ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

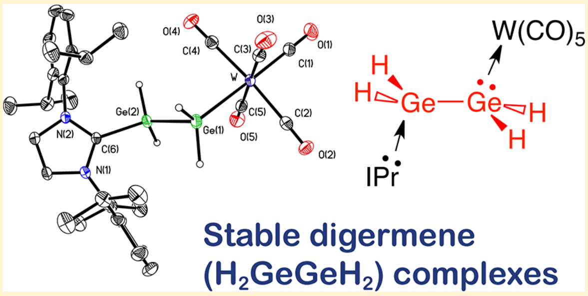
Stable Complexes of Parent Digermene: An Inorganic Analogue of Ethylene

S. M. Ibrahim Al-Rafia, Mohammad R. Momeni, Michael J. Ferguson, Robert McDonald, Alex Brown,* and Eric Rivard*

Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada T6G 2G2

Ⓢ *Supporting Information*

ABSTRACT: The elusive parent inorganic ethylene H_2GeGeH_2 has been isolated in the form of a stable complex for the first time via donor−acceptor coordination with suitable Lewis base/acid combinations ($LB{\cdot}H_2Ge\text{-}GeH_2{\cdot}LA$; LB = N-heterocyclic carbene or N-heterocyclic olefin; LA = $W(CO)_5$). The nature of the bonding in these species was investigated by density functional theory calculations and revealed the presence of polarized Ge−Ge covalent σ-bonds within the $H_2Ge{-}GeH_2$ arrays and dative Ge−C interactions between the digermene and the carbon-based Lewis bases.



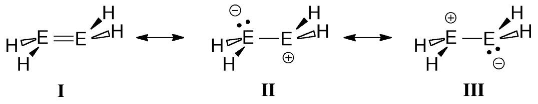
INTRODUCTION

The study of low-oxidation-state main-group hydrides has benefitted considerably from the discovery of new kinetic and electronic stabilization protocols which act to suppress undesired decomposition pathways that are commonly available to these reactive species.[1] In addition, low-oxidation-state group 14 element compounds of Si, Ge, and Sn (including their hydrides) have been actively explored by various groups with novel small-molecule activation processes uncovered; these studies serve to bridge the reactivity gap that once existed between main-group elements and their transition-metal counterparts.[2] Higher oxidation state group 14 hydrides have also received attention from industrial and academic realms due to their use as precursors to metal surfaces and nanoparticles via controlled thermolysis chemistry.[3] Our group has contributed to the field of main-group hydride chemistry by applying a general donor−acceptor route to access complexes of parent inorganic analogues of methylene (EH_2; E = Si, Ge, Sn) and ethylene (H_2SiGeH_2 and H_2SiSnH_2).[4] In this paper we now describe our successful efforts to prepare the first stable adducts of the parent digermene H_2GeGeH_2 using traditional Schlenk and glovebox techniques.[5] In order to provide further insight into the bonding of the reported encapsulated digermenes, computational studies using density functional theory (DFT) are presented.

RESULTS AND DISCUSSION

In a series of pioneering theoretical studies, the bonding in the heavy inorganic ethylene analogues H_2EEH_2 (E = Si−Pb) was determined to be vastly different from that of ethylene, $H_2C{=}CH_2$.[6] Notably, the heavier Group 14 element dimetallenes are predicted to adopt stable *trans*-bent geometries, as illustrated by the canonical forms **I**−**III** (Scheme 1), leading to concomitantly low HOMO−LUMO gaps.[7]

Scheme 1. Illustration of the *trans* Bending and Representative Canonical Forms for the Parent Group 14 Alkene Derivatives H_2EEH_2 (E = Si−Pb)

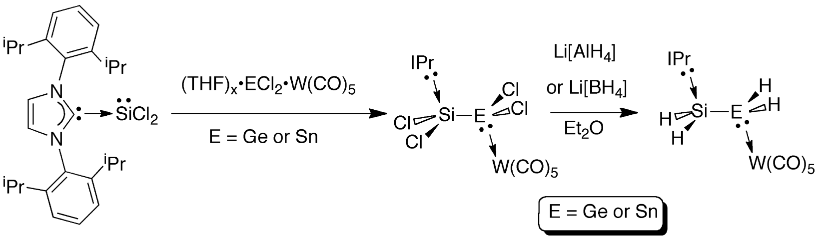

I **II** **III**

In a previous study we were able to prepare stable complexes containing the parent inorganic dimetallene units H_2SiEH_2 (E = Ge, Sn) in the formal bonding arrangement **III** shown in Scheme 1.[4e] Due to the inherent reactivity of the free parent species,[7] the presence of additional coordinative interactions between the $H_2Si{-}EH_2$ arrays and Lewis acids and bases (donor−acceptor stabilization) was required to intercept these main-group hydrides. As shown in Scheme 2, a key aspect of this synthetic approach was the formation of the E−E bond (E = group 14 element) by attack of a Lewis basic carbene−ECl_2 unit (e.g., $IPr{\cdot}SiCl_2$) onto an electron-deficient $ECl_2{-}W(CO)_5$ moiety; this reaction represents a nice illustration of the Umpolung effect,[8] whereby coordination chemistry can be used to confer either nucleophilic or electrophilic character at an element. Specifically, the nucleophilic silylene adduct $IPr{\cdot}SiCl_2$[9] was reacted with the tetrel element complexes $(THF)_xECl_2{\cdot}W(CO)_5$ (E = Ge, Sn; x = 1, 2) to yield the desired perhaloethylene adducts $IPr{\cdot}Cl_2Si{-}ECl_2{\cdot}W(CO)_5$ with the concomitant loss of THF (Scheme 2). Treatment of these species with hydride sources readily converted the E−Cl

Special Issue: Applications of Electrophilic Main Group Organometallic Molecules

Received: April 25, 2013

Scheme 2. Synthesis of the Silagermene and Silastannene Adducts IPr·H_2Si−EH_2·W$(CO)_5$ (E = Ge, Sn)[4e]



residues to E−H groups to afford the dimetallene complexes IPr·H_2Si−EH_2·W$(CO)_5$ (E = Ge, Sn).[4e]

We began this study by attempting to extend the approach outlined in Scheme 2 to prepare other H_2E−EH_2 complexes with alternate E−E linkages via replacement of the IPr·$SiCl_2$ donor unit with the known heavy element congeners IPr·$GeCl_2$ and IPr·$SnCl_2$.[4a,10] When IPr·$SnCl_2$ was combined with (THF)$_2$$SnCl_2$·W$(CO)_5$ in toluene, the immediate formation of a copious amount of white precipitate was noted. Analysis of this reaction mixture by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy confirmed the presence of the known Sn(II) dichloride donor−acceptor complex IPr·$SnCl_2$·W$(CO)_5$ as the only identifiable carbene-containing product (Scheme 3, eq 1).[4b] We also investigated mixed Ge/Sn reagent combinations, and in each case, $SnCl_2$ extrusion chemistry transpired to yield the stable germylene adduct IPr·$GeCl_2$·W$(CO)_5$ in place of the target adducts IPr·Cl_2Sn−$GeCl_2$·W$(CO)_5$ and IPr·Cl_2Ge−$SnCl_2$·W$(CO)_5$ (Scheme 3, eqs 2 and 3). Although IPr·$GeCl_2$·W$(CO)_5$ is a previously reported compound,[4b] we were subsequently able to obtain crystals of this complex that were suitable for single-crystal X-ray diffraction and the refined structure has been included as part of the Supporting Information (Figure S1).[11]

Scheme 3. Attempted Synthesis of Mixed Ge/Sn and Sn/Sn Dimetallene Adducts

$$\mathrm{(THF)_2SnCl_2{\bullet}W(CO)_5} + \mathrm{IPr{\bullet}SnCl_2} \xrightarrow[\substack{-\ \mathrm{SnCl_2} \\ -\ 2\ \mathrm{THF}}]{\text{toluene}} \mathrm{IPr{\bullet}SnCl_2{\bullet}W(CO)_5} \tag{1}$$

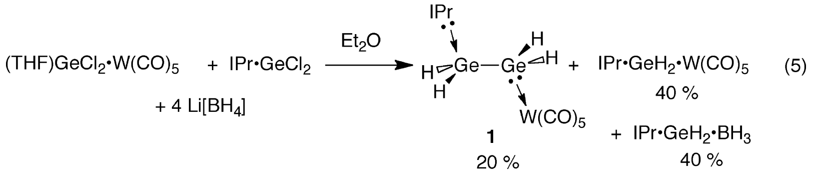
$$\mathrm{(THF)_2SnCl_2{\bullet}W(CO)_5} + \mathrm{IPr{\bullet}GeCl_2} \xrightarrow[\substack{-\ \mathrm{SnCl_2} \\ -\ 2\ \mathrm{THF}}]{\text{toluene}} \mathrm{IPr{\bullet}GeCl_2{\bullet}W(CO)_5} \tag{2}$$

$$\mathrm{(THF)GeCl_2{\bullet}W(CO)_5} + \mathrm{IPr{\bullet}SnCl_2} \xrightarrow[\substack{-\ \mathrm{SnCl_2} \\ -\ \mathrm{THF}}]{\text{toluene}} \mathrm{IPr{\bullet}GeCl_2{\bullet}W(CO)_5} \tag{3}$$

From the aforementioned chemistry, we noted that there was a preference for $GeCl_2$ units to bind to the Lewis acidic W$(CO)_5$ moieties in comparison to $SnCl_2$ donors; therefore, we used this property to our advantage to develop an improved route to the germylene precursor (THF)$GeCl_2$·W$(CO)_5$. The pre-existing route to (THF)$GeCl_2$·W$(CO)_5$ required the photolysis of W$(CO)_6$ in the presence of THF to give THF·W$(CO)_5$, followed by addition of Cl_2Ge·dioxane;[12] however, this preparation in our hands gave very low yields of (THF)$GeCl_2$·W$(CO)_5$. Our alternate route to (THF)$GeCl_2$·W$(CO)_5$ involved combining the readily available Sn(II) precursor (THF)$_2$$SnCl_2$·W$(CO)_5$[13] with Cl_2Ge·(dioxane) in toluene. This reaction immediately resulted in the formation of a white precipitate ($SnCl_2$), and the soluble target germylene adduct (THF)$GeCl_2$·W$(CO)_5$ was recovered as an analytically pure pale yellow solid (98% yield) after filtration and removal of the volatiles from the filtrate (eq 4); the generation of insoluble $SnCl_2$ was confirmed by melting point analysis.

$$\mathrm{(THF)_2SnCl_2{\bullet}W(CO)_5} + \mathrm{Cl_2Ge{\bullet}dioxane} \xrightarrow[\substack{-\ \text{dioxane} \\ -\ \mathrm{SnCl_2}\downarrow \\ -\ \mathrm{THF}}]{\text{toluene}} \mathrm{(THF)GeCl_2{\bullet}W(CO)_5} \tag{4}$$

Following a synthetic procedure related to that found in Scheme 2, IPr·$GeCl_2$ was combined with (THF)$GeCl_2$·W$(CO)_5$ in an attempt to prepare the donor−acceptor complex IPr·Cl_2Ge−$GeCl_2$·W$(CO)_5$. However, large quantities of unreacted IPr·$GeCl_2$ and the known species IPr·$GeCl_2$·W$(CO)_5$[4b] were detected by ^{1}H NMR along with some unidentified carbene-bound species. Positing that this reaction mixture could contain minor quantities of IPr·Cl_2Ge−$GeCl_2$·W$(CO)_5$, a somewhat unorthodox three-component reaction (eq 5) was initiated among IPr·$GeCl_2$, (THF)$GeCl_2$·W$(CO)_5$, and the hydride source Li[BH_4] in diethyl ether solvent in order to intercept the digermene complex IPr·H_2Ge−GeH_2·W$(CO)_5$ (**1**). Analysis of the resulting product mixture by NMR spectroscopy identified the previously reported Ge(II) species IPr·GeH_2·BH_3 and IPr·GeH_2·W$(CO)_5$ (ca. 40% each)[4a,b] along with a new carbene-containing product (ca. 20%). This latter species possessed distinctive multiplet resonances at 3.05 and 4.08 ppm in the ^{1}H NMR spectrum consistent with the presence of four magnetically inequivalent germanium-bound hydrides (i.e., in a H_2Ge−GeH_2 environment). Related AA′XX′ spectral features were observed for the SiH_2 and EH_2 units within the silagermene and silastannene adducts IPr·H_2Si−EH_2·W$(CO)_5$ (E = Ge, Sn),[4e] suggesting that the above mentioned reaction indeed produced the target digermene complex IPr·H_2Ge−GeH_2·W$(CO)_5$ (**1**) as a minor product. Fortunately we were able to isolate this species in pure form via fractional crystallization and obtain structural authentication by X-ray crystallography (Figure 1). The expected ν(Ge−H) stretching bands were located at 1954 and 1961 cm^{-1} by IR spectroscopy, and in order to confirm our spectral assignments, the deuterium isotopologue IPr·D_2Ge−GeD_2·W$(CO)_5$ (**1D**) was also prepared; this perdeuterated digermene complex displayed spectroscopically shifted IR ν(Ge−D) bands at 1405 and 1407 cm^{-1}. The Ge−H stretching frequencies in **1** are at the low end of the range typically found in other low-oxidation-state germanium hydrides in the literature (ca. 1900−2100 cm^{-1}).[2e,4,14] Although complex **1** can be handled in solution for short periods of time, it undergoes decomposition in benzene at ambient temperature after 48 h to yield IPr·GeH_2·W$(CO)_5$ and an insoluble product that is presumably elemental germanium. We attempted to trap GeH_2 by allowing **1** to decompose in the presence of either excess cyclohexene and



(5)

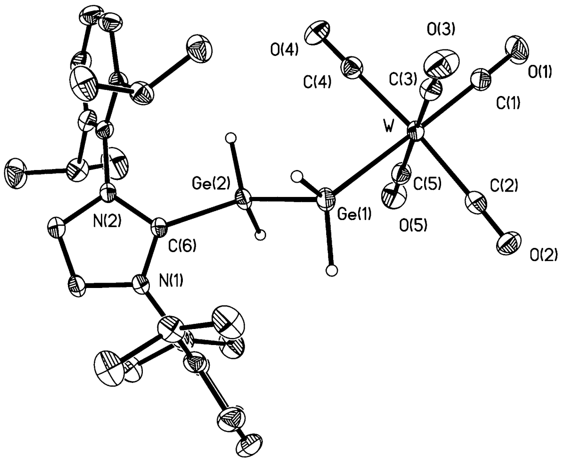


Figure 1. Thermal ellipsoid plot (30% probability level) of IPr·H_2Ge–GeH_2·W$(CO)_5$ (**1**). All carbon-bound hydrogen atoms have been omitted for clarity, and the Ge–H distances have been restrained to 1.500(2) Å. Selected bond lengths (Å) and angles (deg): C(6)–Ge(2) = 2.001(5), Ge(1)–Ge(2) = 2.4212(7), Ge(1)–W(1) = 2.6351(5), W(1)–C(1) = 1.994(5), W(1)–C(2–5) = 2.023(6)–2.059(5); C(6)–Ge(2)–Ge(1) = 120.06(10), Ge(2)–Ge(1)–W(1) = 107.80(2), Ge(1)–W(1)–C(1) = 177.60(14), Ge(1)–W(1)–C(2–5) = 86.01(13)–90.63(14); C(6)–Ge(2)–Ge(1)–W(1) torsion angle = 165.18(12).

2,3-dimethyl-1,3-butadiene (2 equiv) in C_6D_6 and did not see any evidence for GeH_2-trapped products. Moreover, compound **1** decomposes in the solid state to form a dark metallic byproduct upon heating to 65 °C.

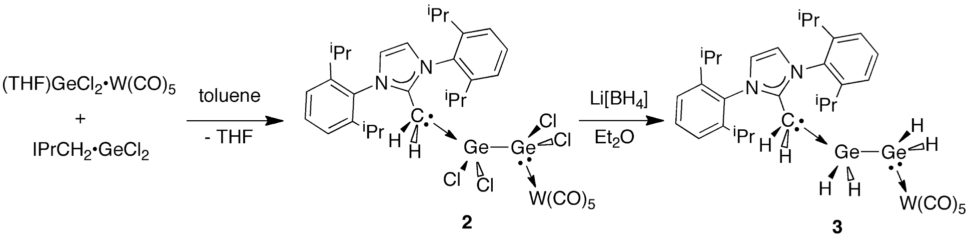
The structural parameters of IPr·H_2Ge–GeH_2·W$(CO)_5$ (**1**) (Figure 1) do not give any clear indication as to why this species is considerably less stable than other low-oxidation-state group 14 hydrides isolated by the donor–acceptor approach (e.g., IPr·GeH_2·W$(CO)_5$ or IPr·H_2Si–GeH_2·W$(CO)_5$).[4] Specifically, the C_{IPr}–Ge distance in **1** (2.001(5) Å) is actually shorter than the dative C_{IPr}-Ge interaction in the thermally stable Ge(II) complex IPr·GeCl_2 (2.112(2) Å).[4a] Moreover, the central Ge–Ge bond in **1** (2.4217(7) Å) lies within the accepted bond length range for Ge–Ge single bonds (ca. 2.40–2.50 Å).[15] However, it is salient to mention the computational work by Baines and co-workers, who studied various N-heterocyclic carbene–germylene complexes ImMe_2·GeR_2 (R = various electron donating and withdrawing groups; ImMe_2 = [$(HCNMe)_2$C:]) and could not find any clear correlation between the calculated C_{ImMe_2}–Ge bond lengths and the carbene–germylene interaction energies.[16] The Geerlings group also noted poor correlations between bond lengths and interaction strengths when soft donors (e.g., PH_3 and AsH_3) were bound to germylenes.[17] Therefore, some caution is required in drawing conclusions on complex stability solely from carbene carbon–germanium bond lengths.

Our prior observations in the donor–acceptor stabilization of group 14 methylenes EH_2 indicate that both N-heterocyclic carbenes (e.g., IPr) and nucleophilic olefins (IPrCH_2) are suitable Lewis bases for the preparation of stable EH_2 complexes.[4c] As a result, we explored chemistry complementary to that described above with the ylidic donor IPrCH_2. The stable tetrachlorodigermene adduct IPrCH_2·Cl_2Ge–GeCl_2·W$(CO)_5$ (**2**) was synthesized in 93% yield by combining the recently prepared Ge(II) dichloride adduct[18] IPrCH_2·GeCl_2 with (THF)GeCl_2·W$(CO)_5$ in toluene (Scheme 4). Compound **2** was isolated as an air- and moisture-sensitive pale yellow solid, and crystals suitable for X-ray diffraction were obtained from CH_2Cl_2/hexanes (Figure 2).

Compound **2** represents the first formal inorganic ethylene complex supported by the nucleophilic olefin donor IPrCH_2. The average Ge–Ge bond length in **2** is 2.4478(14) Å (two independent molecules in the unit cell), which is elongated by ca. 0.02 Å with respect to the Ge–Ge distance in IPr·H_2Ge–GeH_2·W$(CO)_5$ (**1**) (2.4212(7) Å). For comparison, the Ge–Ge distances in the perhalogenated pentagermane Ge$(GeCl_3)_4$ average to 2.420(6) Å;[19] thus, one can consider the Ge–Ge linkage in **2** as having considerable covalent character. For further reference, the recently prepared Lewis acid free carbodiphosphorane–digermene adduct $(Ph_3P)_2$C·GeCl_2GeCl_2 has a significantly longer Ge–Ge bond length (2.567 Å) relative to **2**.[20] Both Ge centers in **2** adopt slightly distorted tetrahedral environments, while the C_{IPrCH_2}–Ge (1.982(8) Å) and Ge–W (2.5452(10) Å) bonds in **2** are noticeably shorter than the respective C_{IPrCH_2}–Ge and Ge–W interactions in the germylene adduct IPrCH_2·GeCl_2·W$(CO)_5$ (2.056(3) and 2.5803(3) Å, respectively).[4c]

With the requisite perhalogenated digermene IPrCH_2·Cl_2Ge–GeCl_2·W$(CO)_5$ (**2**) in hand, halide/hydride metathesis chemistry to afford IPrCH_2·H_2Ge–GeH_2·W$(CO)_5$

Scheme 4. Synthesis of the Donor–Acceptor Complexes IPrCH_2·Cl_2Ge–GeCl_2·W$(CO)_5$ (2) and IPrCH_2·H_2Ge–GeH_2·W$(CO)_5$ (3)



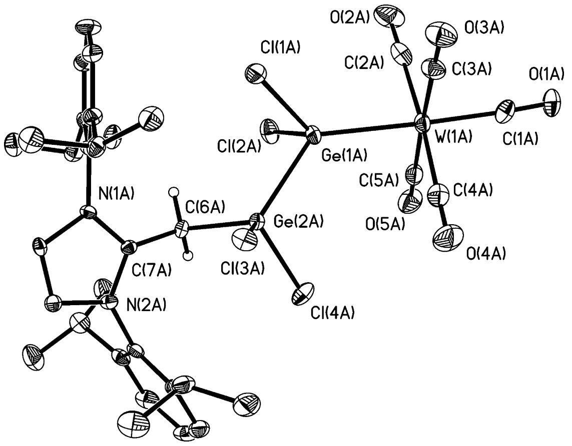


Figure 2. Thermal ellipsoid plot (30% probability level) of $IPrCH_2{\cdot}Cl_2Ge{-}GeCl_2{\cdot}W(CO)_5$ (**2**). Selected carbon-bound hydrogen atoms have been omitted for clarity. Only one molecule in the asymmetric unit is presented, with metrical parameters for the second molecule given in brackets. Selected bond lengths (Å) and angles (deg): C(6)−C(7) = 1.465(8) [1.462(8)], C(6)−Ge(2) = 1.991(6) [1.972(6)], Ge(1)−Ge(2) = 2.4486(10) [2.4469(10)], Ge(2)−Cl(3) = 2.1562(17) [2.1601(18)], Ge(2)−Cl(4) = 2.1653(19) [2.1715(19)], Ge(1)−Cl(1) = 2.2274(19) [2.2274(19)], Ge(1)−Cl(2) = 2.2412(19) [2.2339(18)], Ge(1)−W = 2.5551(7) [2.5393(7)], W−C(1) = 1.988(8) [1.996(9)], W−C(2−5) = 2.024(8)−2.051(9) [2.026(10)−2.048(9)]; C(6)−Ge(2)−Ge(1) = 118.02(18) [113.93(18)], Ge(2)−Ge(1)−W = 128.45(3) [126.88(3)], Ge(1)−W−C(1) = 174.6(2) [178.1(2)]; C(6)−Ge(2)−Ge(1)−W(1) torsion angle = 150.25(19) [162.8(2)].

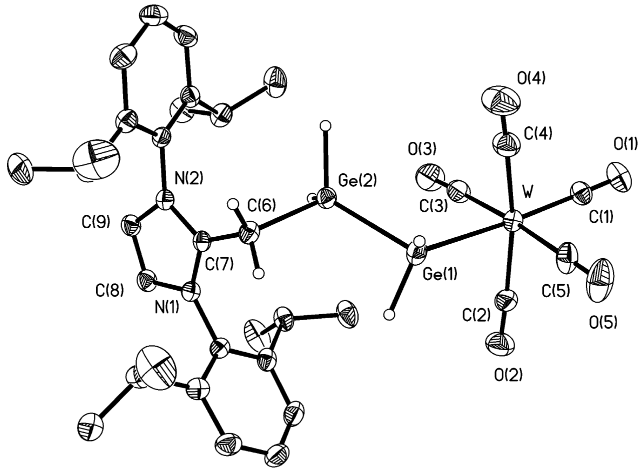


Figure 3. Thermal ellipsoid plot (30% probability level) of $IPrCH_2{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ (**3**). Selected carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(6)−C(7) = 1.462(4), C(6)−Ge(2) = 2.013(3), Ge(1)−H(1) = 1.63(3), Ge(1)−H(2) = 1.48(4), Ge(2)−H(3) = 1.60(4), Ge(2)−H(4) = 1.50(4), Ge(1)−Ge(2) = 2.4098(5), Ge(1)−W = 2.6295(4), W−C(1) = 1.992(4), W−C(2−5) = 2.014(4)−2.043(4); C(6)−Ge(2)−Ge(1) = 111.10(9), Ge(2)−Ge(1)−W = 114.706(17), H(1)−Ge(1)−H(2) = 98.2(18), H(3)−Ge(2)−H(4) = 97(2), Ge(1)−W−C(1) = 176.36(10), Ge−W−C(2−5) = 81.27(12)−89.58(11); W−Ge(1)−Ge(2)−C(6) torsion angle = 172.81(9).

(**3**) was readily accomplished using $Li[BH_4]$ as a hydride source (Scheme 4). Compound **3** was structurally authenticated by X-ray crystallography (Figure 3, vide infra); however, some comment about the spectral data and thermal stability of this parent digermene ($H_2Ge{-}GeH_2$) complex is warranted. Specifically, a single IR Ge−H stretch in **3** was located at 2028 cm^{-1}, which lies at a higher frequency than the ν(Ge−H) stretches in the carbene-capped IPr analogue $IPr{\cdot}GeH_2GeH_2{\cdot}W(CO)_5$ (**1**) (1954 and 1961 cm^{-1}). The ^1H NMR data for **3** are particularly informative, as the tungsten-bound GeH_2 residue in $IPrCH_2{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ (**3**) appears as a triplet at 3.23 ppm due to coupling ($^3J_{HH}$ = 4.0 Hz) to neighboring hydrogen atoms within the adjacent GeH_2 unit; the remaining GeH_2 group yields a pseudopentet resonance stemming from coupling to two proximal GeH_2 and two CH_2 hydrogen atoms (with nearly coincident $^3J_{HH}$ values). As noted with the IPr analogue **1**, $IPrCH_2{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ (**3**) exhibits only modest stability in the solid state (decomposes at 61−63 °C), while heating a toluene solution of **3** to 60 °C for 24 h led to the complete conversion of **3** into the known adduct $IPrCH_2{\cdot}GeH_2{\cdot}W(CO)_5$[4c] and presumably elemental germanium and hydrogen.

Figure 3 contains the refined structure of $IPrCH_2{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ (**3**). The Lewis base $IPrCH_2$ and Lewis acid $W(CO)_5$ in **3** are bound to the digermene unit to give an *anti* configuration (W−Ge(1)−Ge(2)−C(6) torsion angle = 172.81(9)°). The quality of the data was suitable to enable the location of the germanium-bound hydrides and their isotropic refinement. The core Ge−Ge distance in **3** is 2.4098(5) Å and is similar in length to the Ge−Ge interaction in $IPr{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ (**1**) (2.4217(7) Å). As with the other $W(CO)_5$ adducts of EH_2 and $H_2EE'H_2$ (E = Si, Ge, and/or Sn),[4] the tungsten center adopts a nearly ideal local C_{4v} geometry with approximately linear Ge(1)−W−C(1) (176.36(10)°) and orthogonal Ge−W−C(2−5) angles.

As a complement to the experimental studies presented above, we decided to investigate structural models of the $H_2Ge{-}GeH_2$ adducts **1** and **3** by density functional theory (at the M06-2X/cc-pVTZ level).[21] The two models chosen were structurally modified by replacing the flanking Dipp groups of the IPr and $IPrCH_2$ donors in **1** and **3** with less hindered Me substituents: $ImMe_2{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ ($\mathbf{1_{Me}}$) and $ImMe_2CH_2{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ ($\mathbf{3_{Me}}$) ($ImMe_2$ = $[(HCNMe)_2C:]$). In both instances there was good agreement between the calculated metrical parameters in the models and the values for **1** and **3** derived by X-ray crystallography (ca. 0.02−0.05 Å deviations in the bond lengths). The slightly canted *anti* configuration observed for $IPr{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ (**1**) in the solid state (W−Ge−Ge−C torsion angle = 165.18(12)°) was reproduced in the calculated gas-phase structure of $ImMe_2{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ ($\mathbf{1_{Me}}$) (179.85°). The truncated model $ImMe_2CH_2{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ ($\mathbf{3_{Me}}$) adopted a C−Ge−Ge−W arrangement that approached a *gauche* conformation (torsion angle = 39.05°), while an *anti* structure is found in the solid-state structure of **3**. Notably, both *anti* and *gauche* forms have been observed within the related aminoborane adducts $LB{\cdot}H_2B{-}NH_2{\cdot}LA$ (LB = Lewis base; LA = Lewis acid) with low energy differences calculated between the two forms.[22]

The IR spectrum of $\mathbf{1_{Me}}$ was calculated, and low-intensity Ge−H stretches were found at 1986 and 2120/2117 cm^{-1} (closely spaced vibrations), while in the more hindered species $IPr{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$, ν(Ge−H) bands were located at 1954 and 1961 cm^{-1}. The related nucleophilic olefin adduct $ImMe_2CH_2{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ ($\mathbf{3_{Me}}$) afforded a moderately intense calculated Ge−H stretching band at 2041 cm^{-1} in the gas phase, which correlated well with the experimentally determined Ge−H vibrational frequency of 2028 cm^{-1} in **3**. Note that the calculated Ge−H band in **3_{Me}** results from coupled motion among all four H atoms within the H_2GeGeH_2 unit, thus complicating comparative analyses between the IR data of **1** and **3** (see Figures S11 and S12 in the Supporting Information for diagrammatic representations of the Ge−H stretching modes in **1_{Me}** and **3_{Me}**).

Natural bond orbital (NBO) analyses were also conducted on both **1_{Me}** and **3_{Me}** and revealed striking similarities between the Ge−Ge bonds in each of these digermene (H_2GeGeH_2) complexes. In each model complex, polar Ge−Ge linkages were present with ca. 60% of the electron density in these bonds residing on the $W(CO)_5$-bound germanium centers; this observation follows what would be expected due to the electron-withdrawing nature of the metal carbonyl groups. Wiberg bond indices (WBI) of 0.87 and 0.91 were found for the Ge−Ge bonds in **1_{Me}** and **3_{Me}**, respectively, and these values are significantly larger than the bond index calculated for $IPr{\cdot}Cl_2Ge{-}GeCl_2$ (0.68), wherein a dative Ge→Ge interaction is present; thus, the bonding in both **1_{Me}** and **3_{Me}** (and by extension the digermene complexes **1** and **3**) can be regarded as being polar covalent in nature.[23] One interesting feature of the bonding in $ImMe_2{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ (**1_{Me}**) is that the WBI for the C−Ge interaction (0.73) is somewhat higher than that expected for typical carbene−germanium interactions (where values around 0.55−0.60 are generally obtained),[21] and close inspection of the calculated molecular orbitals in **1_{Me}** show a Ge→C back-bonding interaction of π symmetry (see HOMO-6 in Figure S5 in the Supporting Information). In both models **1_{Me}** and **3_{Me}**, the HOMO to HOMO-2 orbital sets are predominantly W−CO bonding in character. We also calculated the WBI values for the Ge−Ge bonding interactions in $H_3Ge{-}GeH_3$ and $H_2Ge{=}GeH_2$ (see Table S5 in the Supporting Information) and obtained values of 0.97 and 1.79, respectively, adding support for the formulation of Ge−Ge single bonds in **1** and **3**.

In addition, we calculated the UV−vis spectra for $H_3Ge{-}GeH_3$, $H_2Ge{=}GeH_2$, **1_{Me}**, and **3_{Me}** (see Table S6 and Figures S7−S10 in the Supporting Information[21]). Intense Ge−Ge $\sigma \rightarrow \sigma^*$ transitions were obtained for both H_3Ge-GeH_3 and $H_2Ge{=}GeH_2$ (162 and 150 nm, respectively), and a Ge−Ge $\pi \rightarrow \pi^*$ transition was located at 364 nm in $H_2Ge{=}GeH_2$. In comparison, both models of **1** and **3** (**1_{Me}** and **3_{Me}**) did not give any significant Ge−Ge $\sigma \rightarrow \sigma^*$ or $\pi \rightarrow \pi^*$ transitions in the UV−vis region, and the calculated absorption maxima (309 and 314 nm, respectively) were each derived from electronic transitions involving the filled d-orbitals on the W centers.[21]

The bonding in **1_{Me}** and **3_{Me}** was also analyzed by the AIM (atoms in molecules) method.[21] Two parameters were used in our evaluation: (a) the $\rho(r)$ values, which represent the minimum electron density along a bond path, and (b) the Laplacian, $\nabla^2\rho(r)$, which gives an indication of the degree of covalent or ionic character in a bond. The Ge−Ge bonds in **1_{Me}** and **3_{Me}** gave AIM parameters which are consistent with the presence of covalent bonds that contain less orbital overlap relative to the digermane $H_3Ge{-}GeH_3$ (Figures S13−S16 in the Supporting Information). Specifically, a $\rho(r)$ value of 0.082 is found for the Ge−Ge bond in $H_3Ge{-}GeH_3$, whereas $ImMe_2{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ (**1_{Me}**) has $\rho(r)$ = 0.069; similar minimum Ge−Ge bonding electron density is present in $ImMe_2CH_2{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ (**3_{Me}**) ($\rho(r)$ = 0.073). In addition, covalent interactions appear to be dominant in the Ge−Ge linkages in **1_{Me}** and **3_{Me}**, as negative $\nabla^2\rho(r)$ values are calculated (−0.026 and −0.033, respectively). Negative $\nabla^2\rho(r)$ terms indicate covalent interactions (e.g., the $\nabla^2\rho(r)$ value for the Ge−Ge bond in H_3GeGeH_3 is −0.081),[21] while positive terms indicate that ionic bonding is dominant. These data, when taken in conjunction with the NBO analyses, point toward the presence of polar covalent Ge−Ge single bonds in the hindered digermene complexes **1** and **3**.

CONCLUSION

In summary, the synthesis of two stable parent digermene donor−acceptor complexes $LB{\cdot}H_2Ge{-}GeH_2{\cdot}W(CO)_5$ (LB = IPr, $IPrCH_2$) is reported. Both complexes are stable in the solid state for indefinite periods of time. However, mild heating in arene solvents leads to the formal extrusion of 1 equiv of GeH_2 to produce the germanium(II) dihydride adducts $LB{\cdot}GeH_2{\cdot}W(CO)_5$. The bonding in both of the H_2GeGeH_2 complexes was analyzed via DFT studies on structurally truncated model systems, and this investigation revealed the presence of polar covalent Ge−Ge bonds with significant electron density shuttled toward the $W(CO)_5$-bound Ge atoms. This work highlights the generality of the donor−acceptor methodology in intercepting complexes of novel main-group species that are typically unstable in the condensed phase as free entities. We are currently expanding the range of reactive species that can be isolated using this approach with a long-term goal of using these metastable complexes as molecular precursors to functional clusters and nanomaterials.

EXPERIMENTAL SECTION

Materials and Instrumentation. All reactions were performed using standard Schlenk line techniques under an atmosphere of nitrogen or in an inert-atmosphere glovebox (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system[24] manufactured by Innovative Technology, Inc., degassed (freeze−pump−thaw method), and stored under an atmosphere of nitrogen prior to use. $Li[BH_4]$, $Li[BD_4]$, $SnCl_2$, and $Cl_2Ge{\cdot}(dioxane)$ were purchased from Aldrich and used as received; cyclohexene and 2,3-dimethyl-1,3-butadiene were each obtained from Aldrich, dried over molecular sieves, and degassed prior to use. $IPr{\cdot}GeCl_2$,[4a] $IPr{\cdot}SnCl_2$,[4a] $(THF)_2SnCl_2{\cdot}W(CO)_5$,[13] and $IPrCH_2{\cdot}GeCl_2$[18] were prepared following literature procedures. ^1H, $^2H\{^1H\}$, ^{11}B, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian iNova-400 spectrometer and referenced externally to $SiMe_4$ (^1H and $^{13}C\{^1H\}$), $Si(CD_3)_4$ ($^2H\{^1H\}$), and $F_3B{\cdot}OEt_2$ (^{11}B), respectively. X-ray crystallographic analyses were performed by the X-ray Crystallography Laboratory at the University of Alberta. Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Infrared spectra were recorded on a Nicolet IR100 FTIR spectrometer as Nujol mulls between NaCl plates. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected.

X-ray Crystallography. Crystals of suitable quality for X-ray diffraction studies were removed from a vial in a glovebox and immediately covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was selected, mounted on a glass fiber, and quickly placed in a low -temperature stream of nitrogen on an X-ray diffractometer.[25] All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo Kα (compounds **2** and **3**) or Cu Kα (compound **1**) radiation with the crystals cooled to −100 °C. The data were corrected for absorption through Gaussian integration from the indexing of the crystal faces.[26] Structures were solved using the direct methods program SHELXS-97[27] (compounds **1** and **2**) or using the Patterson search/structure expansion facilities within the DIRDIF-2008 program suite[28] (compound **3**); structure refinement was accomplished using SHELXL-97.[27] The germanium-bound hydrogen atoms in **1** and **3** were located in the electron difference map and refined isotropically; however, the Ge−H distances in **1** were restrained to be 1.500(2) Å. All carbon-bound hydrogen atoms were assigned positions based on the sp^2 or sp^3 hybridization geometries of their attached carbon atoms and were given thermal parameters 20% greater than those of their parent atoms. A tabular listing of the crystallographic data for compounds **1**−**3** can be found in the Supporting Information (Table S1).

Synthetic Details. *Alternate Preparation of (THF)GeCl$_2$·W(CO)$_5$.* To a mixture of Cl_2Ge·(dioxane) (161 mg, 0.694 mmol) and $(THF)_2SnCl_2\cdot W(CO)_5$ (450 mg, 0.684 mmol) was added 6 mL of toluene. The reaction mixture was stirred for 3 h at room temperature to give a pale yellow solution over a white precipitate ($SnCl_2$).[29] The mother liquor was then filtered through Celite, and removal of the volatiles from the filtrate afforded $(THF)GeCl_2\cdot W(CO)_5$ as a pale yellow crystalline solid (361 mg, 98%). ^1H NMR (C_6D_6): δ 1.12 (m, 4H, C_4H_8O, THF), 3.59 (m, 4H, C_4H_8O, THF). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 24.7 (C_4H_8O, THF), 72.4 (C_4H_8O, THF), 195.5 (equat CO, $^1J_{W-C}$ = 124.9 Hz), 198.3 (ax CO). Anal. Calcd. for $C_9H_8Cl_2GeO_6W$: C, 20.03; H, 1.49. Found: C, 20.20; H, 1.51.

General Procedure for the Reaction of (THF)$_n$ECl$_2$·W(CO)$_5$ (n = 1, 2; E = Ge, Sn) with IPr·GeCl$_2$ and IPr·SnCl$_2$. In each case, 0.15−0.20 mmol of IPr·ECl_2 (E = Ge, Sn) was combined with an equimolar quantity of $(THF)_nECl_2\cdot W(CO)_5$ (n = 1, 2; E = Ge, Sn) in 6 mL of toluene. The reaction mixtures were then stirred for 6 h to give copious amounts of white precipitate. The volatiles were then removed, and the soluble fractions were extracted into C_6D_6 for ^1H and $^{13}C\{^1H\}$ NMR spectroscopic analysis, which indicated the exclusive presence of either IPr·$SnCl_2\cdot W(CO)_5$[4b] (eq 1) or IPr·$GeCl_2\cdot W(CO)_5$[4b] (eqs 2 and 3) as carbene-containing products.

*Synthesis of IPr·H$_2$Ge-GeH$_2$·W(CO)$_5$ (**1**).* To a mixture of IPr·$GeCl_2$ (56 mg, 0.11 mmol), $(THF)GeCl_2\cdot W(CO)_5$ (57 mg, 0.11 mmol), and Li[BH_4] (9.4 mg, 0.43 mmol) was added 6 mL of Et_2O. The reaction mixture was stirred for 20 min to give a yellow solution over a pale yellow precipitate (presumably LiCl). The reaction mixture was allowed to settle, and the mother liquor was filtered through Celite. Removal of the volatiles from the filtrate afforded a yellow solid, which was identified as a mixture of **1** (ca. 20%), IPr·$GeH_2\cdot W(CO)_5$ (ca. 40%), and IPr·$GeH_2\cdot BH_3$ (ca. 40%) by ^1H NMR spectroscopy. Spectroscopically pure **1** was isolated by fractional crystallization, by cooling a saturated Et_2O solution of the crude material layered with hexanes to −35 °C (18 mg, 20%). Despite the low yield, this preparation was reproducible. ^1H NMR (C_6D_6): δ 0.82 (d, $^3J_{HH}$ = 7.0 Hz, 12H, $CH(CH_3)_2$), 1.19 (d, $^3J_{HH}$ = 7.0 Hz, 12H, $CH(CH_3)_2$), 2.27 (septet, $^3J_{HH}$ = 7.0 Hz, 4H, $CH(CH_3)_2$), 3.05 (m, AA′XX′ pattern, 2H, $-GeH_2-$), 4.08 (m, AA′XX′ pattern, 2H, $-GeH_2-$), 6.30 (s, 2H, N−CH−), 6.96 (d, $^3J_{HH}$ = 7.5 Hz, 4H, ArH), 7.14 (t, $^3J_{HH}$ = 7.5 Hz, 2H, ArH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 22.8 ($CH(CH_3)_2$), 25.4 ($CH(CH_3)_2$), 29.2 ($CH(CH_3)_2$), 125.1 (−N−CH−), 125.4 (ArC), 132.2 (ArC), 132.5 (ArC), 144.9 (ArC), 163.7 (N-C-N), 201.7 (equat CO, $^1J_{W-C}$ = 125 Hz), 202.2 (ax CO). IR (Nujol/cm^{-1}): 1887 (br, ν(C−O)), 1945 (br, ν(C−O)), 1954 (sh, ν(Ge−H)), 1961 (s, ν(Ge−H)), 2047 (s, ν(C−O)). Anal. Calcd for $C_{32}H_{40}Ge_2N_2O_5W$: C, 44.60; H, 4.68; N, 3.25. Found: C, 44.17; H, 4.70; N, 3.13. Mp (°C): 65−67 (dec, turns red), 149−151 (melts).

*Synthesis of IPr·D$_2$Ge-GeD$_2$·W(CO)$_5$ (**1D**).* To a mixture of IPr·$GeCl_2$ (63 mg, 0.12 mmol), $(THF)GeCl_2\cdot W(CO)_5$ (64 mg, 0.12 mmol), and Li[BD_4] (13 mg, 0.51 mmol) was added 6 mL of Et_2O. The reaction mixture was stirred for 20 min at room temperature to give a yellow solution over a pale yellow precipitate (LiCl). The reaction mixture was allowed to settle, and the mother liquor was filtered through Celite to give a yellow filtrate. Removal of the volatiles from the filtrate afforded a yellow solid, which was identified as a mixture of **1D** (ca. 20%), IPr·$GeD_2\cdot W(CO)_5$ (ca. 40%),[4b] and IPr·$GeD_2\cdot BD_3$ (ca. 40%)[4b] by ^1H and ^{11}B NMR spectroscopy. Spectroscopically pure **1D** was isolated by fractional crystallization, by cooling a saturated Et_2O solution of the crude material layered with hexanes to −35 °C (19 mg, 19%). ^1H NMR (C_6D_6): essentially same as for **1** with the absence of the $-GeH_2-$ resonances at 3.05 and 4.08 ppm. $^2H\{^1H\}$ NMR (C_6H_6): δ 3.05 (s, $-GeD_2-$), 4.08 (s, $-GeD_2-$). IR (Nujol/cm^{-1}): similar to that for **1** except for the absence of the $-GeH_2-$ vibrations at 1961 and 1954 cm^{-1}, while $-GeD_2-$ stretching bands were observed at 1405 and 1407 cm^{-1}.

*Synthesis of IPrCH$_2$·Cl$_2$Ge-GeCl$_2$·W(CO)$_5$ (**2**).* To a mixture of IPr$CH_2\cdot GeCl_2$ (250 mg, 0.46 mmol) and $(THF)GeCl_2\cdot W(CO)_5$ (246 mg, 0.46 mmol) was added 8 mL of toluene. The reaction mixture was then stirred for 20 min at room temperature to give a pale solution over a yellow precipitate. The precipitate was isolated by filtration and dried under vacuum to yield **2** as a pale yellow powder (430 mg, 93%). Crystals suitable for X-ray crystallography were grown by cooling (−35 °C) a saturated solution of **2** in CH_2Cl_2 layered with hexanes. ^1H NMR (CD_2Cl_2): δ 1.19 (d, $^3J_{HH}$ = 7.0 Hz, 12H, $CH(CH_3)_2$), 1.40 (d, $^3J_{HH}$ = 7.0 Hz, 12H, $CH(CH_3)_2$), 2.60 (septet, $^3J_{HH}$ = 7.0 Hz, 4H, $CH(CH_3)_2$), 3.15 (s, 2H, $-CH_2-$), 7.40 (s, 2H, N−CH−), 7.45 (d, $^3J_{HH}$ = 7.5 Hz, 4H, ArH), 7.63 (t, $^3J_{HH}$ = 7.5 Hz, 2H, ArH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 21.9 ($-CH_2-$), 22.8 ($CH(CH_3)_2$), 26.6 ($CH(CH_3)_2$), 29.6 ($CH(CH_3)_2$), 124.6 (−N−CH−), 126.2 (ArC), 129.9 (ArC), 132.9 (ArC), 145.6 (ArC), 150.3 (N−C−N), 197.1 (equat CO), 201.6 (ax CO). IR (Nujol/cm^{-1}): 1919 (br, ν(C−O)), 1941 (br, ν(C−O)), 1983 (sh, ν(C−O)), 2065 (s, ν(C−O)). Anal. Calcd for $C_{33}H_{38}Cl_4Ge_2N_2O_5W$: C, 39.10; H, 3.78; N, 2.76. Found: C, 39.80; H, 3.88; N, 2.80. Mp (°C): 189−191 (dec, turns dark brown), 201−203 (melts).

*Synthesis of IPrCH$_2$·H$_2$Ge-GeH$_2$·W(CO)$_5$ (**3**).* To a mixture of IPr$CH_2\cdot Cl_2Ge-GeCl_2\cdot W(CO)_5$ (102 mg, 0.101 mmol) and Li[BH_4] (9.1 mg, 0.43 mmol) was added 10 mL of Et_2O. The reaction mixture was stirred for 30 min at room temperature to give a pale yellow slurry. The resulting precipitate was then allowed to settle, and the mother liquor was filtered through Celite to yield a pale yellow filtrate. Removal of the volatiles from the filtrate afforded **3** as a pale yellow powder (82 mg, 93%). Crystals suitable for X-ray crystallography were grown by cooling a saturated Et_2O solution of **3** layered with hexanes to −35 °C for 5 days. ^1H NMR (C_6D_6): δ 0.82 (d, $^3J_{HH}$ = 7.0 Hz, 12H, $CH(CH_3)_2$), 1.91 (d, $^3J_{HH}$ = 7.0 Hz, 12H, $CH(CH_3)_2$), 2.29 (t, $^3J_{HH}$ = 4.0 Hz, 2H, $-CH_2-$), 2.32 (septet, $^3J_{HH}$ = 7.0 Hz, 4H, $CH(CH_3)_2$), 3.23 (t, $^3J_{HH}$ = 4.0 Hz, 2H, $GeH_2-GeH_2-W(CO)_5$), 3.97 (pseudopentet, $^3J_{HH}$ = 4.0 Hz, 2H, $CH_2-GeH_2-GeH_2$), 6.13 (s, 2H, N−CH−), 6.97 (d, $^3J_{HH}$ = 7.2 Hz, 4H, ArH), 7.14 (t, $^3J_{HH}$ = 7.2 Hz, 2H, ArH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 9.9 ($-CH_2-$), 22.4 ($CH(CH_3)_2$), 25.7 ($CH(CH_3)_2$), 29.3 ($CH(CH_3)_2$), 121.9 (−N−CH−), 125.5 (ArC), 129.6 (ArC), 132.6 (ArC), 145.1 (ArC), 156.5 (N−C−N), 202.8 (equat CO), 205.5 (ax CO). IR (Nujol/cm^{-1}): 1865 (br, ν(C−O)), 1896 (br, ν(C−O)), 1950 (sh, ν(C−O)), 2028 (sh, ν(Ge−H)), 2044 (sh, ν(C−O)). Anal. Calcd for $C_{33}H_{42}Ge_2N_2O_5W$: C, 45.26; H, 4.83; N, 3.20. Found: C, 45.54; H, 4.99; N, 3.20. Mp (°C): 61−63 (dec, turns red), 87−89 (melts).

*Synthesis of IPrCH$_2$·D$_2$Ge-GeD$_2$·W(CO)$_5$ (**3D**).* To a mixture of IPr$CH_2\cdot Cl_2Ge-GeCl_2\cdot W(CO)_5$ (75 mg, 0.074 mmol) and Li[BD_4] (7.8 mg, 0.30 mmol) was added 6 mL of Et_2O. The reaction mixture was stirred for 30 min at room temperature to give a pale yellow slurry. The resulting precipitate was then allowed to settle, and the resulting mother liquor was filtered through Celite to give a pale yellow filtrate. Removal of the volatiles from the filtrate afforded **3D** as a pale yellow powder (62 mg, 95%). ^1H NMR (C_6D_6): essentially the same as for **3** with the absence of the $-GeH_2-$ resonances at 3.23 and 3.97 ppm. $^2H\{^1H\}$ NMR (C_6H_6): δ 3.23 (s, $-GeD_2-$), 3.97 (s, $-GeD_2-$). IR (Nujol/cm^{-1}): similar to that for **3** except for the absence of the $-GeH_2-$ vibration at 2028 cm^{-1} and the $-GeD_2-$ stretching frequency could not be located due to overlap with aromatic C═C vibrations.

*Thermolysis of IPr·H$_2$Ge-GeH$_2$·W(CO)$_5$ (**1**).* A solution of IPr·$H_2Ge-GeH_2\cdot W(CO)_5$ (ca. 8 mg) in C_6D_6 was kept in a J. Young NMR tube at room temperature for 48 h. ^1H NMR analysis (C_6D_6) after that period showed the complete conversion of **1** into IPr·$GeH_2\cdot W(CO)_5$.[4b]

*Thermolysis of IPrCH$_2$·H$_2$Ge-GeH$_2$·W(CO)$_5$ (**3**).* A solution of IPr$CH_2\cdot H_2Ge-GeH_2\cdot W(CO)_5$ (20 mg, 0.022 mmol) in 8 mL of toluene was heated to 60 °C for 24 h to give a pale yellow solution along with a dark brown precipitate on the walls of the reaction flask. The reaction mixture was filtered through Celite, and the volatiles were then removed from the filtrate under vacuum to yield a pale yellow powder. ^{1}H NMR analysis (C_6D_6) of the powder showed the formation of $IPrCH_2{\cdot}GeH_2{\cdot}W(CO)_5$[4c] as the sole soluble decomposition product.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables, text, figures, and CIF files giving full crystallographic details for compounds **1**−**3** and $IPr{\cdot}GeCl_2{\cdot}W(CO)_5$, and computational studies on the model systems $ImMe_2{\cdot}H_2Ge\text{-}GeH_2{\cdot}W(CO)_5$ (**1$_{Me}$**) and $ImMe_2CH_2{\cdot}H_2Ge\text{-}GeH_2{\cdot}W(CO)_5$ (**3$_{Me}$**) and the parent hydrides $H_3Ge{-}GeH_3$ and $H_2Ge{=}GeH_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*A.B.: e-mail, alex.brown@ualberta.ca; tel, (+1) 780-492-1854.
*E.R.: e-mail, erivard@ualberta.ca; tel, (+1) 780-492-4255.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada (Discovery Grants to A.B. and E.R.), the Canada Foundation of Innovation, and Alberta Innovates-Technology Futures (New Faculty Award to E.R.). Compute/Calcul Canada is acknowledged for providing computational resources.

■ REFERENCES

(1) (a) Vogel, U.; Timoshkin, A. Y.; Scheer, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4409. (b) Bonyhady, S. J.; Collis, D.; Frenking, G.; Holzmann, N.; Jones, C.; Stasch, A. *Nat. Chem.* **2010**, *2*, 865. (c) Präsang, C.; Stoelzel, M.; Inoue, S.; Meltzer, A.; Driess, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 10002. (d) Kinjo, R.; Donnadieu, B.; Celik, M. A.; Frenking, G.; Bertrand, G. *Science* **2011**, *333*, 610.

(2) (a) Power, P. P. *Nature* **2010**, *463*, 171. (b) Rivard, E.; Power, P. P. *Dalton Trans.* **2008**, 4336. (c) Protchenko, A. V.; Birjkumar, K. H.; Dange, D.; Schwarz, A. D.; Vidovic, D.; Jones, C.; Kaltsoyannis, N.; Mountford, P.; Aldridge, S. *J. Am. Chem. Soc.* **2012**, *134*, 6500. (d) Abraham, M. Y.; Wang, Y.; Xie, Y.; Wei, P.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2011**, *133*, 8874. (e) Zhang, S.-H.; Yeong, H.-X.; Xi, H.-W.; Lim, K. H.; So, C.-W. *Chem. Eur. J.* **2010**, *16*, 10250. (f) Rodriguez, R.; Gau, D.; Contie, Y.; Kato, T.; Saffron-Merceron, N.; Baceiredo, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 11492. (g) Stoelzel, M.; Präsang, C.; Inoue, S.; Enthaler, S.; Driess, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 399. (h) Jana, A.; Ghoshal, D.; Roesky, H. W.; Objartel, I.; Schwab, G.; Stalke, D. *J. Am. Chem. Soc.* **2009**, *131*, 1288. (i) Eichler, B. E.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 8785. (j) Khan, S.; Samuel, P. P.; Michel, R.; Dieterich, J. M.; Mata, R. A.; Demers, J.-P.; Lange, A.; Roesky, H. W.; Stalke, D. *Chem. Commun.* **2012**, *48*, 4890.

(3) (a) Jasinski, J. M.; Gates, S. M. *Acc. Chem. Res.* **1991**, *24*, 9. (b) Xu, C.; Beeler, R. T.; Grzybowski, G. J.; Chizmeshya, A. V. G.; Smith, D. J.; Menéndez, J.; Kouvetakis, J. *J. Am. Chem. Soc.* **2012**, *134*, 20756. (c) Chizmeshya, A. V. G.; Ritter, C. J.; Hu, C.; Tice, J. B.; Tolle, J.; Nieman, R. A.; Tsong, I. S. T.; Kouvetakis, J. *J. Am. Chem. Soc.* **2006**, *128*, 6919. (d) Gencarelli, F.; Vincent, B.; Souriau, L.; Richard, O.; Vandervorst, W.; Loo, R.; Caymax, M.; Heyns, M. *Thin Solid Films* **2012**, *520*, 3211. (e) Veinot, J. G. C. *Chem. Commun.* **2006**, 4160. (f) Wang, C.-F.; Xie, S.-Y.; Lin, S.-C.; Cheng, X.; Zhang, X.-H.; Huang, R.-B.; Zheng, L.-S. *Chem. Commun.* **2004**, 1766.

(4) (a) Thimer, K. C.; Al-Rafia, S. M. I.; Ferguson, M. J.; McDonald, R.; Rivard, E. *Chem. Commun.* **2009**, 7119. (b) Al-Rafia, S. M. I.; Malcolm, A. C.; Liew, S. K.; Ferguson, M. J.; Rivard, E. *J. Am. Chem. Soc.* **2011**, *133*, 777. (c) Al-Rafia, S. M. I.; Malcolm, A. C.; Liew, S. K.; Ferguson, M. J.; McDonald, R.; Rivard, E. *Chem. Commun.* **2011**, 6987. (d) Al-Rafia, S. M. I.; Malcolm, A. C.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Chem. Commun.* **2012**, *48*, 1308. (e) Al-Rafia, S. M. I.; Malcolm, A. C.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 8354. (f) Inoue, S.; Driess, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 5614.

(5) (a) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354. (b) Fischer, R. C.; Power, P. P. *Chem. Rev.* **2010**, *110*, 3877. (c) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479. (d) Grev, R. S. *Adv. Organomet. Chem.* **1991**, *33*, 125.

(6) (a) Dolgonos, G. *Chem. Phys. Lett.* **2008**, *466*, 11. (b) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130. (c) Grev, R. S.; Schaefer, H. F., III; Baines, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 9458. (d) Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1994**, *116*, 3667.

(7) For reviews covering the experimental validation of *trans*-bent geometries within the heavier group 14 element alkenes, see: (a) Power, P. P. *J. Chem. Soc., Dalton Trans.* **1998**, 2939. (b) Weidenbruch, M. *Organometallics* **2003**, *22*, 4348. The parent systems, H_2EEH_2 have also been isolated in inert matrices: (c) Maier, G.; Reisenauer, H. P.; Glatthaar, J. *Chem. Eur. J.* **2002**, 4383. (d) Andrews, L.; Wang, X. *J. Phys. Chem. A* **2002**, *106*, 7696. (e) Carrier, W.; Zheng, W.; Osamura, Y.; Kaiser, R. I. *Chem. Phys.* **2006**, *330*, 275. (f) Wang, X.; Andrews, L. *J. Am. Chem. Soc.* **2003**, *125*, 6581. (g) Sari, L.; McCarthy, M. C.; Schaefer, H. F., III; Thaddeus, P. *J. Am. Chem. Soc.* **2003**, *125*, 11409.

(8) (a) Cowley, A. H. *Chem. Commun.* **2004**, 2369. (b) Burford, N.; Ragogna, P. J. *Dalton Trans.* **2002**, 4307. (c) Protasiewicz, J. D. *Eur. J. Inorg. Chem.* **2012**, 4539.

(9) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 5683.

(10) For an alternate preparation of $IPr{\cdot}GeCl_2$, see: Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 9701.

(11) See the Supporting Information for full crystallographic details.

(12) (a) Jutzi, P.; Steiner, W. *Chem. Ber.* **1976**, *109*, 3473. (b) Strohmeier, W.; Müller, F.-J. *Chem. Ber.* **1969**, *102*, 3608.

(13) Balch, A. L.; Oram, D. E. *Organometallics* **1988**, *7*, 155.

(14) (a) Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G *Organometallics* **2001**, *20*, 4806. (b) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232. (c) Leung, W.-P.; So, C.-W.; Chong, K.-H.; Kan, K.-W.; Chan, H.-S.; Mak, T. C. W. *Organometallics* **2006**, *25*, 2851. (d) Arii, H.; Nakadate, F.; Mochida, K. *Organometallics* **2009**, *28*, 4909. (e) Al-Rafia, S. M. I.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Chem. Eur. J.* **2012**, *18*, 13810. (f) Lower Ge−H stretching frequencies (1722 and 1733 cm^{-1}) were recently found within hindered nacnac Ge(II) hydride complexes: Choong, S. L.; Woodul, W. D.; Schenk, C.; Stasch, A.; Richards, A. F.; Jones, C. *Organometallics* **2011**, *30*, 5543.

(15) Amadoruge, M. L.; Weinert, C. S. *Chem. Rev.* **2008**, *108*, 4253.

(16) Ruddy, A. J.; Rupar, P. A.; Bladek, K. J.; Allan, C. J.; Avery, J. C.; Baines, K. M. *Organometallics* **2010**, *29*, 1362.

(17) Oláh, J.; De Proft, F.; Veszprémi, T.; Geerlings, P. *J. Phys. Chem. A* **2005**, *109*, 1608.

(18) Al-Rafia, S. M. I.; Momeni, M. R.; McDonald, R.; Ferguson, M. J.; Brown, A.; Rivard, E. *Angew. Chem., Int. Ed.* **2013**, DOI: 10.1002/anie.201302767.

(19) Beattie, I. R.; Jones, P. J.; Reid, G.; Webster, M. *Inorg. Chem.* **1998**, *37*, 6032.

(20) Khan, S.; Gopakumar, G.; Thiel, W.; Alcarazo, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 5644.

(21) See the Supporting Information for full computational details.

(22) (a) Nutt, W. R.; McKee, M. L. *Inorg. Chem.* **2007**, *46*, 7633. (b) Malcolm, A. C.; Sabourin, K. J.; McDonald, R.; Ferguson, M. J.;

Rivard, E. *Inorg. Chem.* **2012**, *51*, 12905. (c) Chen, X.; Gallucci, J.; Campana, C.; Huang, Z.; Kumar Lingam, H.; Shore, S. G.; Zhao, J.-C. *Chem. Commun.* **2012**, *48*, 7943.

(23) For a summary of dative vs covalent bonding modes in the main group, see: Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992.

(24) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(25) Hope, H. *Prog. Inorg. Chem.* **1994**, *41*, 1.

(26) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(27) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(28) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Smits, J. M. M.; Garcia-Garcia, S.; Gould, R. O. *DIRDIF-2008*; Crystallography Laboratory, Radboud University, Nijmegen, The Netherlands, 2008.

(29) The melting point of the precipitate matched that reported for commercially available $SnCl_2$ (mp 246 °C; Aldrich Chemical Co., 99% purity).