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We report the synthesis of a trimetallic mixed-valence Ge(I)/Ge(II)/Ge(III) trihydride, which presents a structural novel motif among systems of the type (XMH)_n (M = group 14 metal). In terms of reactivity (Ar^{NiPr2})₂GeGe(Ar^{NiPr2})(H)Ge(Ar^{NiPr2})(H)₂ can act as a source of both the Ge(II) and Ge(IV) hydrides via Ge–H reductive elimination from the central metal centre involving two different regiochemistries.



Subvalent germanium hydrides (*i.e.* hydrides in formal metal oxidation states <4) have played a central role in establishing methodologies for bond activation and catalysis by main group compounds.¹ The digermene (Ar^{Dipp})₂Ge₂ reported by Power and co-workers in 2005 (where Ar^{Dipp} = 2,6-Dipp₂C₆H₃ and Dipp = 2,6-ⁱPr₂C₆H₃) offered the first example of facile main group dihydrogen activation, generating a mixture of hydride products (Ar^{Dipp}GeH₃, (Ar^{Dipp}GeH₂)₂ and (Ar^{Dipp}GeH)₂) depending on the reaction stoichiometry.² Orbital comparisons with transition metal complexes offered a rationale for initial H₂ activation occurring at one of the germanium centres in (Ar^{Dipp})₂Ge₂,³ and structural validation of this type of unsymmetrical Ge(I)/Ge(III) mixed-valence dihydride was subsequently obtained for {Ar*(Me₃Si)N}GeGe(H)₂{N(SiMe₃)Ar*} (where Ar* = 4-Me-2,6-(Ph₂CH)₂C₆H₂).⁴ Two-coordinate Ge(II) hydride systems can be accessed by employing an even greater degree of steric bulk, as in the case of (for example) {Ar*((^tBuO)₃Si)N}GeH,⁵ and concurrent access to a Ge–H bond and a vacant coordination site is thought to be important in related systems which act as very active catalysts for carbonyl hydroboration.⁶

In the presence of less sterically demanding X ligands, aggregation of [XGeH] monomers is common (Scheme 1); dimerization *via* Ge=Ge bond formation is prevalent for germanium (type II systems),^{2,4b,7} while H-bridged structures of the type XSn(μ-H)₂SnX are known for heavier tin congeners.^{7a,8,9}

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† Electronic supplementary information (ESI) available: Full synthetic/characterizing data[†] representative spectra; CIFs. CCDC 2242325–2242328. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3cc01411h>

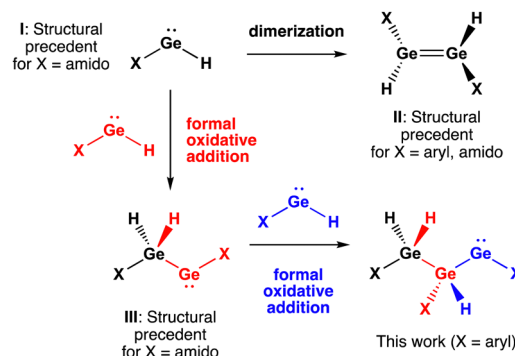
Redox flexibility in a germanium hydride manifold: hydrogen shuttling *via* oxidative addition and reductive elimination†

 Alexa Caise, Jamie Hicks,  Andreas Heilmann and Simon Aldridge *

Unsymmetrical Ge(I)/Ge(III) systems (type III) can also *formally* be regarded as a product assembled from two [XGeH] monomers *via* Ge–H oxidative addition at a Ge(II) centre.

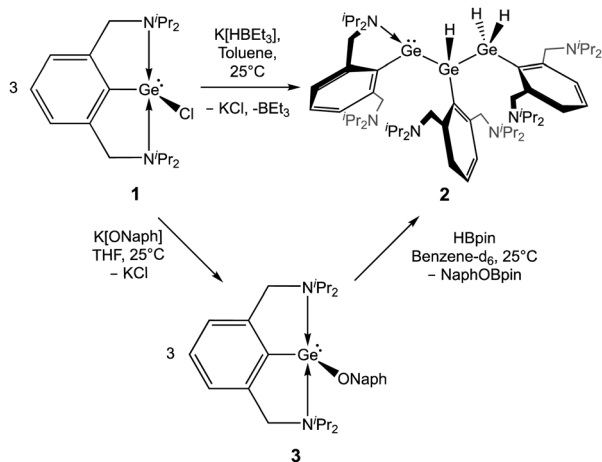
In recent work we have been interested in the use in low-valent group 14 chemistry of hemi-labile pincer ligands, 2,6-(R₂NCH₂)₂C₆H₃ (R = Et, ⁱPr), and have shown how these can be exploited to control catenation, and to effect reversible E–H bond activation and the reversible uptake of CO₂.¹⁰ Here we show that these supporting ligands can be used to support a novel mixed-valence variant of [XGeH]_n, in the form of a trimetallic aggregate of type (X)Ge–Ge(X)(H)–Ge(X)(H)₂. This system formally contains Ge(I), Ge(II) and Ge(III) centres, and, remarkably, can act as a source of both Ge(II) and Ge(IV) hydrides by reductive Ge–H elimination from the central metal centre with two different regio-chemistries. As such, it offers a demonstration of unprecedented redox flexibility within a germanium hydride manifold.

The reaction of Ar^{NiPr2}GeCl (1; Ar^{NiPr2} = 2,6-(ⁱPr₂NCH₂)₂-C₆H₃)^{10a} with K[HBET₃] in toluene at room temperature over a period of 3 h gives rise to a single new species, 2 (Scheme 2), characterized by ¹H and ¹³C NMR spectra indicating a low degree of molecular symmetry.‡ The ¹³C spectrum, for example, features four ⁱPr CH and eight ⁱPr CH₃ signals, together with



Scheme 1 Conceptual link between various isomeric forms of (putative) germanium(II) hydrides.





Scheme 2 Synthesis of trinuclear germanium hydride **2** from either Ge–Cl or Ge–O containing precursors *via* metathesis with B–H bonds.

four resonances due to the methylene carbons of the $-\text{CH}_2\text{N}$ tethers. By means of comparison, the corresponding ^{13}C spectrum at room temperature for ‘simple’ mononuclear species (such as **1** itself)^{10a} typically features one ^1Pr CH, two ^1Pr CH_3 and one $-\text{CH}_2\text{N}$ signals. In addition, the ^1H NMR spectrum of the product contains three signals (each integrating to 1H) assigned to germanium-bound hydrogen atoms, namely doublets at $\delta_{\text{H}} = 4.70$ and 4.88 (with coupling constants of 7.1 and 9.7 Hz, respectively) and a doublet of doublets at $\delta_{\text{H}} = 4.99$ ($J = 7.1, 9.7$ Hz). **2** can also be prepared from precursors containing Ge–O bonds *via* metathesis reactions with pinacolborane. Thus, reactions of the naphthoxide derivative $\text{Ar}^{\text{N}^i\text{Pr}_2}\text{Ge}(\text{ONaph}-1)$ (**3**) or the formate complex $\text{Ar}^{\text{N}^i\text{Pr}_2}\text{Ge}(\text{OC}(\text{O})\text{H})$ (**4**) with HBpin yield (1-NaphO)Bpin and HC(O)OBpin, respectively,¹¹ together with the same $\text{Ar}^{\text{N}^i\text{Pr}_2}\text{Ge}$ -containing species. The identity of the product was definitively established by a combination of elemental microanalysis, IR spectroscopy and X-ray crystallography (Fig. 1).

The solid-state structure shows **2** to be a trinuclear species, $(\text{Ar}^{\text{N}^i\text{Pr}_2})\text{GeGe}(\text{Ar}^{\text{N}^i\text{Pr}_2})(\text{H})\text{Ge}(\text{Ar}^{\text{N}^i\text{Pr}_2})(\text{H})_2$, featuring a chain of three metal atoms, two of which engage in no short contacts ($< 4 \text{ \AA}$) with the amine donors of the pendant ligand arms. The third germanium centre, Ge(1), is coordinated by a single amine donor, with the associated Ge–N distance (2.166(1) Å) being similar to those found for the terminal, N-donor ‘capped’ metal centres in di- or tetra-nuclear Ge(I) chains featuring the same (or related) pincer ligands.^{10a} The Ge(1)–Ge(2) separation (2.531(1) Å) is consistent with a relatively long single bond (*cf.* 2.5052(3) Å for the corresponding linkage in $(\text{Ar}^{\text{N}^i\text{Pr}_2}\text{Ge})_4$ and *ca.* 2.40 Å for the sum of the covalent radii.^{10a,12} The lack of coordinated amine arms at either Ge(2) or Ge(3) suggests the presence of metal-bound hydrogen atoms, and notwithstanding the uncertainties in the location of hydrogens by X-ray crystallography, the presence of two H atoms at Ge(3) and one at Ge(2) is consistent with (i) peaks located in the difference Fourier map; (ii) the presence of three Ge–H stretching bands (at 1981, 2003 and 2042 cm^{-1}) in the solid-state IR spectrum of **2**; and (iii) with the coupling patterns observed for the three germanium bound hydrogens in the ^1H NMR spectrum of **2**. A similar pattern of

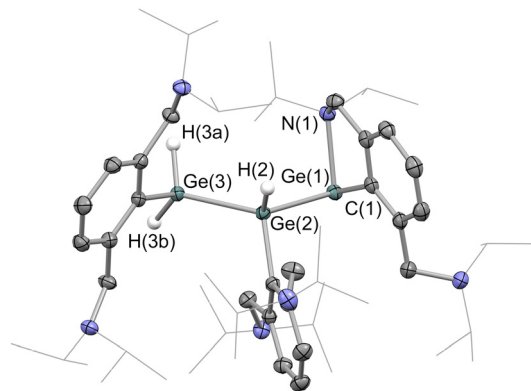


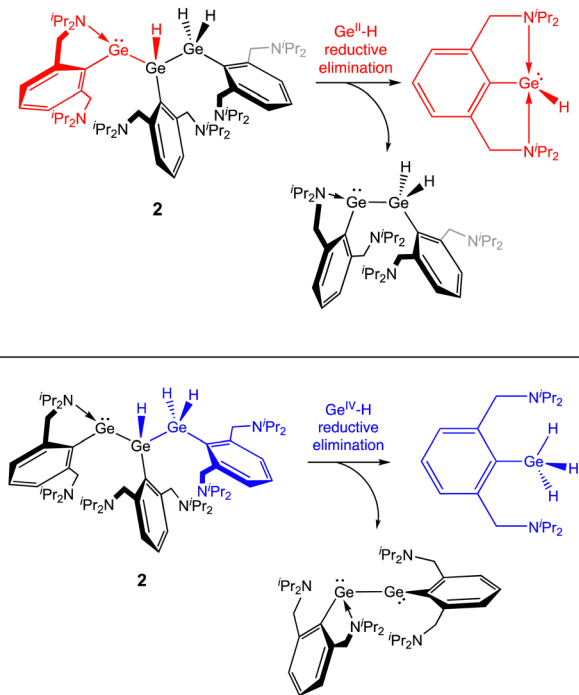
Fig. 1 Molecular structure of **2** in the solid state as determined by X-ray crystallography. ^1Pr groups shown in wireframe format and most hydrogen atoms omitted for clarity; thermal ellipsoids plotted at the 40% probability level. Key bond lengths (Å): Ge(1)–Ge(2) 2.531(1), Ge(2)–Ge(3) 2.433(1), Ge(1)–N(1) 2.166(1), Ge(1)–C(1) 1.996(1), Ge(2)–C(2) 1.991(2), Ge(3)–C(4) 1.973(1), Ge(2)–H(2) 1.45(2), Ge(3)–H 1.43(2), 1.47(2).

resonances (two doublets and a doublet of doublets) has been reported previously for $\{(\text{HCDippN})_2\text{B}\}\text{Ge}(\text{H})_2\text{Ge}(\text{H})\{\text{N}(\text{SiMe}_3)_2\}\{\text{B}(\text{NDippCH})_2\}$,¹² with the larger doublet splitting (9.7 Hz for **2**, *cf.* 12.0 Hz) being attributed to the geminal $^2J_{\text{HH}}$ coupling, and the smaller one (7.1 Hz for **2**, *cf.* 2.8 Hz) to the *trans* $^3J_{\text{HH}}$ coupling. The two compounds feature similar alignments of the Ge–H bonds across the Ge_2 unit in the solid state (**2**: H(2)–Ge(2)–Ge(3)–H torsion angles of 166.1, 77.2°, *cf.* 175.6 and 46.7°).¹³

Assignment of formal oxidation states to the metal centres in **2**, implies the presence of a central Ge(II) unit (labelled Ge(2)), flanked by Ge(I) and Ge(III) centres bearing zero and two hydrogen atoms, respectively (*i.e.* Ge(1) and Ge(3)). Such a description is also consistent with the shorter Ge(2)–Ge(3) distance (2.433(1) Å, *cf.* 2.531(1) Å for Ge(1)–Ge(2)), reflecting the smaller covalent radius associated with Ge(III) over Ge(I).

The structure of **2** represents a novel motif added to the family of known isomeric hydride systems of the type $(\text{XGeH})_n$ (X = aryl, amido *etc.*). In addition to monomeric and Ge=Ge bonded digermene Ge(II) systems (*e.g.* **I** and **II**, Scheme 1),^{2,4b,5,7,9} unsymmetrical Ge(I)/Ge(III) derivatives of the type $\text{XGeGe}(\text{H})_2\text{X}$ (III) have been postulated as key intermediates in the activation of H_2 by digermynes,³ and have been structurally characterized for X = $\text{N}(\text{SiMe}_3)\text{Ar}^*$.⁴ Conceptually, type III systems could be regarded as dimeric species, $(\text{XGeH})_2$, formed *via* formal oxidative addition of the Ge–H bond of one monomeric hydridogermylene to the germanium centre of another (Scheme 1). By extension, a subsequent Ge–H activation step at the unsaturated metal centre of the resulting (germyl)germylene could then generate a species akin to **2**, featuring a linear chain of three Ge centres. With this in mind – and given the *reversibility* demonstrated recently for E–H oxidative addition at related Sn centres^{10b} – we were interested to probe the scope for **2** to act as a source of monomeric germanium hydride species. Given the presence of both Ge(I) and Ge(III) centres in the terminal positions in **2**, we hypothesized that this system might act as a source of germanium hydride moieties in different formal oxidation states *via* Ge–H reductive elimination from

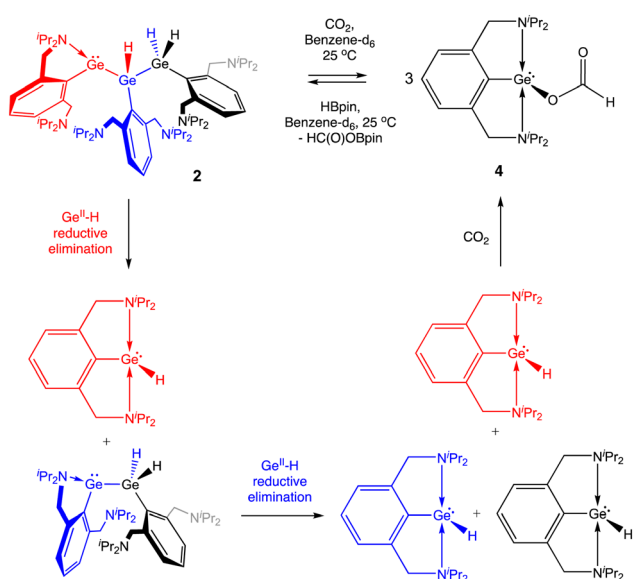




Scheme 3 Potential Ge–H reductive elimination processes leading to the cleavage of **2**.

the central metal centre occurring *via* different regio-chemistries (Scheme 3).

In the case of related tin(II) systems, it has been shown that reaction with CO₂ (to give a tin formate complex) offers a viable route for trapping hydride species of the type Ar^{NiPr₂}SnH.^{10b} With this in mind, we examined the reactivity of **2** towards CO₂, aiming to probe the viability of the trinuclear framework to act as a synthon for [Ar^{NiPr₂}GeH]. In the event, this reaction



Scheme 4 Chemically reversible cleavage of **2** into Ge(II) products by the insertion of CO₂ into Ge–H bonds.

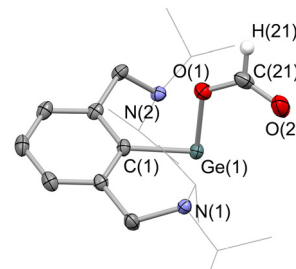


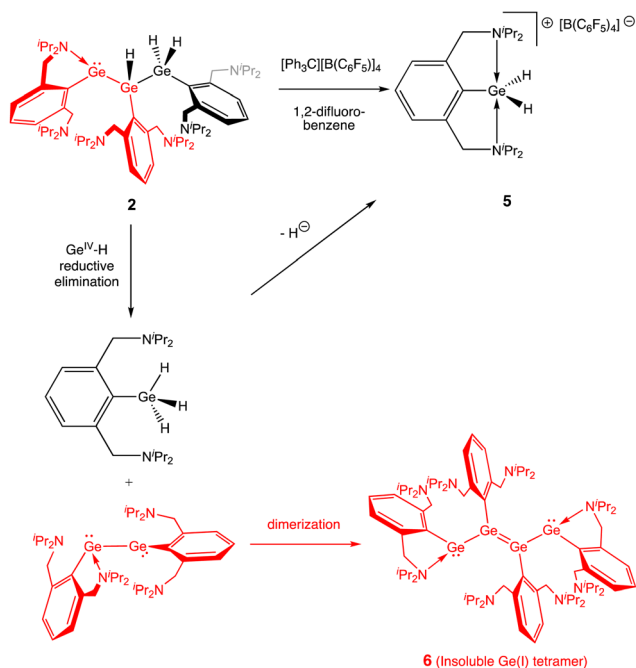
Fig. 2 Molecular structure of **4** in the solid state as determined by X-ray crystallography. ⁱPr groups shown in wireframe format and most hydrogen atoms omitted for clarity; thermal ellipsoids plotted at the 40% probability level. Key bond lengths (Å): Ge(1)–C(1) 1.993(2), Ge(1)–O(1) 1.952(1), O(1)–C(21) 1.273(2), C(21)–O(2) 1.223(3), Ge(1)–N(1) 2.341(1), 2.832(1).

proceeds rapidly and quantitatively at room temperature to generate the formate complex Ar^{NiPr₂}Ge{OC(O)H} (**4**; Scheme 4). The same compound can also be generated *via* the metathesis reaction between Ar^{NiPr₂}GeCl and K[O₂CH], and its molecular structure (and κ¹ coordination mode of the formate ligand) confirmed crystallographically (Fig. 2). Interestingly, while the formation of **4** in this way is consistent with the idea of **2** acting as the synthetic equivalent of three molecules of Ar^{NiPr₂}GeH, it is noteworthy that this reaction is chemically reversible, such that **4** can be re-converted into **2** (and HC(O)OBpin) by the action of pinacolborane.

Ge–H reductive elimination from **2** in the opposite sense to generate a Ge(IV) hydride species can also be demonstrated (Schemes 3 and 5). Thus, the reaction of **2** with the hydride abstraction agent [Ph₃C][B(C₆F₅)₄] in 1,2-difluorobenzene leads to precipitation of the insoluble Ge(I) tetramer (Ar^{NiPr₂}Ge)₄,^{10a} accompanied by the formation of the cation [Ar^{NiPr₂}GeH₂]⁺, as the [B(C₆F₅)₄][−] salt (**5**; Scheme 5). **5** has been characterized by standard spectroscopic methods and its structure in the solid state confirmed by X-ray crystallography (Fig. 3). The presence of two germanium-bound hydrogen atoms within an overall trigonal bipyramidal metal coordination environment is implied by the presence of (i) a single resonance (integrating to 2H) in the ¹H NMR spectrum at δ_H = 5.92 ppm and (ii) bands due to Ge–H stretching modes at 2162 and 2179 cm^{−1} in the IR spectrum of solid **5**. The bond lengths associated with the germanium centre (*d*(Ge(1)–C(1)) = 1.895(2) Å, Ge(1)–N(1) 2.263(2), 2.272(1) Å) are somewhat shorter than those found in (for example) **1**, presumably reflecting the smaller size and greater Lewis acidity of Ge(IV) over Ge(II), and the effect of the overall cationic charge.

In conclusion, we report the synthesis of a trimetallic mixed-valence Ge(I)/Ge(II)/Ge(III) trihydride, the structure of which represents a novel motif among systems of the type (XMH)_n (M = group 14 metal). (Ar^{NiPr₂}GeGe(Ar^{NiPr₂})(H)Ge(Ar^{NiPr₂})(H)₂ (**2**) can be viewed conceptually as being formed from monomeric [(Ar^{NiPr₂}GeH)] units by successive Ge–H oxidative addition processes occurring at Ge(II), *via* the intermediacy of the (germyl)germylene, (Ar^{NiPr₂}GeGe(Ar^{NiPr₂})(H)₂. Consistent with this idea, **2** can act as a source of the [(Ar^{NiPr₂}GeH)] fragment in reactions with CO₂ (generating the formate Ar^{NiPr₂}Ge{OC(O)H}, **4**,





Scheme 5 Cleavage of **2** leading to the formation of a Ge(IV) dihydride cation via reaction with [Ph₃C][B(C₆F₅)₄].

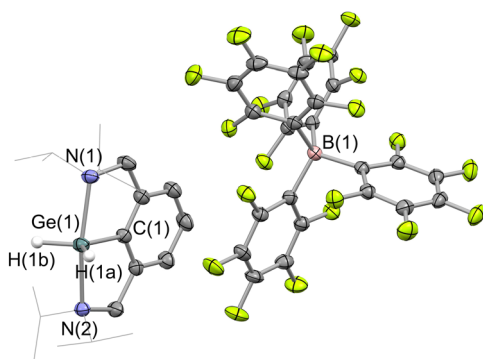


Fig. 3 Molecular structure of **5** in the solid state as determined by X-ray crystallography. ⁱPr groups shown in wireframe format and solvent molecule/most hydrogen atoms omitted for clarity; thermal ellipsoids plotted at the 40% probability level. Key bond lengths (Å): Ge(1)–C(1) 1.895(2), Ge(1)–H(1a) 1.46(2), 1.49(2), Ge(1)–N(1) 2.263(2), 2.272(1).

and **4** can be re-converted back into **2** via Ge–O/B–H metathesis with pinacolborane. On the other hand, Ge–H reductive elimination from **2** occurring with a different regiochemistry can be used as a source of the Ge(IV) hydride (Ar^{NiPr₂})GeH₃, which undergoes hydride abstraction with [Ph₃C][B(C₆F₅)₄] to generate the trigonal bipyramidal cation [Ar^{NiPr₂}GeH₂]⁺. The chemically reversible and regiochemically flexible nature of this Ge–H activation chemistry

therefore facilitates unprecedented redox flexibility within a germanium hydride manifold.

AC carried out the synthetic experiments and spectroscopic characterization of new compounds; AH and JH carried out the crystallographic measurements; SA managed the project and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Synthetic and characterizing data for new compounds can be found in the ESI.† Crystallographic data for compounds **2**, **3**, **4** and **5** can be obtained from the CCDC (citing reference numbers 2242325–2242328).

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