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Parent Heavy Methylenes: Chemical Tricks to Access Isolable Complexes of Elusive H_2E: Species (E = Ge and Sn)**

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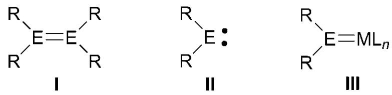
carbenes · germanium · main-group elements · metallenes · tin

Olefins, $R_2C{=}CR_2$, are one of the simplest classes of unsaturated organic compounds with a C–C π bond and represent indispensible building blocks in the molecular sciences. Their heavier analogues $R_2E{=}ER_2$ ("dimetallenes" **I**; Scheme 1), however, are regarded as one of the most important types of reactive intermediates in main-group chemistry.[1] Such dimetallenes **I**, bearing hydrogen atoms or sterically small substituents at the heavier Group 14 element, are elusive. However, the introduction of sterically congesting substituents at the metal centers can bring about higher kinetic stabilization of the E=E bonds, which has led to the astonishingly facile isolation of stable disilenes, digermenes, and distannes.[2–4] Moreover, the latter groundbreaking work by Lappert et al.[4] has stimulated the synthesis of a vast number of isolable dimetallenes, including an air-stable disilene, which was reported recently by Tamao and coworkers.[2b] Despite the impressive progress made in the chemistry of doubly bonded compounds of the heavier elements, the experimental access and exploration of the simplest of these species, the parent heavy ethenes $H_2E{=}EH_2$, remain attractive for two main reasons: The isolation of such ethene analogues could bring about a better fundamental understanding of structure–property relationships (e.g., experimental analysis of the interconversion of several valence isomers) and may also inspire new applications in molecular synthesis (e.g., hydrometalation of unsaturated substrates with HE=E subunits) and materials chemistry.



Scheme 1. Heavier Group 14 elements analogue of alkenes (**I**), carbenes (**II**), and carbene complexes (**III**). E = Si, Ge, Sn; M = transition metal, L = ligand.

Homolytic dissociation of the E=E bond in dimetallenes could generate two molar equivalents of the heavy carbene analogues **II** (Scheme 1), which, in turn, are also important reactive intermediates in organic and organometallic chemistry and have been the subject of several notable studies.[5] In fact, there are numerous examples of both dimetallenes being used to generate two equivalents of the corresponding heavy carbene analogue and the generation of dimetallenes by facile dimerization of metastable heavy carbene species.[5] Naturally the relative stabilities of **I** and **II** are controlled by the steric and electronic properties of the substituents at the Group 14 atom E; additionally, the tendency of **II** to undergo facile dimerization is indicated by its singlet–triplet energy gap.[1] In both cases, sterically congested substituents kinetically stabilize these reactive species, but in the latter case electronic stabilization plays a particularly important role, as shown by π-donor substituents that are capable of stabilizing an empty valence p orbital at the metal center.[5]

Despite the considerable research in this area, the parent heavy methylenes EH_2 have remained unattainable, because the hydrogen atoms can satisfy neither the steric nor the electronic requirements. However, stabilization can also be achieved with external electron donors (Lewis bases) and acceptors (Lewis acids). In fact, by employing electron-donating N-heterocyclic carbenes (NHCs), a large variety of small main-group molecules, which are unstable otherwise, have been isolated and fully characterized (B_2H_2, Si_2, silanones ($R_2Si{=}O$), dioxasiliranes, Ge_2, P_2, and NP).[6] The fruitful concept of donor–acceptor stabilization of carbene species is even more prevalent and was first brought to the forefront of chemical research through the seminal discovery of transition-metal–carbene complexes by Fischer and Schrock, for which they received Nobel Prizes in 1973 and 1995[10] and which has subsequently been expanded to the development of heavy-carbene–metal complexes **III** (Scheme 1).[7–9] Transition-metal–carbene and –heavy-carbene complexes are very important reactive intermediates in organic synthesis and organometallic chemistry and play a vital role in many catalytic processes. However, the chemistry of the heavier congeners **III** is still in its infancy relative to

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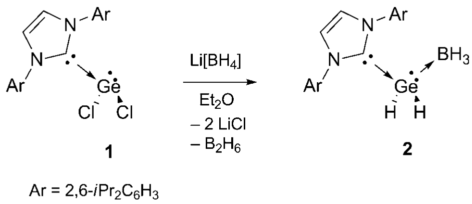
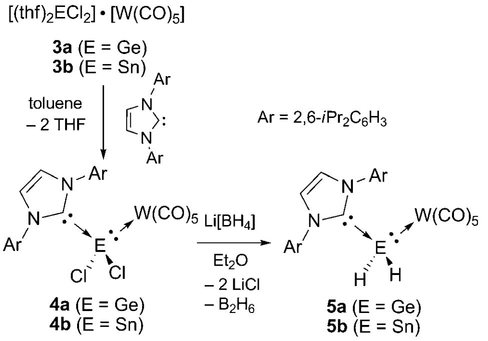
that of Fischer and Schrock complexes owing to their intrinsically lower stabilities. Therefore, while methylene complexes are well known and studied, there have been no reports on parent heavy methylene complexes $H_2E{=}ML_n$.

Taking advantage of both of these chemical tricks, Rivard and co-workers reported the first parent germylene complex **2** using an NHC as donor and BH_3 as acceptor ligand; compound **2** was synthesized by the Cl/H metathesis reaction of carbene-stabilized dichlorogermylene **1** with lithium tetrahydroborate in diethyl ether (Scheme 2).[11] Very recently, Rivard's group reported on the synthesis of the parent heavy methylenes GeH_2 and SnH_2 by employing the same NHC donor while changing to a transition metal (tungsten) as acceptor site (Scheme 3).[12] These species represent the first examples of a new class of compounds, namely donor-stabilized heavy-methylene–transition-metal complexes. The heavy dichlorocarbene tungsten complexes **4** can be obtained by the reaction of the corresponding pentacarbonyltungsten complexes **3** with one molar equivalent NHC (Scheme 3). Subsequent reaction of **4** with $LiBH_4$ afforded the donor–acceptor-stabilized heavy methylenes **5**.



Scheme 2. Donor–acceptor-stabilized parent germylene **2**.

The molecular structures of complexes **2** and **5** were determined by NMR spectroscopy and single-crystal X-ray diffraction. In the ^1H NMR spectra, the characteristic EH_2 signals were observed at $\delta = 3.92$ (**2**), 4.23 (**5a**), and 5.56 ppm (**5b**), respectively. Furthermore, in the IR spectra, weak E−H vibration bands could be observed at 1987 (**2**), 1981 (**5a**), and 1786 cm^{-1} (**5b**). These bands were assigned by calculations and deuterium-labeling experiments. The divalent metal atoms E of these complexes are tetrahedrally surrounded and connected to one NHC and one $W(CO)_5$ or BH_3 moiety. On the basis of bond lengths in **5** and DFT calculations of model compounds, the complexes are concluded to consist of a dative $E \leftarrow C(NHC)$ bond and a σ-donating $E \rightarrow W$ bond. Of particular note is that the Sn−H bonds in **5b**, despite the steric protection afforded by the NHC and $W(CO)_5$ groups, are capable of reacting with three molar equivalents of benzaldehyde to give a hydrostannylation product that has been isolated. These exciting results demonstrate that the chemistry of elusive H_2E: species can be explored by taking advantage of the chemical trick of donor–acceptor stabilization. Further reactivity studies with other organic small molecules should be feasible and could pave the way to new and important products. It remains to be seen whether the same methodology can be applied to isolate elusive SiH_2 species as well.



Scheme 3. Synthesis of donor–acceptor-stabilized heavy chlorocarbenes **4** and heavy methylenes **5**.

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