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

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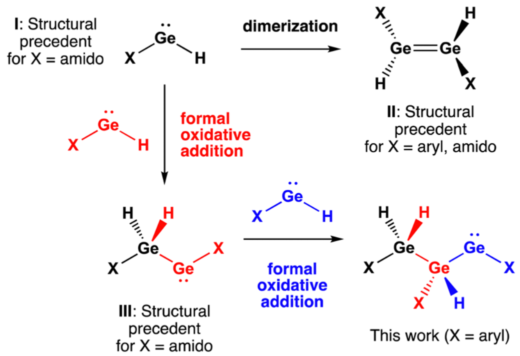
We report the synthesis of a trimetallic mixed-valence Ge(I)/Ge(II)/Ge(III) trihydride, which presents a structural novel motif among systems of the type $(XMH)_n$ (M = group 14 metal). In terms of reactivity $(Ar^{NiPr2})GeGe(Ar^{NiPr2})(H)Ge(Ar^{NiPr2})(H)_2$ can act as a source of both the Ge(II) 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 digermyne $(Ar^{Dipp}Ge)_2$ reported by Power and co-workers in 2005 (where Ar^{Dipp} = 2,6-$Dipp_2C_6H_3$ and Dipp = 2,6-$^iPr_2C_6H_3$) offered the first example of facile main group dihydrogen activation, generating a mixture of hydride products ($Ar^{Dipp}GeH_3$, $(Ar^{Dipp}GeH_2)_2$ and $(Ar^{Dipp}GeH)_2$) depending on the reaction stoichiometry.[2] Orbital comparisons with transition metal complexes offered a rationale for initial H_2 activation occurring at one of the germanium centres in $(Ar^{Dipp}Ge)_2$,[3] and structural validation of this type of unsymmetrical Ge(I)/Ge(III) mixed-valence dihydride was subsequently obtained for $\{Ar^*(Me_3Si)N\}Ge$-$Ge(H)_2\{N(SiMe_3)Ar^*\}$ (where Ar* = 4-Me-2,6-$(Ph_2CH)_2C_6H_2$).[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 $XSn(\mu\text{-}H)_2SnX$ are known for heavier tin congeners.[7a,8,9] 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-$(R_2NCH_2)_2C_6H_3$ (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 CO_2.[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-$(^iPr_2NCH_2)_2$-C_6H_3)[10a] with $K[HBEt_3]$ 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 ^{13}C NMR spectra indicating a low degree of molecular symmetry.‡ The ^{13}C spectrum, for example, features four ^iPr CH and eight ^iPr CH_3 signals, together with



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

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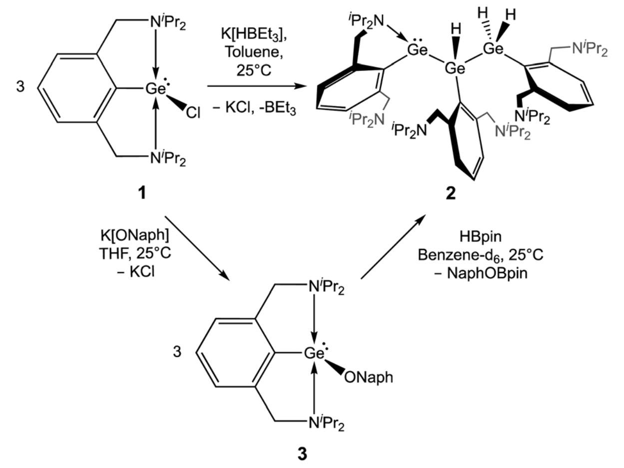


Scheme 2 Synthesis of trinuclear germanium hydride **2** from either Ge–Cl or Ge–O containing precursors *via* metathesis with B–H bonds.

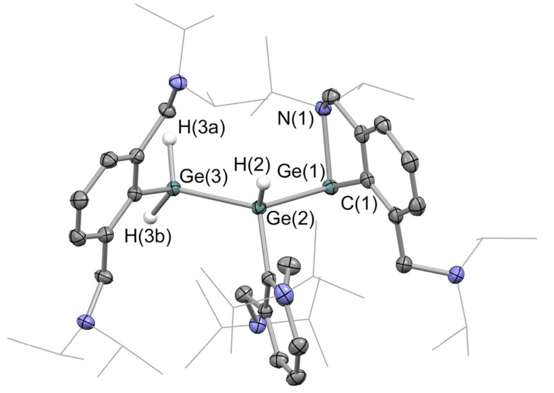


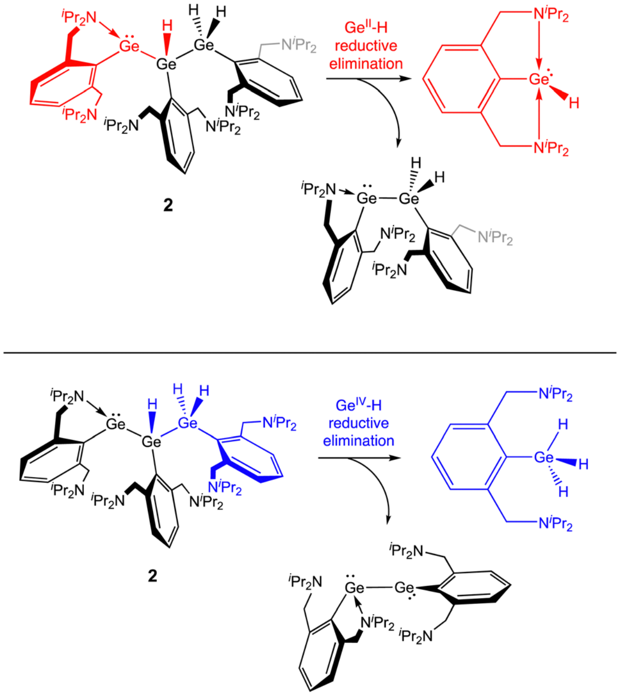
Fig. 1 Molecular structure of **2** in the solid state as determined by X-ray crystallography. ^{i}Pr groups shown in wireframe format and most hydrogen atoms omitted for clarity; thermal ellipsoids plotted at the 40% probability level. Key bond lengths (Å): Ge(1)–Ge(2) 2.531(1), Ge(2)–Ge(3) 2.433(1), Ge(1)–N(1) 2.166(1), Ge(1)–C(1) 1.996(1), Ge(2)–C(21) 1.991(2), Ge(3)–C(41) 1.973(1), Ge(2)–H(2) 1.45(2), Ge(3)–H 1.43(2), 1.47(2).

four resonances due to the methylene carbons of the –CH_2N 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 ^{i}Pr CH, two ^{i}Pr CH_3 and one –CH_2N 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 δ_H = 4.70 and 4.88 (with coupling constants of 7.1 and 9.7 Hz, respectively) and a doublet of doublets at δ_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 $\mathrm{Ar}^{\mathrm{NiPr2}}$Ge(ONaph-1) (**3**) or the formate complex $\mathrm{Ar}^{\mathrm{NiPr2}}$Ge(OC(O)H) (**4**) with HBpin yield (1-NaphO)Bpin and HC(O)OBpin, respectively,[11] together with the same $\mathrm{Ar}^{\mathrm{NiPr2}}$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, $(\mathrm{Ar}^{\mathrm{NiPr2}})\mathrm{GeGe}(\mathrm{Ar}^{\mathrm{NiPr2}})(\mathrm{H})\mathrm{Ge}(\mathrm{Ar}^{\mathrm{NiPr2}})(\mathrm{H})_2$, featuring a chain of three metal atoms, two of which engage in no short contacts (< 4 Å) 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 $(\mathrm{Ar}^{\mathrm{NiPr2}}\mathrm{Ge})_4$ 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 resonances (two doublets and a doublet of doublets) has been reported previously for $\{(\mathrm{HCDippN})_2\mathrm{B}\}\mathrm{Ge}(\mathrm{H})_2\mathrm{Ge}(\mathrm{H})\{\mathrm{N}(\mathrm{SiMe}_3)_2\}\{\mathrm{B}(\mathrm{NDippCH})_2\}$,[12] with the larger doublet splitting (9.7 Hz for **2**, *cf.* 12.0 Hz) being attributed to the geminal $^2J_{HH}$ coupling, and the smaller one (7.1 Hz for **2**, *cf.* 2.8 Hz) to the *trans* $^3J_{HH}$ 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 as 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).

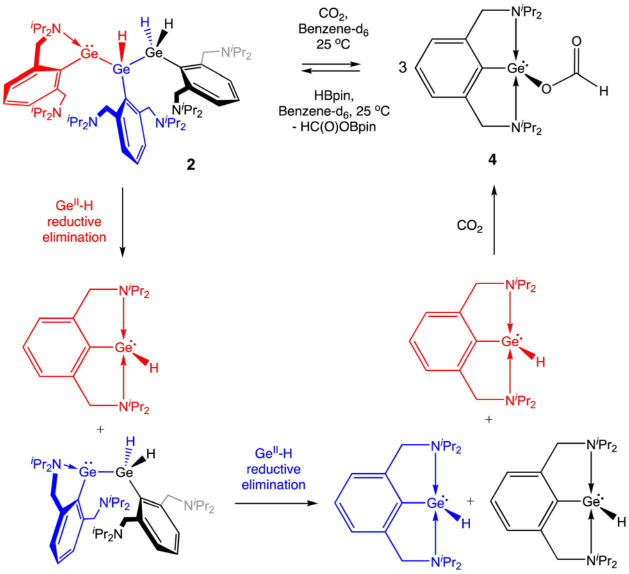
The structure of **2** represents a novel motif added to the family of known isomeric hydride systems of the type $(\mathrm{XGeH})_n$ (X = aryl, amido *etc.*). In addition to monomeric and Ge═Ge bonded digermene Ge(II) systems (*e.g.* **I** and **II**, Scheme 1),[2,4b,5,7,9] unsymmetrical Ge(I)/Ge(III) derivatives of the type $\mathrm{XGeGe}(\mathrm{H})_2\mathrm{X}$ (**III**) have been postulated as key intermediates in the activation of H_2 by digermynes,[3] and have been structurally characterized for X = $\mathrm{N}(\mathrm{SiMe}_3)\mathrm{Ar}^\star$.[4] Conceptually, type **III** systems could be regarded as dimeric species, $(\mathrm{XGeH})_2$, 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 CO_2 (to give a tin formate complex) offers a viable route for trapping hydride species of the type Ar$^{\mathrm{NiPr2}}$SnH.[10b] With this in mind, we examined the reactivity of **2** towards CO_2, aiming to probe the viability of the trinuclear framework to act as a synthon for [Ar$^{\mathrm{NiPr2}}$GeH]. In the event, this reaction proceeds rapidly and quantitatively at room temperature to generate the formate complex Ar$^{\mathrm{NiPr2}}$Ge{OC(O)H} (**4**; Scheme 4). The same compound can also be generated *via* the metathesis reaction between Ar$^{\mathrm{NiPr2}}$GeCl and K[O_2CH], and its molecular structure (and κ^1 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$^{\mathrm{NiPr2}}$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.



Scheme 4 Chemically reversible cleavage of **2** into Ge(II) products by the insertion of CO_2 into Ge–H bonds.

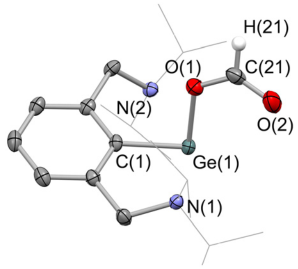
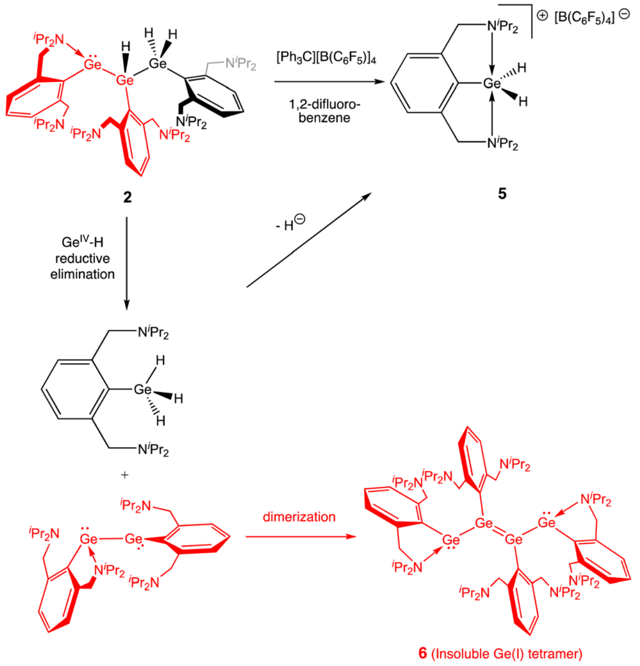


Fig. 2 Molecular structure of **4** in the solid state as determined by X-ray crystallography. ^{i}Pr groups shown in wireframe format and most hydrogen atoms omitted for clarity; thermal ellipsoids plotted at the 40% probability level. Key bond lengths (Å): Ge(1)–C(1) 1.993(2), Ge(1)–O(1) 1.952(1),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

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 [Ph_3C][$B(C_6F_5)_4$] in 1,2-difluorobenzene leads to precipitation of the insoluble Ge(I) tetramer (Ar$^{\mathrm{NiPr2}}$Ge)$_4$,[10a] accompanied by the formation of the cation [Ar$^{\mathrm{NiPr2}}$GeH$_2$]$^+$, as the [$B(C_6F_5)_4$]$^-$ 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 ^{1}H NMR spectrum at $\delta_H = 5.92$ 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 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$^{\mathrm{NiPr2}}$)GeGe(Ar$^{\mathrm{NiPr2}}$)(H)Ge(Ar$^{\mathrm{NiPr2}}$)(H)$_2$ (**2**) can be viewed conceptually as being formed from monomeric [(Ar$^{\mathrm{NiPr2}}$)GeH] units by successive Ge–H oxidative addition processes occurring at Ge(II), *via* the intermediacy of the (germyl)germylene, (Ar$^{\mathrm{NiPr2}}$)GeGe(Ar$^{\mathrm{NiPr2}}$)(H)$_2$. Consistent with this idea, **2** can act as a source of the [(Ar$^{\mathrm{NiPr2}}$)GeH] fragment in reactions with CO_2 (generating the formate Ar$^{\mathrm{NiPr2}}$Ge{OC(O)H}, **4**),



Scheme 5 Cleavage of **2** leading to the formation of a Ge(IV) dihydride cation *via* reaction with $[Ph_3C][B(C_6F_5)_4]$.

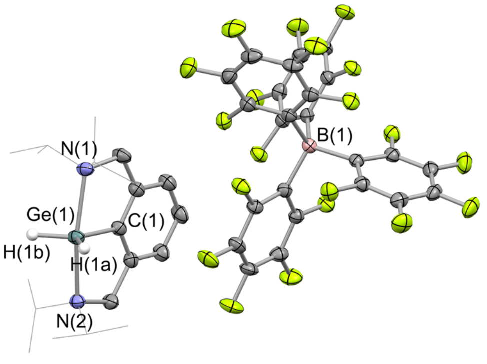


Fig. 3 Molecular structure of **5** in the solid state as determined by X-ray crystallography. ^{i}Pr groups shown in wireframe format and solvent molecule/most hydrogen atoms omitted for clarity; thermal ellipsoids plotted at the 40% probability level. Key bond lengths (Å): Ge(1)–C(1) 1.895(2), Ge(1)–H 1.46(2), 1.49(2), Ge(1)–N 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 $(Ar^{NiPr2})GeH_3$, which undergoes hydride abstraction with $[Ph_3C][B(C_6F_5)_4]$ to generate the trigonal bipyramidal cation $[Ar^{NiPr2}GeH_2]^+$. 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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