Main-Group Compounds

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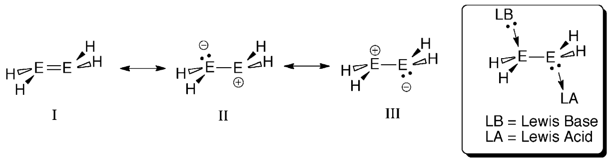
Trapping the Parent Inorganic Ethylenes H_2SiGeH_2 and H_2SiSnH_2 in the Form of Stable Adducts at Ambient Temperature**

*S. M. Ibrahim Al-Rafia, Adam C. Malcolm, Robert McDonald, Michael J. Ferguson, and Eric Rivard**

Ethylene is a key industrial precursor to numerous value-added chemicals,[1] and is a regulatory component for plant growth.[2] Moreover, ethylene has played an important role in shaping our general knowledge of transition-metal coordination chemistry.[3] By comparison, the heavier Group 14 element ethylene analogues, $H_2E=EH_2$ (E = Si–Pb), have remained elusive owing to a lack of suitable synthetic routes for their preparation and the expected instability of these entities in the condensed phase.[4,5] Despite such synthetic obstacles, these species are of considerable interest as they serve as structural models for Si and Ge surfaces (where E=E bonds are likely present),[6] and are potential precursors to new inorganic hybrid materials.[7]

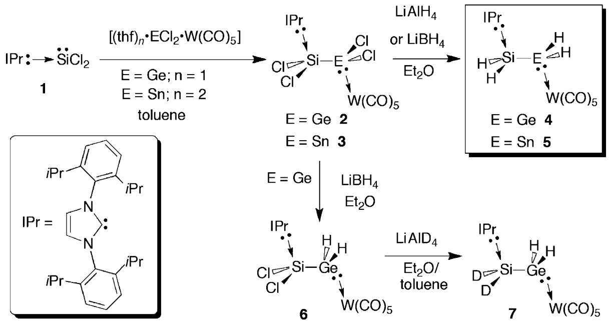
Pioneering work by Lappert and others revealed that the heavy Group 14 element dimetallenes $R_2E=ER_2$ only become stable to sacrificial oligomerization and/or E=E bond activation processes when bulky groups are present (for example, $R = CH(SiMe_3)_2$).[8] Furthermore, the bonding within these compounds are often vastly different from that of traditional olefins. For example, the heavy ethylene congeners $R_2E=ER_2$ (E = Ge, Sn, or Pb) have a propensity to dissociate into monomeric, singlet R_2E: fragments in solution, while elongated E=E distances and *trans*-bent geometries are present in the solid state (Scheme 1).[8] These observations are consistent with the presence of weak E=E bonds,[9] and theoretical investigations on the parent systems $H_2E=EH_2$ echo these findings.[10] Herein we provide experimental verification of the first inorganic analogues of ethylene, H_2SiEH_2 (E = Ge and Sn), in the form of stable complexes at ambient temperature.

The inorganic ethylenes $H_2E=EH_2$ (E = Si–Pb) have been predicted to adopt *trans*-bent geometries, wherein both E centers can act either as electron donors or acceptors. This unusual bonding feature is illustrated by the resonance forms **I–III** in Scheme 1;[9–11] consequently, we reasoned that the isolation of bottleable complexes of these species could be possible in the presence of suitable Lewis acidic and basic groups.[12,13]



Scheme 1. Resonance description of the bonding within the heavy ethylene analogues $H_2E=EH_2$ (E = Si–Pb).

The synthetic pathway used to access stable complexes of H_2SiGeH_2 and H_2SiSnH_2 is presented in Scheme 2, and relies upon the ability of N-heterocyclic carbenes such as IPr (IPr = $(HCNAr)_2C$:; Ar = 2,6-iPr$_2C_6H_3$), to stabilize highly reactive species in the p block.[14] To construct the requisite Si–Ge and Si–Sn linkages, we reacted Roesky's nucleophilic Si(II) halide adduct, IPr·$SiCl_2$ (**1**),[14h] with the coordinatively labile tungsten complexes, $[(thf)_n\cdot ECl_2\cdot W(CO)_5]$ (E = Ge and Sn);[15] the resulting perhalogenated complexes $[IPr\cdot Cl_2Si{-}ECl_2\cdot W(CO)_5]$ (E = Ge and Sn; **2** and **3**) were isolated in high yield as pale yellow solids.[16] Treatment of **2** and **3** with $LiAlH_4$ or $LiBH_4$, respectively, led to the installation of hydride functionality onto the Group 14 elements and the formation of the desired inorganic ethylene adducts, $[IPr\cdot H_2Si{-}EH_2\cdot W(CO)_5]$ (E = Ge and Sn; **4** and **5**) as air- and moisture-sensitive solids. Conclusive evidence for the formation of the parent hydride adducts **4** and **5** was obtained by X-ray crystallography, NMR and IR spectroscopy, theoretical calculations, and deuterium labeling.[17]



Scheme 2. Synthesis of the Group 14 dimetallene adducts **2–7**.

As shown in Figure 1, $[IPr\cdot H_2Si{-}GeH_2\cdot W(CO)_5]$ (**4**) features a coordinated H_2SiGeH_2 silagermene unit within a canted transoid C_{IPr}–Si–Ge–W array. The corresponding Si–Ge distance in **4** was 2.3717(14) Å, and is similar in length to

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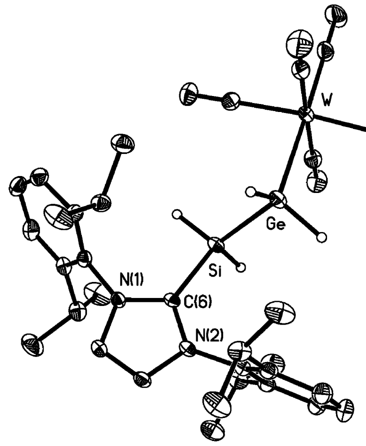


Figure 1. ORTEP plot of [IPr·H$_2$Si–GeH$_2$·W(CO)$_5$] (**4**). Ellipsoids set at 30% probability; all carbon-bound hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: C6–Si 1.915(5), Si–Ge 2.3717(14), Si–H 1.38(5) and 1.37(5), Ge–H distances fixed to 1.460(4) Å, Ge–W 2.6479(6), W–C1 1.996(5), W–(C2–C5) 2.014(5) to 2.049(6); C6-Si-Ge 119.96(13), Si-Ge-W 107.84(4), Ge-W-C1 177.26(12); W-Ge-Si-C6 −164.77(15).

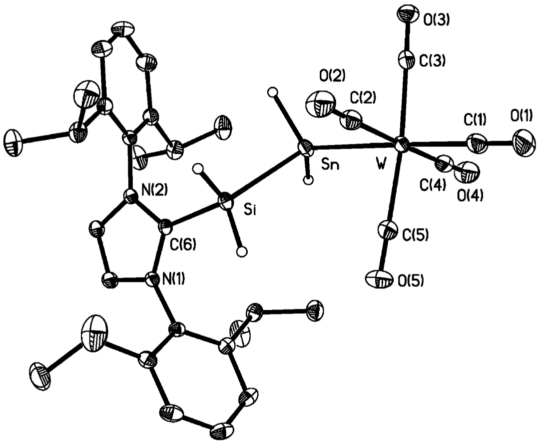


Figure 2. ORTEP plot of [IPr·H$_2$Si–SnH$_2$·W(CO)$_5$] (**5**). Ellipsoids set at 30% probability; all carbon-bound hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: C6–Si 1.9128(17), Si–Sn 2.5808(5), Si–H 1.35(2) and 1.36(2), Sn–H 1.67(2) and 1.65(2), Sn–W 2.79631(17), W–C1 1.986(2), W–(C2–C5) 2.0217(19) to 2.0467(18); C6-Si-Sn 120.14(5), Si-Sn-W 101.101(11), Sn-W-C1 177.82(6); W-Sn-Si-C6 −164.67(5).

the Si–Ge single bond found in H$_3$Si–GeH$_3$ (2.357(4) Å).[16,17] The flanking C$_{\mathrm{IPr}}$–Si interaction was determined to be at a distance of 1.915(5) Å, and is notably shorter than the C–Si bond lengths within the previously known silicon(II) dihalide adducts IPr·SiCl$_2$ (**1**; 1.985(4) Å)[14h] and IPr·SiBr$_2$ (1.989(3) Å).[14i]

^{1}H and ^{13}C{^{1}H} NMR spectroscopy confirmed the presence of peripheral IPr and W(CO)$_5$ groups in [IPr·H$_2$Si–GeH$_2$·W(CO)$_5$] (**4**). Interestingly, the ^{1}H NMR resonances associated with the Si*H*$_2$ and Ge*H*$_2$ units appeared as second-order resonances at 3.73 and 1.90 ppm, respectively (in [D$_8$]THF); these spectroscopic features arise from the mutually restricted rotation of the SiH$_2$ and GeH$_2$ groups on the NMR timescale, resulting in inequivalence of each of the four hydride moieties.[17] Furthermore, a clearly resolved triplet resonance was detected at −71.9 ppm ($^1J_{\mathrm{Si\text{-}H}} = 192.2$ Hz) in the proton-coupled ^{29}Si NMR spectrum, while Si–H (2140 and 2150 cm^{-1}) and Ge–H (1959 cm^{-1}) stretching bands were located by IR spectroscopy. The perdeutero complex [IPr·D$_2$Si–GeD$_2$·W(CO)$_5$] **4D** was also prepared and yielded isotopically shifted Si–D (1549 and 1567 cm^{-1}) and Ge–D (1404 cm^{-1}) IR bands, thereby supporting our initial assignment of the Ge–H vibration in **4** amongst proximal ν(CO) vibrations.

The related silastannene complex [IPr·H$_2$Si–SnH$_2$·W(CO)$_5$] (**5**) was prepared using the strategy outlined in Scheme 2. The isolation of **5** was complicated by the routine formation of the known adduct IPr·SiCl$_2$·BH$_3$ as a by-product (ca. 40%);[18] therefore isolation of **5** in pure form necessitated additional recrystallization steps, resulting in a substantially reduced, yet reproducible, yield of about 9%.

As shown in Figure 2, compound **5** adopts a nearly isostructural motif as its Si–Ge congener **4**, with a Si–Sn distance of 2.5808(5) Å. This value supports the presence of Si–Sn single bonding in **5**,[19] while the corresponding Si=Sn bond length in (tBu$_2$MeSi)$_2$Si=SnTrip$_2$ (Trip = 2,4,6-iPr$_3$C$_6$H$_2$) is, as expected, considerably shorter (2.4188(14) Å).[20] The adjacent C$_{\mathrm{IPr}}$–Si bond length in **5** (1.9128(17) Å) is comparable to the related bond in **4** (1.915(5) Å), suggesting that a similar, formally dative, interaction is present in each adduct. The Sn–W linkage in **5** (2.79631(17) Å) is slightly longer than the Sn–W bond in [IPr·SnH$_2$·W(CO)$_5$] (2.7703(9) Å),[12b] congruent with the stronger donating ability of IPr relative to the silylene adduct, IPr·SiH$_2$. Furthermore, the Sn–W distance in **5** is much shorter than the Sn–W distance of 2.9030(8) Å in Power's Sn$^{\mathrm{II}}$ complex [(η^5-C$_5$H$_5$)W(CO)$_3$–SnAr*] (Ar* = 2,6-Trip$_2$C$_6$H$_3$), and is consistent with an increase in tin-derived s-orbital character within the Sn–W bond in **5**.[21] In each of the reported W(CO)$_5$ adducts **4** and **5**, quasi octahedral geometries were found about the tungsten centers with nearly colinear E-W-C1 arrangements.

The NMR spectra for **5** were particularly informative due to the presence of many different NMR-active nuclei. Specifically, second-order spin systems were observed for the SiH$_2$ and SnH$_2$ groups by ^{1}H NMR spectroscopy, with added flanking satellites resulting from coupling with NMR-active ^{117}Sn and ^{119}Sn nuclei. Moreover a distinct triplet of triplets pattern was noted in the proton-coupled ^{119}Sn NMR spectrum ($\delta = -537$) owing to coupling between the ^{119}Sn nuclei and the hydrogen atoms of the Sn*H*$_2$ ($^1J_{\mathrm{Sn\text{-}H}} = 1109$ Hz) and Si*H*$_2$ ($^2J_{\mathrm{Sn\text{-}H}} = 62$ Hz) groups; of note, the magnitude of the $^1J_{\mathrm{Sn\text{-}H}}$ coupling in **5** is comparable to that in [IPr·SnH$_2$·W(CO)$_5$] ($^1J_{\mathrm{Sn\text{-}H}} = 1158$ Hz; $\delta = -309$).[12b] The IR spectrum of **5** contained the expected number of ν(CO) vibrations for an L·W(CO)$_5$ coordination environment (L = monodentate ligand),[12c] while a Si–H stretching mode was detected at 2136 cm^{-1}. For comparison, the recently reported silicon(II) hydride adduct [PhC(NtBu)$_2$]Si(H)·BH$_3$ has a Si–H vibration at 2107 cm^{-1}.[22] Despite NMR and crystallographic evidence for the presence of a SnH$_2$ group in **5**, the anticipated Sn–H vibrations could not be conclusively identified, which is presumably due to their low oscillator strengths.

The mixed halo/hydride adduct [IPr·Cl_2Si–GeH_2·W$(CO)_5$] **6**, and its deuterium analogue [IPr·Cl_2Si–GeD_2·W$(CO)_5$] **6D**, were readily prepared from **2** and the mild reducing agents $LiBH_4$ and $LiBD_4$ (Scheme 2; see the Supporting Information, Figure S2 for a thermal ellipsoid plot of **6**).[17] This chemistry follows previously studies wherein the Ge–Cl bonds in IPr·$GeCl_2$ are rapidly reduced by $LiBH_4$ to give IPr·GeH_2·BH_3,[12a] while recent work by Roesky and co-workers indicates that the Si–Cl groups in IPr·$SiCl_2$ remain largely unchanged in the presence of $LiBH_4$.[18] To date, our attempts to induce HCl elimination from **6** have been unsuccessful; however, treatment of **6** with the deuteride source $LiAlD_4$ generated the novel silagermene isotopomer [IPr·D_2Si–GeH_2·W$(CO)_5$] (**7**) in high yield. The formation of **7** was accompanied by discernable H/D exchange at Ge (as judged by ^{1}H and ^{2}H NMR spectroscopy), and the nature of this exchange process is currently under investigation in our group.

Theoretical studies (B3LYP/cc-pVDZ-pp)[17] were also performed on the structurally truncated models of **4** and **5**: [$(HCNMe)_2$C·H_2Si–EH_2·W$(CO)_5$] (E = Ge and Sn). In each complex, no evidence for Si–E multiple bonding could be found, and accordingly, the calculated Wiberg bond indices for the Si–Ge (0.88) and Si–Sn (0.79) interactions suggested the presence of single bonds.[23] This data when taken with the highly polarized (dative) nature of the C_{IPr}–Si ($C^{\delta-}$–$Si^{\delta+}$) and $E^{\delta-}$–$W^{\delta+}$ bonds, support the bonding mode for **4** and **5** given in Scheme 2. As anticipated on the basis of electronegativity differences, each of the Si–H, Ge–H, and Sn–H bonds in the model complexes contained significant hydridic, $H^{\delta-}$, character (by natural population analyses).

The silagermene [IPr·H_2Si–GeH_2·W$(CO)_5$] (**4**) exhibited considerable thermal stability in the solid state ($T_{dec} \approx 135\,°C$), and is stable for extended periods of time in refluxing toluene. The tin analogue [IPr·H_2Si–SnH_2·W$(CO)_5$] (**5**), however, is significantly less stable, with decomposition in Et_2O solvent noted even at −30 °C to give the known adduct [IPr·SnH_2·W$(CO)_5$][12b] and unidentified insoluble by-product(s). As a result of the instability of **5** in solution, subsequent reactivity studies were focused on the silagermene adduct **4**.

Attempts to induce H_2 elimination from **4** and generate the dimetallyne adduct [IPr·HSi=GeH·W$(CO)_5$] by photolysis led only to the recovery of unreacted **4**. Furthermore, no reactivity was observed between **4** and either HC≡CPh or CNXyl (Xyl = 2,6-$Me_2C_6H_4$). Yet in the presence of acetylacetone, compound **4** underwent a surprisingly clean hydrosilylation reaction to yield the novel anionic adduct [{MeC(O)H–CH=C(Me)O}SiH–GeH_2·W$(CO)_5$]$^-$ as a salt with the known imidiazolium countercation [IPrH]$^+$ (Figure 3).

As evidenced by the formation of [IPrH]$^+$, the hydrosilylation reaction (Scheme 3) involves the deprotonation of the acetylacetone group by the basic carbene IPr.[24] The fate of the activated Si–H and backbone C–H groups was confirmed by repeating the same reaction with the isotopomer, [IPr·D_2Si–GeD_2·W$(CO)_5$] **4D**, whereby deuteride migration from the SiD_2 unit to the ketonic carbon of acetylacetonate was observed. This transformation suggests that the C_{IPr}–Si interaction in **4** is sufficiently labile to allow productive hydrosilylation chemistry to transpire while illustrating the stable nature of the Si–Ge linkage. The presence of strong Si–Ge bonding in **4** should facilitate the future preparation of new SiGe hybrid nanomaterials by the decomplexation/dehydrogenation of the H_2SiGeH_2 unit in **4**.[7]

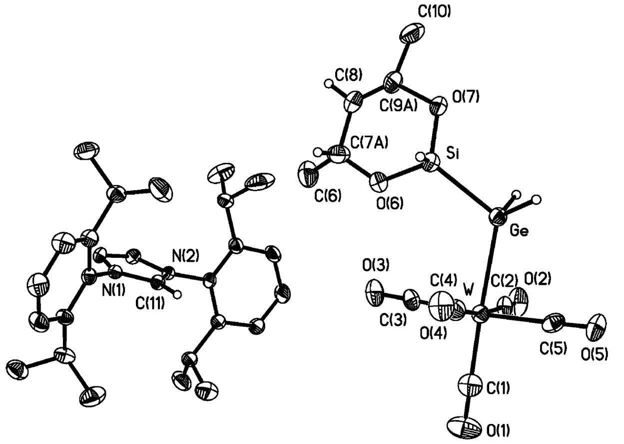
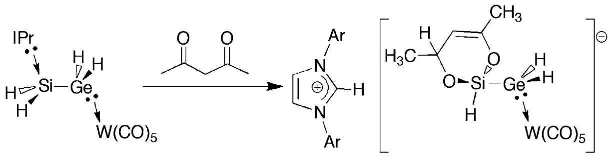


Figure 3. ORTEP plot of [IPrH][{MeC(O)H–CH=C(Me)O}SiH–GeH_2·W$(CO)_5$] (**8**). Ellipsoids set at 30% probability; selected carbon-bound hydrogen atoms and Et_2O solvate omitted for clarity; one view of the disordered silicon heterocycle is shown. Selected bond lengths [Å] and angles [°]: Si–Ge 2.3620(12), Si–H 1.33(4), Ge–H 1.44(4) and 1.47(4), Ge–W 2.6464(6), Si–O6 1.641(3), Si–O7 1.645(3), W–C1 1.948(6), W–(C2–C5) 2.012(5) to 2.045(5); O6-Si-O7 104.54(17), Si-Ge-W 118.43(3), Ge-W-C1 177.27(15).



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Scheme 3. Hydrosilylation chemistry involving the dimetallene complex **4**.

In summary, the first stable complexes of the parent inorganic ethylenes H_2SiEH_2 (E = Ge and Sn) have been synthesized. The ability to generate these novel mixed Group 14 element hydrides using readily available techniques should encourage the widespread study of these once elusive species, and thus opens an entirely new avenue of chemical exploration with potential applications in both the realms of molecular and materials chemistry.

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[16] Crystallographic data for **2**, **4**–**6**, and **8**: Recorded at 173 K with $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71073$ Å): **2**·THF: $a = 10.0601(4)$, $b = 11.0700(4)$, $c = 20.4081(7)$ Å, $\alpha = 75.8474(4)$, $\beta = 86.0770(5)$, $\gamma = 76.1582(5)°$, triclinic, space group $P\bar{1}$, $Z = 2$, $R1 = 0.0282$ for 9783 ($I > 2\sigma(I)$) data, $wR2$ (all data) $= 0.0670$; **4**: $a = 20.608(3)$, $b = 15.168(2)$, $c = 22.932(4)$ Å; orthorhombic, space group *Pbca*, $Z = 8$, $R1 = 0.0432$ for 8390 ($I > 2\sigma(I)$) data, $wR2$ (all data) $= 0.1275$; **5**: $a = 20.9929(11)$, $b = 15.0611(8)$, $c = 22.9501(12)$ Å; orthorhombic, space group *Pbca*, $Z = 8$, $R1 = 0.0147$ for 8348 ($I > 2\sigma(I)$) data, $wR2$ (all data) $= 0.0403$; **6**·$\mathrm{Et_2O}$: $a = 37.006(5)$, $b = 10.7703(13)$, $c = 21.044(3)$ Å, $\beta = 92.8633(16)°$; monoclinic, space group *C*2/*c*, $Z = 8$, $R1 = 0.0370$ for 8578 ($I > 2\sigma(I)$) data, $wR2$ (all data) $= 0.0902$; **8**·$\mathrm{Et_2O}$: $a = 11.1107(4)$, $b = 9.9270(3)$, $c = 21.7330(7)$ Å, $\beta = 104.4957(4)°$; monoclinic, space group *Pn*, $Z = 2$, $R1 = 0.0263$ for 10628 ($I > 2\sigma(I)$) data, $wR2$ (all data) $= 0.0517$, flack parameter $= 0.011(5)$. CCDC 826394 (**2**), 826395 (**4**), 826396 (**5**), 826397 (**6**), and 826398 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] See the Supporting Information for full details.

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[23] Compounds **4** and **5** could also have considerable silylene character resulting in coordinative Si–E interactions, as represented by the bonding model: $[\mathrm{IPr{:}{\rightarrow}H_2Si{:}{\rightarrow}H_2E{:}{\rightarrow}W(CO)_5}]$. We are currently investigating the reactivity of **4** and **5** to uncover if such a bonding descriptor is suitable.

[24] For an analogous insertion reaction involving $\mathrm{(Me_5C_5)_2Si}$: and acetylacetone, see: P. Jutzi, E. A. Bunte, U. Holtmann, B. Neumann, H. G. Stammler, *J. Organomet. Chem.* **1993**, *446*, 139.