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Communication

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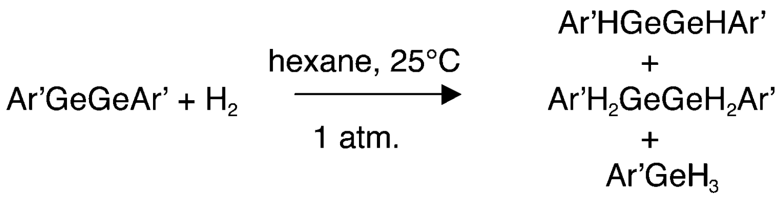

$$\mathrm{Ar'GeGeAr'} + \mathrm{H_2} \xrightarrow[\text{1 atm.}]{\text{hexane, 25°C}} \mathrm{Ar'HGeGeHAr'} + \mathrm{Ar'H_2GeGeH_2Ar'} + \mathrm{Ar'GeH_3}$$

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# Facile Activation of Dihydrogen by an Unsaturated Heavier Main Group Compound

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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.

$$\begin{aligned} \text{Ar}'\text{GeGeAr}'\ (\mathbf{1}) + 1\text{H}_2 \rightarrow\ & 60\%\ \text{Ar}'\text{GeGeAr}'\ (\mathbf{1}) \qquad (1)\\ & + 21\%\ \text{Ar}'\text{HGeGeHAr}'\ (\mathbf{2})\\ & + 10\%\ \text{Ar}'\text{H}_2\text{GeGeH}_2\text{Ar}'\ (\mathbf{3})\\ & + 9\%\ \text{Ar}'\text{GeH}_3\ (\mathbf{4}) \end{aligned}$$

$$\begin{aligned} \text{Ar}'\text{GeGeAr}'\ (\mathbf{1}) + 2\text{H}_2 \rightarrow\ & 2\%\ \text{Ar}'\text{HGeGeHAr}'\ (\mathbf{2}) \qquad (2)\\ & + 85\%\ \text{Ar}'\text{H}_2\text{GeGeH}_2\text{Ar}'\ (\mathbf{3})\\ & + 13\%\ \text{Ar}'\text{GeH}_3\ (\mathbf{4}) \end{aligned}$$

$$\begin{aligned} \text{Ar}'\text{GeGeAr}'\ (\mathbf{1}) + 3\text{H}_2 \rightarrow\ & 65\%\ \text{Ar}'\text{H}_2\text{GeGeH}_2\text{Ar}'\ (\mathbf{3}) \qquad (3)\\ & + 35\%\ \text{Ar}'\text{GeH}_3\ (\mathbf{4}) \end{aligned}$$

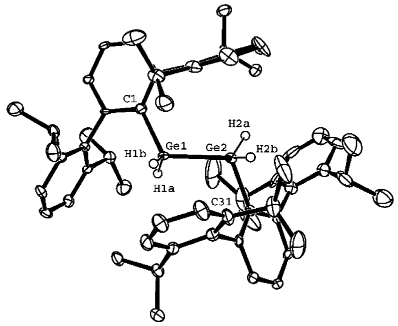

***Figure 1.*** Thermal ellipsoid (50%) drawing of **3**; H atoms (except Ge−H) are not shown. Selected bond lengths (Å) and angles (°): Ge−Ge (avg) 2.4019(10), Ge−Cipso range 1.962(5)−1.997(5), Ge−H (avg) 1.44(4); C−Ge−Ge range 109.85(14)−120.12(16).

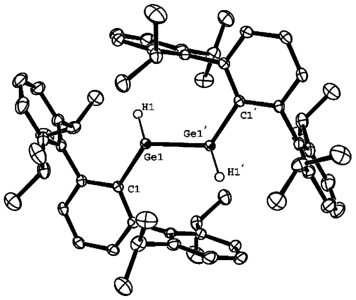

***Figure 2.*** Thermal ellipsoid (50%) drawing of **2**; H atoms (except Ge−H) are not shown. Selected bond lengths (Å) and angles (°): Ge1−Ge1′ 2.3026(3), Ge1−C1 1.9677(12), Ge−H 1.46(2); C1−Ge1−Ge1′ 121.93(4).

The 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′$H_2$GeGe$H_2$Ar′ (**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′Ge$H_3$ (**4**), which was synthesized independently by the reduction of Ar′Ge(OMe)$_3$ with LiAl$H_4$.[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. 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^F$$H_2$GeGe$H_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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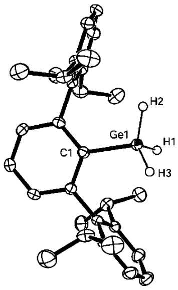

***Figure 3.*** Thermal ellipsoid (50%) drawing of **4**; H atoms (except Ge−H) are not shown. Selected bond lengths (Å): Ge−Cipso (avg) 1.979(2), Ge−H (avg) 1.445(10).

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 $^1H$ 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 $^1H$ 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 $H_2$ $\sigma$-bonding MO with the LUMO of Ar′GeGeAr′ (which is the $n_+$ combination)[17] to generate the digermene Ar′HGeGeHAr′ (**2**). The digermane $Ar'H_2GeGeH_2Ar'$ (**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 $Ar'Ge(\mu\text{-}H)_2GeAr'$. The possibility of the latter type of structure is supported by calculations[18] and by the isolation of the related tin compound $Ar^*Sn(\mu\text{-}H)_2SnAr^*$.[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 $Ar'GeH_3$ (**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. $^1H$ NMR ($C_6D_6$, 300.08 MHz): $\delta$ 1.03 (d, 24H, *J* = 6.9 Hz, CH*Me*$_2$), 1.16 (d, 24H, *J* = 6.9 Hz, CH*Me*$_2$), 2.74 (sept, 8H, *J* = 6.6 Hz, C*H*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): $\delta$ 24.2 (CH*Me*$_2$), 25.7 (CH*Me*$_2$), 31.0 (*C*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′ = $C_6H_3$-2, $6(C_6H_3\text{-}2,6\text{-}Pr^i{}_2)_2$, 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. $^1H$ NMR ($C_6D_6$, 300.08 MHz): $\delta$ 1.00 (d, 24H, *J* = 6.9 Hz, CH*Me*$_2$), 1.15 (d, 24H, *J* = 6.9 Hz, CH*Me*$_2$), 2.64 (sept, 8H, *J* = 6.6 Hz, C*H*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): $\delta$ 23.3 (CH*Me*$_2$), 25.9 (CH*Me*$_2$), 30.9 (*C*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 $LiAlH_4$ 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. $^1H$ NMR ($C_6D_6$, 300.08 MHz): $\delta$ 1.08 (d, 12H, *J* = 6.9 Hz, CH*Me*$_2$), 1.25 (d, 12H, *J* = 6.9 Hz, CH*Me*$_2$), 2.82 (sept, 4H, *J* = 6.6 Hz, C*H*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): $\delta$ 23.2 (CH*Me*$_2$), 25.4 (CH*Me*$_2$), 31.0 (*C*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 $^1H$ NMR spectroscopy.

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(11) Crystal data for **2**−**4** at 90(2) K with Mo Kα ($\lambda$ = 0.71073 Å). (a) **2**: monoclinic, space group $P2_1/n$, $a$ = 11.9597(11) Å, $b$ = 17.5129(15) Å, $c$ = 12.4578(11) Å, $\beta$ = 99.797(2)°, R1 = 0.0297 for 6932 ($I > 2\sigma(I)$) reflections, wR2 = 0.0797 (all data). (b) **3**: orthorhombic, space group $Pna2_1$, $a$ = 16.3425(11) Å, $b$ = 45.579(3) Å, $c$ = 21.2946 Å, R1 = 0.0622 for 24708 ($I > 2\sigma(I)$) reflections, wR2 = 0.1501 (all data). (c) **4**: orthorhombic, space group *Pbca*, $a$ = 15.3043(4) Å, $b$ = 25.3617(7) Å, $c$ = 27.7091(8) Å, R1 = 0.0431 for 8258 ($I > 2\sigma(I)$) reflections, wR2 = 0.1106 (all data).

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