ChemComm

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2023, **59**, 7251

Received 22nd March 2023,
Accepted 16th May 2023

DOI: 10.1039/d3cc01411h

rsc.li/chemcomm

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

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

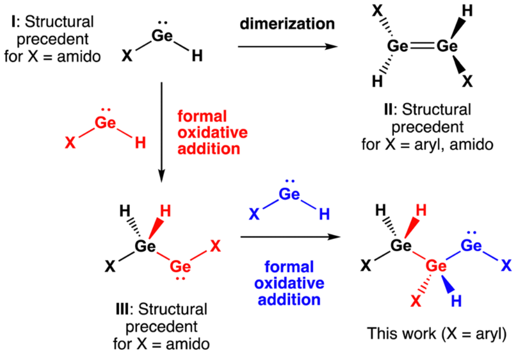
We report the synthesis of a trimetallic mixed-valence Ge(I)/Ge(II)/Ge(III) trihydride, which presents a structural novel motif among systems of the type $(XMH)_n$ (M = group 14 metal). In terms of reactivity $(Ar^{NiPr2})GeGe(Ar^{NiPr2})(H)Ge(Ar^{NiPr2})(H)_2$ can act as a source of both the Ge(II) 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 $\{Ar^*(Me_3Si)N\}Ge\text{-}Ge(H)_2\{N(SiMe_3)Ar^*\}$ (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, ^{i}Pr), 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.

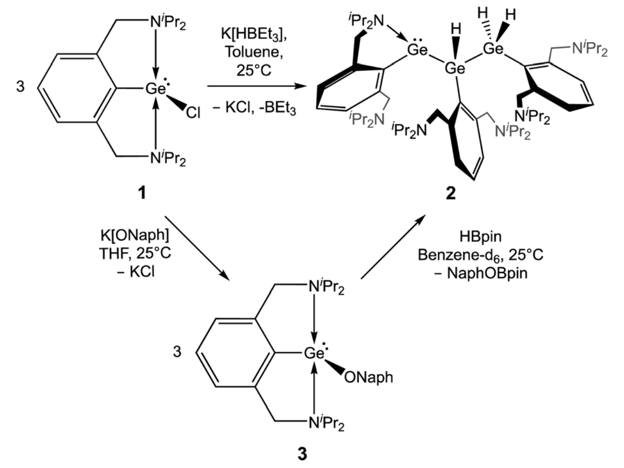
The reaction of $Ar^{NiPr2}GeCl$ (**1**; Ar^{NiPr2} = 2,6-$(^iPr_2NCH_2)_2$-C_6H_3)[10a] with $K[HBEt_3]$ in toluene at room temperature over a period of 3 h gives rise to a single new species, **2** (Scheme 2), characterized by ^1H and ^{13}C NMR spectra indicating a low degree of molecular symmetry.‡ The ^{13}C spectrum, for example, features four ^{i}Pr CH and eight ^{i}Pr CH_3 signals, together with



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

Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK. E-mail: simon.aldridge@chem.ox.ac.uk

† Electronic supplementary information (ESI) available: Full synthetic/characterizing date' 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**



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

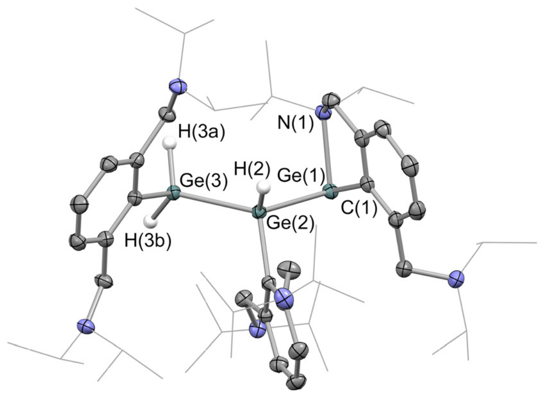


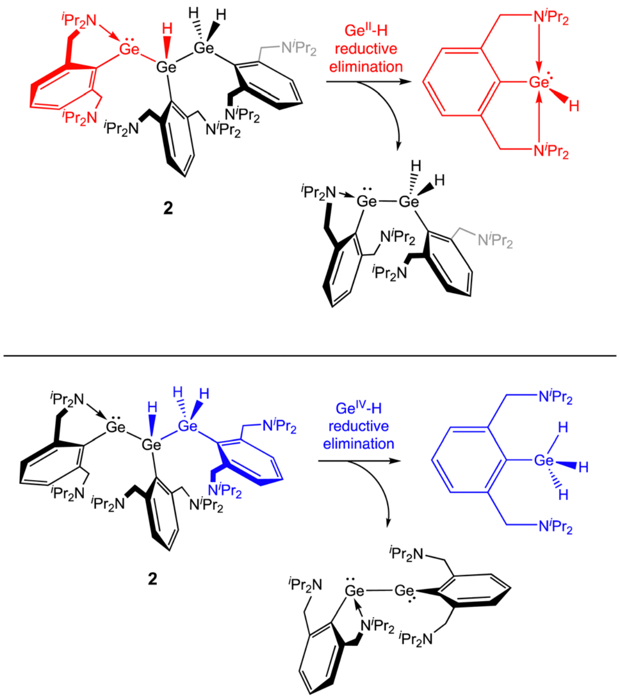
Fig. 1 Molecular structure of **2** in the solid state as determined by X-ray crystallography. ^{i}Pr groups shown in wireframe format and most hydrogen atoms omitted for clarity; thermal ellipsoids plotted at the 40% probability level. Key bond lengths (Å): Ge(1)–Ge(2) 2.531(1), Ge(2)–Ge(3) 2.433(1), 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 $Ar^{NiPr2}Ge(ONaph\text{-}1)$ (**3**) or the formate complex $Ar^{NiPr2}Ge(OC(O)H)$ (**4**) with HBpin yield (1-NaphO)Bpin and HC(O)OBpin, respectively,[11] together with the same Ar^{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, $(Ar^{NiPr2})GeGe(Ar^{NiPr2})(H)Ge(Ar^{NiPr2})(H)_2$, 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 $(Ar^{NiPr2}Ge)_4$ 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 $\{(HCDippN)_2B\}Ge(H)_2Ge(H)\{N(SiMe_3)_2\}\{B(NDippCH)_2\}$,[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).

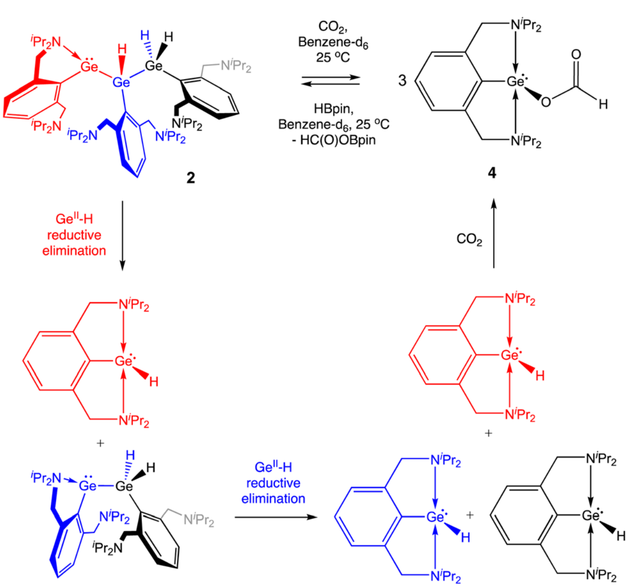
The structure of **2** represents a novel motif added to the family of known isomeric hydride systems of the type $(XGeH)_n$ (X = aryl, amido *etc.*). In addition to monomeric and Ge=Ge bonded digermene Ge(II) systems (*e.g.* **I** and **II**, Scheme 1),[2,4b,5,7,9] unsymmetrical Ge(I)/Ge(III) derivatives of the type $XGeGe(H)_2X$ (**III**) have been postulated as key intermediates in the activation of H_2 by digermynes,[3] and have been structurally characterized for X = $N(SiMe_3)Ar^*$.[4] Conceptually, type **III** systems could be regarded as dimeric species, $(XGeH)_2$, 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^{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^{NiPr2}GeH]. In the event, this reaction 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[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^{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.

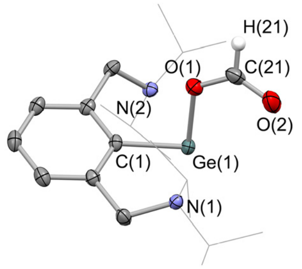
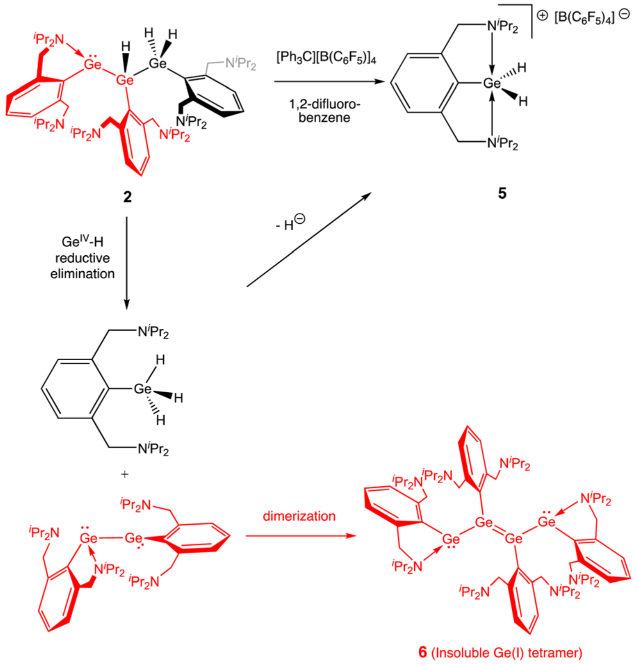


Fig. 2 Molecular structure of **4** in the solid state as determined by X-ray crystallography. ^{i}Pr groups shown in wireframe format and most hydrogen atoms omitted for clarity; thermal ellipsoids plotted at the 40% probability level. Key bond lengths (Å): Ge(1)–C(1) 1.993(2), Ge(1)–O(1) 1.952(1), 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^{NiPr2}Ge)$_4$,[10a] accompanied by the formation of the cation [Ar^{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^{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 CO_2 (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 $[Ph_3C][B(C_6F_5)_4]$.

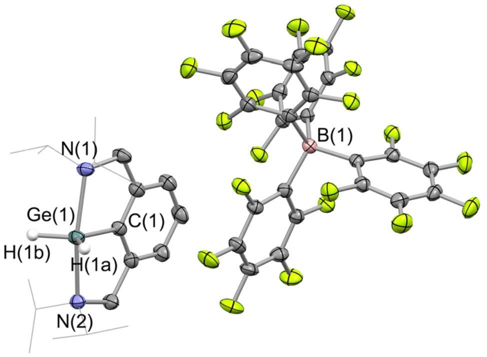


Fig. 3 Molecular structure of **5** in the solid state as determined by X-ray crystallography. ^{i}Pr groups shown in wireframe format and solvent molecule/most hydrogen atoms omitted for clarity; thermal ellipsoids plotted at the 40% probability level. Key bond lengths (Å): Ge(1)–C(1) 1.895(2), Ge(1)–H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

1 For a recent review of main group hydride chemistry, see: M. M. D. Roy, A. A. Omaña, A. S. S. Wilson, M. S. Hill, S. Aldridge and E. Rivard, *Chem. Rev.*, 2021, **121**, 12784–12965.

2 G. H. Spikes, J. C. Fettinger and P. P. Power, *J. Am. Chem. Soc.*, 2005, **127**, 12232–12233.

3 P. P. Power, *Nature*, 2010, **463**, 171–177.

4 (*a*) J. Li, C. Schenk, C. Goedecke, G. Frenking and C. Jones, *J. Am. Chem. Soc.*, 2011, **133**, 18622–18625. For a related system formed in the presence of a Lewis base, see: (*b*) A. F. Richards, A. D. Phillips, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2003, **125**, 3204–3205.

5 T. J. Hadlington, B. Schwarze, E. I. Izgorodina and C. Jones, *Chem. Commun.*, 2015, **51**, 6854–6857.

6 T. J. Hadlington, M. Hermann, G. Frenking and C. Jones, *J. Am. Chem. Soc.*, 2014, **136**, 3028–3031.

7 (*a*) T. J. Hadlington, M. Hermann, J. Li, G. Frenking and C. Jones, *Angew. Chem., Int. Ed.*, 2013, **52**, 10199–10203; (*b*) J. A. Kelly, M. Juckel, T. J. Hadlington, I. Fernández, G. Frenking and C. Jones, *Chem. – Eur. J.*, 2019, **25**, 2773–2785.

8 (*a*) E. Rivard, R. C. Fischer, R. Wolf, Y. Peng, W. A. Merrill, N. D. Schley, Z. Zhu, L. Pu, J. C. Fettinger, S. J. Teat, I. Nowik, R. H. Herber, N. Takagi, S. Nagase and P. P. Power, *J. Am. Chem. Soc.*, 2007, **129**, 16197–16208; (*b*) Y. Peng, B. D. Ellis, X. Wang and P. P. Power, *J. Am. Chem. Soc.*, 2008, **130**, 12268–12269.

9 For a more wide-ranging theoretical discussion of M(II) hydrides of Ge and Sn see: G. Trinquier, *J. Am. Chem. Soc.*, 1990, **112**, 2130–2137.

10 (*a*) A. Caise, L. P. Griffin, A. Heilmann, C. McManus, J. Campos and S. Aldridge, *Angew. Chem., Int. Ed.*, 2021, **60**, 15606–15612; (*b*) A. Caise, A. E. Crumpton, P. Vasko, J. Hicks, C. McManus, N. H. Rees and S. Aldridge, *Angew. Chem., Int. Ed.*, 2022, **61**, e202114926; (*c*) A. Caise, L. P. Griffin, A. Heilmann, C. McManus, J. Campos and S. Aldridge, *Angew. Chem., Int. Ed.*, 2022, **61**, e202117496. For examples of the chemistry of related ligands see: (*d*) R. Jambor, B. Kašná, K. N. Kirschner, M. Schürmann and K. Jurkschat, *Angew. Chem., Int. Ed.*, 2008, **47**, 1650–1653; (*e*) M. Novák, M. Bouška, L. Dostál, A. Růžička, A. Hoffmann, S. Herres-Pawlis and R. Jambor, *Chem. – Eur. J.*, 2015, **21**, 7820–7829; (*f*) M. Novák, L. Dostál, Z. Růžičková, S. Mebs, J. Beckmann and R. Jambor, *Organometallics*, 2019, **38**, 2403–2407.

11 (*a*) C. Bibal, S. Mazières, H. Gornitzka and C. Couret, *Polyhedron*, 2002, **21**, 2827–2834; (*b*) E. A. Romero, J. L. Peltier, R. Jazzar and G. Bertrand, *Chem. Commun.*, 2016, **52**, 10563–10565.

12 B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán and S. Alvarez, *Dalton Trans.*, 2008, 2832–2838.

13 M. Usher, A. V. Protchenko, A. Rit, J. Campos, E. Kolychev, R. Tirfoin and S. Aldridge, *Chem. – Eur. J.*, 2016, **22**, 11685–11698.