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COMMUNICATION

Ge^{II}-H/Si^{IV}-H dehydrocoupling and cycloaddition chemistry of a Ni⁰ bis(hydrido-germylene) complexEmeric Schubert,^a and Terrance J. Hadlington^{a,*}Received 00th January 20xx,
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We report the high-yielding synthesis of bis(hydrido-germylene) complex of Ni⁰ (**2**). In contrast to known hydrido-tetrylene chemistry, this complex demonstrates a unique Ge^{II}-H/Si^{IV}-H dehydrocoupling reaction, in formation of an η³-[Ge₂Si]-Ni complex. On reaction with ethylene, the formal [2+2] cycloaddition across the non-bonded [Ge₂] unit in **2** is observed, forming a heavier metallacyclopentane derivative. These results give new insights into novel E-E bondforming processes, and the effect of metal-coordination on the reactivity of E^{II}-H bonds (E = Si-Pb).

Transition metal (TM) π-complexes are firmly established as key reactive species in organic synthesis.^{1,2} Access is typically achieved by the addition of a π-bonded organyl to a TM synthon – for example, the first well-defined allyl-metal complex, reported in 1959 by Smidt and Hafner,³ was generated through reaction of allyl alcohol with PdCl₂ (Fig 1., **A**). Jointly with the discovery of so-called sandwich complexes and metal-carbene complexes,^{4,5,6,7} this marked an important era in organometallics. Naturally, chemists have since sought heavier derivatives of such π-complexes, whereby carbon centres are substituted either partially or wholly for sub-carbon group 14 elements.⁸ In line with the more recent discovery of *p*-block element congeners to those classic carbon π-systems (e.g. alkenes,^{9,10} alkynes,¹¹ cyclopentadiene¹²) starting in the early 80s, known examples of heavier π-complexes are far outnumbered by carbon derivatives. In part due to the lack of fitting building-blocks, systems bearing η³-E₃ units (E = Si-Pb) are rare (Fig. 1, **B-E**). These and closely related reported compounds (i.e. featuring at least three low-valent heavier group 14 elements coordinating a transition metal (TM)) are heavier Cp,^{13,14,15,16,17,18} cyclobutadiene,^{19,20,21,22} cyclopropene,^{23,24} and

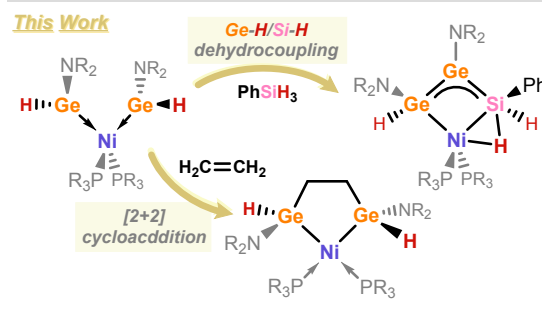
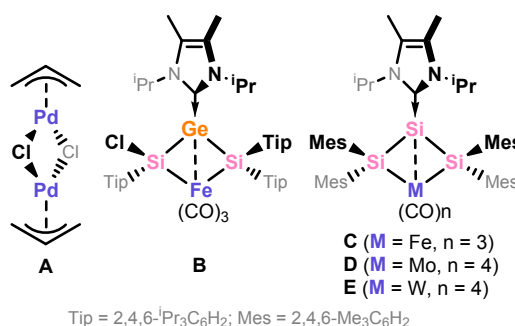


Figure 1. The first well-defined π-allyl-complex, **A**, complexes with Zwitterionic resonance structures akin to allyl-complexes, **B-E**, and a simplified schematic of the complexes and reactivity reported herein.

E-carbene-bound tri(tetrel)allene (E = Ge, Si; Fig 1., **B-E**) complexes.^{25,26} This latter compound class, reported by the groups of Scheschewiz and Lips, is synthesised through coordination of silagermavinylidene and trisilacyclopropylidene analogues, respectively, with TM carbonyl fragments, presumed to form complexes **B-E** via initial κ¹-coordination.^{25,26} Indeed, if one considers resonance forms involving formal C^{NHC}-E covalent bonds, one may describe these as heavier allyl complexes.

In our work, we are interested in the reactivity of TM-bound tetrylene species, with respect to the altered reactivity of the tetrylene-X bond (e.g. X = Cl, Ar, H). This has allowed, for example, σ-metathesis of Ge-X bonds (X = H, OH, NH₂, Cl) with

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oxonium (*i.e.* $[(Et_2O)_2H]^+$) and NH_3 .^{27,28} We sought to approach related chemistry with *hydridic* substrates, *e.g.*, silanes, whereby E_3 -moieties ($E = Ge, Si$) would result. These may stand as fitting starting points for heavy-allyl complexes. Herein we describe a novel form of reactivity at the tetrylene-TM interface, involving a bis(hydridogermylene)-Ni⁰ complex. Reactivity with $PhSiH_3$ proceeds through the formal hetero-dehydrocoupling of Ge^{II} -H and Si^{IV} -H bonds, in the formation of an η^3 - $[Ge_2Si]$ -Ni complex. Divergent reactivity with ethylene, leading to a formal [2+2] cycloaddition, demonstrates no involvement of the Ge-H bond(s); these observations contrast with known Ge^{II} -H chemistry, which may be expected to (a) oxidatively cleave the Si-H bond, and (b) insert into unsaturated C-C bonds. This gives new insights into the effect of TM-coordination on tetrylene-centred chemistry, and opens new methods for constructing E_n units ($E = C-Ge; n > 2$) in the TM coordination sphere.

The starting point for this work was the bis(hydridogermylene)nickel(0) complex $[^{Ph}L(H)Ge]_2Ni$ (**2**; $^{Ph}L = \{[Ph_2PCH_2Si(iPr)_2](Dip)N\}$; Dip = 2,6- $iPr_2C_6H_3$). The direct addition of two equiv. of our previously reported hydridogermylene **1** (*viz.* $^{Ph}L(H)Ge$)²⁹ to $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) leads to the formation of deep red solutions (Fig. 2(a)), from the respectively colourless and pale yellow starting materials. $^{31}P\{^1H\}$ NMR spectroscopic analyses indicate the formation of a single species, with a resonance at $\delta = 20.5$ ppm. Crystallisation from concentrated pentane solutions allowed for the isolation of the single reaction product as deep red blocks. Single crystal X-ray diffraction (SC-XRD) analysis confirmed the formation of the target

bis(hydridogermylene)nickel(0) complex $[^{Ph}L(H)Ge]_2Ni$ (**2**; Fig. 2(b)). Efforts were also made to access the mono-equiv. of $^{Ph}L(H)Ge$, and controlling ligand addition rate, temperature, germylene complex, *i.e.* $^{Ph}L(H)Ge-Ni(cod)$, by employing a single concentration and solvent, but in all cases only **2** is formed, suggesting either that the mono-germylene derivative is unstable relative to redistribution in forming **2**, or that the second ligand substitution is significantly faster than the first. Nevertheless, complex **2** represents a rare example of a bis(hydridotetrylene)-metal complex, closely related stannylene species recently reported by Wesemann and co-workers.³⁰ Observing the molecular structure of **2** (Fig. 2),[†] a Ge-Ge bonding interaction is unlikely given the trigonal planar nature of two Ge centres (sum of angles: $Ge1 = 359^\circ$; $Ge2 = 352^\circ$) and the Ge...Ge distance (3.2477(8) Å), which sits between the sum of the covalent (2.44 Å) and van der Waals (4.22 Å) radii for Ge.³¹ A longer Ge2-Ni1 (2.2356(9) Å) than Ge1-Ni1 distance (2.181(1) Å) would suggest a differing degree of Ni→Ge backbonding in the former, also borne out by the decreased planarity at the Ge2 centre. A τ_4 value of 0.81 indicates a strongly distorted tetrahedral geometry at the Ni centre.³² Significantly deshielded Ge-H resonances are observed in the 1H NMR spectrum at $\delta = 9.45$ ppm, representing a significant shift from the relative signal in the free germylene **1** ($\delta = 7.45$ ppm), perhaps indicative of Ge-H bond weakening upon Ni coordination. Sharp Ge-H stretching bands are observed in the IR spectrum of **2** at 1872 and 1849 cm^{-1} . General broadening of signals and the presence of two Dipp- iPr -CH signals is indicative of hindered ligand rotation.

Following the isolation of compound **2**, we sought to define the reactivity of the coordinated Ge-H fragments. For this we looked towards reactions with phenylsilane, and ethylene. Addition of an excess of $PhSiH_3$ leads to a slow but selective reaction, forming what appears to be two isomers of a single product quantitatively after 3 days at ambient temperature. Bubbling is observed during the course of the reaction, indicative of the formation of dihydrogen, as confirmed by *in-situ* 1H NMR analysis of an NMR-scale reaction (Fig. S16). We note that no di- or oligo-silanes are formed *i.e.* through silane dehydrocoupling, suggesting that H_2 evolution occurs through coupling of a Ge-H moiety with $PhSiH_3$. This is confirmed by a SC-XRD analysis of single crystals grown from saturated pentane solutions, revealing the formation of complex **3** (Fig. 3(a) and (b)). The molecular structure indicates that a single Ge-H fragment has undergone the aforementioned dehydrocoupling reaction, with the second Ge centre still bearing a hydride ligand. In contrast to **2**, a Ge-Ge bonding interaction is now clear in **3**. One terminal Si-H ligand remains, whilst the second is binds Ni (*vide infra*), forming a bridging Ni...H...Si interaction.

In the solid state, **3** exists as two independent diastereoisomers, which are both present in the asymmetric unit (see Fig. S25 in ESI), due to the chiral Ge1 and Si3 centres. Metrical parameters of only one isomer are discussed here. In this molecular structure, a formal Ge-Ge bond is now clearly apparent ($d_{Ge1Ge2} = 2.460(1)$ Å), which sits on the longer side of known Ge-Ge double bonds.* The central Ni1-Ge2 distance

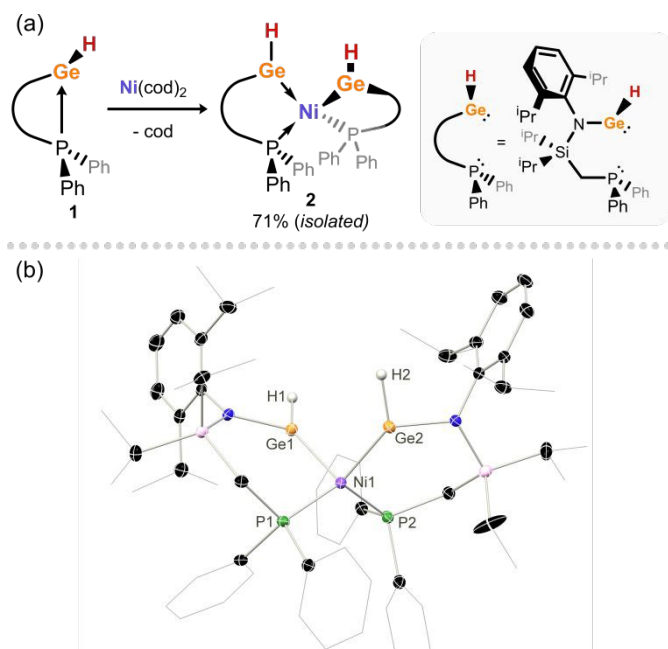


Figure 2. (a) The synthesis of bis(hydridogermylene)-Ni⁰ complex **2**, and (b) the molecular structure of **2**, with thermal ellipsoids at 30% probability, and hydrogen atoms removed for clarity, aside from those direct bound to Ge1 and Ge2. Selected bond lengths (Å) and angles (°) for **2**: Ge1-Ni1 2.181(1); Ge2-Ni1 2.2356(9); Ge1-Ni1-Ge2 94.66(3); P1-Ni1-P2 123.59(4); Ge1-Ni1-P1 94.46(4); Ge1-Ni1-P2 112.86(4); Ge2-Ni1-P1 122.12(4); Ge2-Ni1-P2 104.43(4).



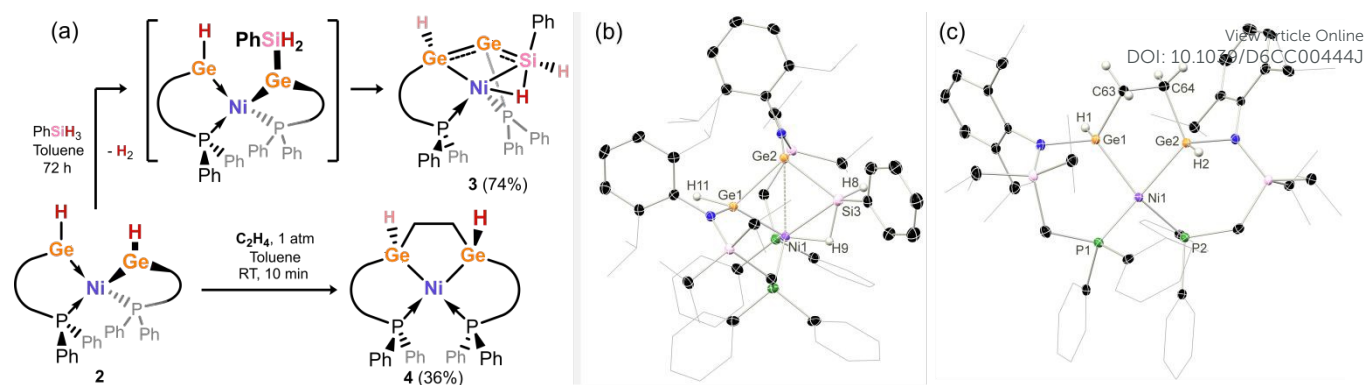


Figure 3. (a) The reactions of **2** towards phenyl silane and ethylene, leading to dehydrocoupling in forming **3**, and [2+2] cycloaddition in forming **4**, respectively (isolated yields given in parentheses); The molecular structures of (b) **3** and (c) **4**, with thermal ellipsoids at 30% probability, and hydrogen atoms removed for clarity, aside from those direct bound to Ge1 and Ge2, and Ni1/Si3. Selected bond lengths (Å) and angles (°) for **3**: Ge1-Ge2 2.460(1); Ge2-Si3 2.374(1); Ge1-Ni1 2.262(1); Ge2-Ni1 2.798(1); Si3-Ni1 2.328(1); Ge1-Ge2-Si3 99.17(3); Ge1-Ni1-Si3 106.63(3); Ni1-Ge1-Ge2 72.53(2); Ni1-Si3-Ge2 73.03(3). For **4**: Ge1-Ni1 2.3430(9); Ge2-Ni1 2.3507(8); Ge1-Ni1-Ge2 77.90(2); P1-Ni1-P2 102.24(4); Ge1-Ni1-P1 97.86(3); Ge1-Ni1-P2 156.46(3); Ge2-Ni1-P1 149.43(3); Ge2-Ni1-P2 90.59(3).

(2.798(1) Å) is significantly longer than the Ni1-Ge1 distance (2.262(1) Å), which would rule out a 'classical' digermene complex. This is further borne out by significant deviation from planarity or *cis*-bending of the $[\text{R}_2\text{GeGeR}_2]$.⁸ The observed Ge2-Si3 contact (2.374(1) Å) sits between reported values for Ge-Si single and double bonds, whilst the Ni1-Si3 bond (2.328(1) Å) aligns with known hydride-bridged silyl complexes of nickel, and as such is longer than a typical Ni-Si single bond. This species is thus significantly distorted from an η^2 -digermene complex,³³ but is formally not a digermasila-allyl complex given the bridging [Ni-H-Si] motif. Still, resonance forms comprising a silyl-digermene complex of Ni^0 are proposed (Fig. 4(a)) – no significant β -Ge-Ni interaction is observed, and a short Ge-Si bond suggests delocalised multiple bond character across the Ge_2Si unit.³³

Additional key aspects of this complex are elucidated through multi-nuclear NMR analyses. The two diastereoisomers of **3** are observed in solution, with clear separation of signals in the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra upon dissolution of crystalline material: bridging Ni-H-Si signals are observed at $\delta = -4.05$ ($^1J_{\text{HSi}} = 80$ Hz) and -4.46 ($^1J_{\text{HSi}} = 72$ Hz) ppm, terminal Si-H signals at 6.26 ($^1J_{\text{HSi}} = 182$ Hz) and 7.19 ppm ($^1J_{\text{HSi}} = 236$ Hz), and Ge-H signals at 9.54 and 10.13 ppm, which are somewhat broadened. The former negatively shifted resonances align with hydride-bridged nickel silyl species,³⁴ the high-field shift indicative of a degree of nickel hydride character. The observed J-coupling constants are in-keeping with bridging, activated Si-H bonds.^{34,35} Four sets of doublets are found in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, with one pair for each isomer ($\delta = 8.6$ and 21.8 [$^2J_{\text{PP}} = 16.6$ Hz]; 11.1 and 23.2 [$^2J_{\text{PP}} = 23.5$ Hz]).

Computational analyses, carried out at the $\omega\text{B97X-D3//def2-SVP(def2-TZVPP}$: Ge, Ni, P) including solvent effects (THF) with the polarizable continuum model (PCM), give further insights into the structure of **3**. An NBO analysis on a reduced structure of **3** yields Mayer Bond Orders (MBOs) for the Ge1-Ge2 and Ge2-Si1 bonds of 0.917 and 0.941, with lower Ge1-Ni1 and Si1-Ni1 values of 0.750 and 0.430. The HOMO and LUMO are both highly delocalised over the [NiGe₂Si] core, the former showing a weak Ge-Si π -interaction (Fig. 4(b)), and the latter representing π^* -symmetry across the Ge-Ge-Si fragment (Fig. 4(c)). This is further borne out, for example, by significant *p*-character of the Ge1-Si3 bond in the NBO analysis (Ge: 89.9% *p*; Si: 67.0% *p*). A lower natural charge at Si3 (+0.59) when compared to the two Si centres of the ligand scaffold (*i.e.*, Si1: +1.96 and Si2: +1.95) would suggest a more anionic nature of the former. Indeed, this value is in keeping with those observed for Ge1 (+0.73) and Ge2 (+0.27).

Given the described Ge-H bond activation in the formation of **3**, and earlier reports on the insertion of alkenes into $\text{Ge}^{\text{II}}\text{-H}$ bonds,^{36,37} potential Ge-H insertion chemistry of **2** was assessed through reactivity with ethylene. No insertion was observed; rather, this reaction leads to what is best referred to as a [2+2] cycloaddition reaction with the $[\text{Ge}_2]$ unit in **2**, forming digermametallacyclopentane derivative **4** (Fig. 3(a)). This

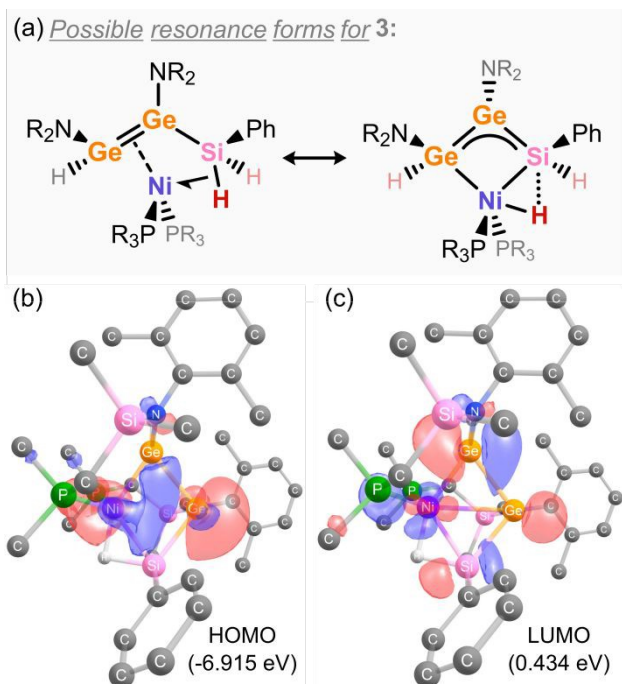


Figure 4. (a) Possible resonance structures of **3**, and graphical representations of (b) the HOMO and (c) LUMO of **3**.



reactivity is rather what one may expect of low-valent Ge-Ge bonded systems such as digermynes.^{38,39} A SC-XRD analysis confirms the connectivity in complex **4** (Fig. 3(c)), which bears a tetradentate bis(phosphino)-bis(germyl) ligand binding a formally Ni^{II} centre. A significant increase in the average Ge-Ni bond lengths in **4** (2.347 Å) when compared with **2** (2.208 Å) aligns with this switch from germylene to germyl ligands, *i.e.* reducing Ni→Ge back-bonding interactions. An additional effect of the ethylene bridge in **4** is a contracted Ge...Ge distance of 2.951(1) Å, compared to 3.2477(8) Å in **2**. Further, due to the increased conformational constraint brought about by the ethylene bridge, **4** tends closer to a square planar geometry, with a τ_4 value of 0.38. This strain, however, does not lead to reversibility in the ethylene cycloaddition process, in contrast to our recently reported bis(gallylene)-Ni⁰ system featuring the closely related ^{Cy}LGa ligand (^{Cy}L = [(Cy₂PCH₂Si(ⁱPr)₂)(Dip)N]).⁴⁰ The ¹H NMR spectrum of **4** deviates from that for **2** in demonstrating a significant high-field shift of the Ge-H moieties, from $\delta = 9.45$ ppm to $\delta = 6.07$ ppm, indicative of the higher valency at Ge.⁴¹ In addition, two broadened 2H multiplet signals are observed for the C₂H₄ fragment. Though we do not include a calculated mechanism for this reaction, we would hypothesise that this proceeds *via* an initial addition to one Ge-Ni moiety, akin to earlier reported Si-Ni and Ga-Ni complexes,^{42,43} followed by migration to Ge in forming **4**. Considering the electron flow on forming **4**, Ni is oxidised (*i.e.* Ni⁰ to Ni^{II}), whilst the oxidation state of Ge in the formally anionic germyl ligands remains +2. As such, one can consider that this reactivity, which diverges from that expected for a Ge^{II}-hydride, is driven by its coordination to low-valent nickel, which mediates electron shuttling.

In summary, we have demonstrated that the reactivity of a bis(hydridogermylene)nickel(0) complex (**2**) is divergent from that expected of a 'free' germylene hydride. This culminates in the Ge^{II}-H/Si^{IV}-H dehydrocoupling reaction with a silane, and [2+2] cycloaddition between ethylene and the [Ge₂] fragment, the former being a previously unobserved class of reactivity for such systems. These results give fresh insights into the effect of metal coordination on the chemistry of functional heavier carbene analogues, which may open new utility moving forward.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information. Crystallographic data for compounds **2**, **3**, and **4** have been deposited at the CCDC under accession numbers 2453067, 2453069, 2453068, respectively, and can be obtained from <https://www.ccdc.cam.ac.uk/structures/>.

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- † The asymmetric unit for **2** contains two full molecules of this species. Only one molecule is discussed here.
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