

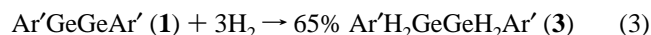
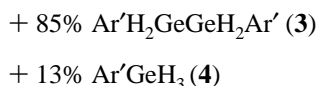
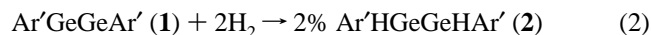
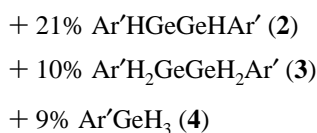
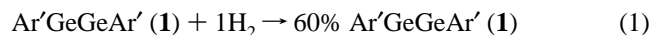
Facile Activation of Dihydrogen by an Unsaturated Heavier Main Group Compound

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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 H₂ 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 H₂ 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' = C₆H₃-2,6(C₆H₃-2,6-Prⁱ)₂),⁴ as well as related tin and lead species,^{5,6} and have shown that the “digermene” (**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, ΔH°_R ca. -250 kJ mol⁻¹, to give H₂GeGeH₂, which in turn displays a ΔH°_R of hydrogenation of ca. -150 kJ mol⁻¹ to afford H₃GeGeH₃.⁸ We now report that **1** reacts directly with H₂ in hexane at room temperature and atmospheric pressure to yield a mixture of a “digermene”, a digermene, and a primary germane.



The addition of 1, 2, or 3 equiv of H₂ 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 ¹H NMR spectroscopy in C₆D₆. The presence of three products was indicated by three different Ge–H signals in the ¹H NMR spectrum at 3.21, 3.58, and 5.87 ppm. For the reaction with 2 equiv of H₂ (eq 2) the intensity ratio 89:10:1 was observed. Recrystallization from a minimum volume of hexane afforded colorless crystals of the digermene Ar'H₂GeGeH₂Ar' (**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'GeH₃ (**4**), which was synthesized independently by the reduction of Ar'Ge(OMe)₃ with LiAlH₄.^{9c} The reactions of **1** with 1 or 3 equiv of H₂ also led to a mixture of products. For 1 equiv of H₂, the red color of **1** faded slightly over 24 h and a large portion of **1** (60%) was found to remain unreacted.

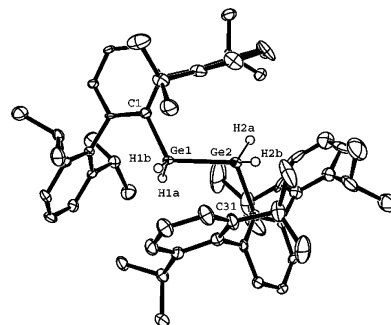


Figure 1. Thermal ellipsoid (50%) drawing of **3**; H atoms (except Ge–H) are not shown. Selected bond lengths (Å) and angles (°): Ge–Ge (avg) 2.4019(10), Ge–Cipso range 1.962(5)–1.997(5), Ge–H (avg) 1.44(4); C–Ge–Ge range 109.85(14)–120.12(16).

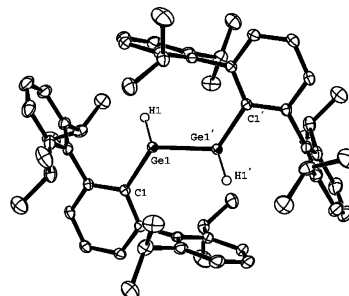


Figure 2. Thermal ellipsoid (50%) drawing of **2**; H atoms (except Ge–H) are not shown. Selected bond lengths (Å) and angles (°): Ge1–Ge1' 2.3026(3), Ge1–C1 1.9677(12), Ge–H 1.46(2); C1–Ge1–Ge1' 121.93(4).

The Ge–H resonances corresponding to **2**, **3**, and **4** were observed in the ¹H NMR spectrum in the intensity ratio 38:38:24. For the addition of 3 equiv of H₂, the color faded over 6 h and only compounds **3** and **4** were observed in the ¹H NMR spectrum in the product ratio 65:35 (eq 3).^{9d}

The digermene **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)°. These may be compared with those of the digermene Ar^FH₂GeGeH₂Ar^F (Ar^F = C₆F₅, Ge–Ge = 2.394(1) Å, C–Ge–Ge = 108.6(2)°).¹² The Ge–H signal in the ¹H 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^{*} = C₆H₃-2,6(C₆H₂-2,4,6-Prⁱ)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°. The IR

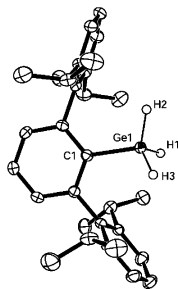


Figure 3. Thermal ellipsoid (50%) drawing of **4**; H atoms (except Ge–H) are not shown. Selected bond lengths (Å): Ge–Cipso (avg) 1.979(2), Ge–H (avg) 1.445(10).

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 digermene **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 $\text{Ar}'\text{GeGeAr}'$ 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 $\text{Ar}'\text{GeGeAr}'$ (which is the n^+ combination)¹⁷ to generate the digermene $\text{Ar}'\text{HGeGeHAr}'$ (**2**). The digermene $\text{Ar}'\text{H}_2\text{GeGeH}_2\text{Ar}'$ (**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 $:\text{GeHAr}'$ or the bridged isomer $\text{Ar}'\text{Ge}(\mu\text{-H})_2\text{GeAr}'$. The possibility of the latter type of structure is supported by calculations¹⁸ and by the isolation of the related tin compound $\text{Ar}^*\text{Sn}(\mu\text{-H})_2\text{SnAr}^*$.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 $\text{Ar}'\text{GeH}_3$ (**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.

Acknowledgment. We thank the National Science Foundation for support of this work.

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 $^\circ\text{C}$. ^1H NMR (C_6D_6 , 300.08 MHz): δ 1.03 (d, 24H, $J = 6.9$ Hz, CHMe_2), 1.16 (d, 24H, $J = 6.9$ Hz, CHMe_2), 2.74 (sept, 8H, $J = 6.6$ Hz, CHMe_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 (CHMe_2), 25.7 (CHMe_2), 31.0 (CHMe_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 $\text{Ar}'\text{GeGeAr}'$ (**1**, $\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6}(\text{C}_6\text{H}_5\text{-2,6-Pr}_2)_2$, 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 $^\circ\text{C}$. ^1H NMR (C_6D_6 , 300.08 MHz): δ 1.00 (d, 24H, $J = 6.9$ Hz, CHMe_2), 1.15 (d, 24H, $J = 6.9$ Hz, CHMe_2), 2.64 (sept, 8H, $J = 6.6$ Hz, CHMe_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 (CHMe_2), 25.9 (CHMe_2), 30.9 (CHMe_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 $\text{Ar}'\text{Ge}(\text{OMe})_3$ (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 $^\circ\text{C}$. ^1H NMR (C_6D_6 , 300.08 MHz): δ 1.08 (d, 12H, $J = 6.9$ Hz, CHMe_2), 1.25 (d, 12H, $J = 6.9$ Hz, CHMe_2), 2.82 (sept, 4H, $J = 6.6$ Hz, CHMe_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 (CHMe_2), 25.4 (CHMe_2), 31.0 (CHMe_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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JA053247A