′GeH_3 (**4**), which was synthesized independently by the reduction of Ar′Ge(OMe)$_3$ with LiAlH_4.[9c] The reactions of **1** with 1 or 3 equiv of H_2 also led to a mixture of products. For 1 equiv of H_2, the red color of **1** faded slightly over 24 h and a large portion of **1** (60%) was found to remain unreacted.

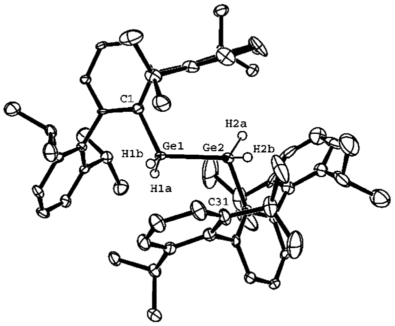

Figure 1. Thermal ellipsoid (50%) drawing of **3**; H atoms (except Ge−H) are not shown. Selected bond lengths (Å) and angles (°): Ge−Ge (avg) 2.4019(10), Ge−Cipso range 1.962(5)−1.997(5), Ge−H (avg) 1.44(4); C−Ge−Ge range 109.85(14)−120.12(16).

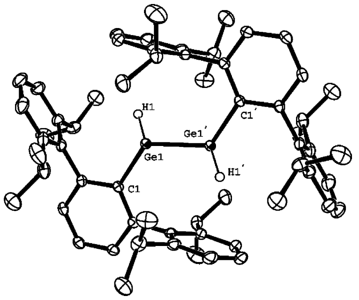

Figure 2. Thermal ellipsoid (50%) drawing of **2**; H atoms (except Ge−H) are not shown. Selected bond lengths (Å) and angles (°): Ge1−Ge1′ 2.3026(3), Ge1−C1 1.9677(12), Ge−H 1.46(2); C1−Ge1−Ge1′ 121.93(4).

The Ge−H resonances corresponding to **2**, **3**, and **4** were observed in the ^{1}H NMR spectrum in the intensity ratio 38:38:24. For the addition of 3 equiv of H_2, the color faded over 6 h and only compounds **3** and **4** were observed in the ^{1}H NMR spectrum in the product ratio 65:35 (eq 3).[9d]

The digermane **3**, synthesized via eq 2, crystallizes with three independent molecules in the asymmetric unit. One of these is given in Figure 1, which shows that there is a trans-bent Ar′GeGeAr′ arrangement with an average Ge−Ge bond distance of 2.4019(10) Å and C−Ge−Ge angles ranging from 109.79(14) to 120.17(14)°.[11a] These may be compared with those of the digermane Ar^FH_2GeGeH_2-Ar^F (Ar^F = C_6F_5, Ge−Ge = 2.394(1) Å, C−Ge−Ge = 108.6(2)°).[12] The Ge−H signal in the ^{1}H NMR spectrum at 3.21 ppm is slightly upfield of the 4−6 ppm range previously observed for Ge(IV) hydrides.[13] The IR spectrum displayed absorptions due to the Ge−H vibrations at 2120 and 2060 cm^{-1}.

Compound **2** (Figure 2)[11b] features a trans-pyramidal, “dimetallene” core arrangement with a Ge−Ge distance of 2.3026(3) Å,[14] which is comparable to those in the terphenyl-substituted digermene derivatives previously isolated by our group: Ar*RGeGeRAr*, Ge−Ge = 2.3173(3)−2.347(3) Å (Ar* = C_6H_3-2,6(C_6H_2-2,4,6-$Pr^i{}_3$)$_2$; R = Me, Et, Ph).[15] The presence of lone pair character at Ge is indicated by an out-of-plane angle of 45.0°.[16] The IR

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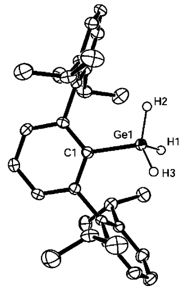

Figure 3. Thermal ellipsoid (50%) drawing of **4**; H atoms (except Ge−H) are not shown. Selected bond lengths (Å): Ge−Cipso (avg) 1.979(2), Ge−H (avg) 1.445(10).

absorptions for Ge−H were observed at 2100 and 2060 cm^{-1}, which are close to the values for **3**. However, GeGe multiple bonding was further supported by an $n_- \rightarrow n_+$ absorption at 434 nm ($\epsilon = 17\,000$). In the ^{1}H NMR spectrum, the Ge−H signal is observed at 5.87 ppm, which is close to those previously observed for Ge(II) hydrides.[13] The structure of **4** (Figure 3)[11c] features Ge−C distances (Ge1−C1 = 1.976(2) Å and Ge2−C31 = 1.983(2) Å) that resemble those observed for **2** and **3**. The IR absorption for Ge−H was observed at 2080 cm^{-1}, which is similar to that of the digermane **3**. The Ge−H resonance in the ^{1}H NMR spectrum at 3.58 ppm is comparable to that of **3** and is near the range previously observed for Ge(IV) hydrides.[13]

The data described above show clearly that H_2 reacts readily with unsaturated Ar′GeGeAr′ at room temperature and pressure. The direct addition of H_2 to an unsaturated, closed shell main group compound under such mild conditions appears to be unprecedented.[2] The initial step in this reaction is currently unknown, but it may involve the symmetry-allowed interaction of the H_2 σ-bonding MO with the LUMO of Ar′GeGeAr′ (which is the n_+ combination)[17] to generate the digermene Ar′HGeGeHAr′ (**2**). The digermane $\mathrm{Ar'H_2GeGeH_2Ar'}$ (**3**) can be produced by direct addition of H_2 to Ge−Ge bonded **2**. The inclusion of **4**, which has no Ge−Ge bond, among the products may be accounted for by the fact that the digermene **2** exists in equilibrium with either monomeric :GeHAr′ or the bridged isomer Ar′Ge(μ-H)$_2$GeAr′. The possibility of the latter type of structure is supported by calculations[18] and by the isolation of the related tin compound Ar*Sn(μ-H)$_2$SnAr*.[19] In these germanium species there is no Ge−Ge bond, and their reaction with H_2 could be expected to afford the primary germane $\mathrm{Ar'GeH_3}$ (**4**). An alternative explanation of the highly reactive nature of **1** lies in the possible singlet diradical character of the Ge−Ge bonding, which is supported by calculations.[20] The ready addition of H_2 to **1** or **2** suggests that it may be possible to add H_2 to other unsaturated heavier group 14 compounds. Work to elucidate the details of the mechanism of the reactions of H_2 with **1** or other unsaturated heavier main group compounds and their possible reversibility is in hand.

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Supporting Information Available: X-ray data and infrared spectra for **2**, **3**, and **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) All manipulations were carried out under anaerobic and anhydrous conditions. (a) **2**: This compound was prepared as previously reported.[10] Orange crystals of **2** were obtained at −18 °C from diethyl ether (0.213 g, 45%). mp: 201−202 °C. ^{1}H NMR (C_6D_6, 300.08 MHz): δ 1.03 (d, 24H, J = 6.9 Hz, $\mathrm{CH}Me_2$), 1.16 (d, 24H, J = 6.9 Hz, $\mathrm{CH}Me_2$), 2.74 (sept, 8H, J = 6.6 Hz, $\mathrm{C}H\mathrm{Me_2}$), 5.87 (s, 2H, Ge−*H*), 6.99 (m, 6H, Ar−H), 7.17 (m, 8H, Ar−H), 7.21 (t, 4H, J = 6.9 Hz, Ar−H). ^{13}C NMR (C_6D_6, 100.52 MHz): δ 24.2 ($\mathrm{CH}Me_2$), 25.7 ($\mathrm{CH}Me_2$), 31.0 ($C\mathrm{HMe_2}$), 124.1, 125.3, 129.3, 129.6, 141.2, 146.7, 147.7, 172.0 (unsaturated carbon). IR (KBr, Nujol): 2100 (w, Ge−H), 2060 (w, Ge−H), 1590 (w), 1570 (w), 1560 (w), 870 (w), 760 (s), 750 (s), 460 (m), 390 (m) cm^{-1}. UV−vis (*n*-hexane): 434 nm ($\epsilon = 17\,000$). (b) **3**: To a solution of Ar′GeGeAr′ (**1**, Ar′ = $\mathrm{C_6H_3}$-2, 6($\mathrm{C_6H_3}$-2,6-$\mathrm{Pr^i_2}$)$_2$, 0.300 g, 0.320 mmol) in *n*-hexane (50 mL) was added H_2 (14.3 mL, 0.640 mmol), and the mixture was stirred at room temperature for 6 h. The resulting pale yellow solution was concentrated and stored at ca. −18 °C overnight to give colorless crystals of **3** (0.250 g, 82.8%). mp: 244−245 °C. ^{1}H NMR (C_6D_6, 300.08 MHz): δ 1.00 (d, 24H, J = 6.9 Hz, $\mathrm{CH}Me_2$), 1.15 (d, 24H, J = 6.9 Hz, $\mathrm{CH}Me_2$), 2.64 (sept, 8H, J = 6.6 Hz, $\mathrm{C}H\mathrm{Me_2}$), 3.21 (s, 4H, Ge−*H*), 7.04 (m, 8H, Ar−H), 7.19 (m, 6H, Ar−H), 7.25 (d, 4H, J = 6.9 Hz, Ar−H). ^{13}C NMR (C_6D_6, 100.52 MHz): δ 23.3 ($\mathrm{CH}Me_2$), 25.9 ($\mathrm{CH}Me_2$), 30.9 ($C\mathrm{HMe_2}$), 123.3, 127.4, 128.7, 129.5, 141.1, 146.5, 147.7 (unsaturated carbon). IR (KBr, Nujol): 2120 (w, Ge−H), 2060 (w, Ge−H), 1590 (w), 1570 (w), 1560 (w), 860 (w), 760 (s), 750 (s), 670 (s), 460 (m), 380 (m) cm^{-1}. (c) **4**: To a Schlenk tube charged with excess $\mathrm{LiAlH_4}$ was added a solution of Ar′Ge(OMe)$_3$ (1.000 g, 0.320 mmol) in diethyl ether (50 mL). The resultant suspension was subsequently stirred for 3 h and filtered, and the volatile materials were removed under reduced pressure. The residue was extracted with a minimum volume of *n*-hexane, which yielded **4** as colorless crystals on storage at ca. −18 °C (0.790 g, 94%). mp: 106−107 °C. ^{1}H NMR (C_6D_6, 300.08 MHz): δ 1.08 (d, 12H, J = 6.9 Hz, $\mathrm{CH}Me_2$), 1.25 (d, 12H, J = 6.9 Hz, $\mathrm{CH}Me_2$), 2.82 (sept, 4H, J = 6.6 Hz, $\mathrm{C}H\mathrm{Me_2}$), 3.58 (s, 3H, Ge−*H*), 7.11 (d, 4H, J = 7.5 Hz, Ar−H), 7.18 (m, 3H, Ar−H), 7.31 (t, 2H, J = 6.9 Hz, Ar−H). ^{13}C NMR (C_6D_6, 100.52 MHz): δ 23.2 ($\mathrm{CH}Me_2$), 25.4 ($\mathrm{CH}Me_2$), 31.0 ($C\mathrm{HMe_2}$), 123.1, 128.5, 128.7, 128.9, 140.7, 146.5, 148.1 149.9 (unsaturated carbon). IR (KBr, Nujol): 2080 (w, Ge−H), 1590 (w), 1570 (w), 1560 (w), 880 (w), 760 (s), 750 (s) cm^{-1}. (d) To solutions of **1** (0.150 g, 0.160 mmol) in *n*-hexane (50 mL) was added 1 or 3 equiv of H_2, and the mixtures were stirred overnight. Subsequently, the volatile materials were removed under reduced pressure, and the resulting mixtures were analyzed by ^{1}H NMR spectroscopy.
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