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Application of the Donor−Acceptor Concept to Intercept Low Oxidation State Group 14 Element Hydrides using a Wittig Reagent as a Lewis Base

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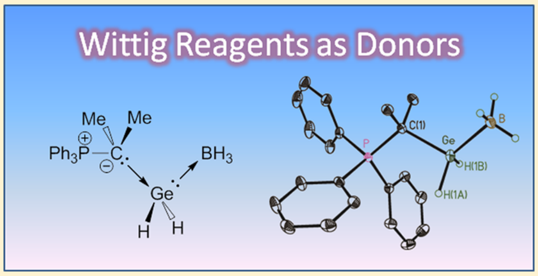
Supporting Information

ABSTRACT: This article outlines our attempts to stabilize the Group 14 element dihydrides, GeH_2 and SnH_2, using commonly employed phosphine and pyridine donors; in each case, elemental Ge and Sn extrusion was noted. However, when these phosphorus and nitrogen donors were replaced with the ylidic Wittig ligand $Ph_3P{=}CMe_2$, stable inorganic methylene complexes (EH_2) were obtained, demonstrating the utility of this under-explored ligand class in advancing main group element coordination chemistry.

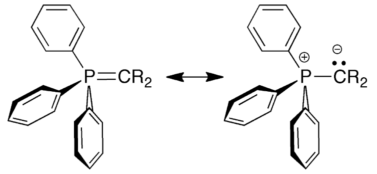


INTRODUCTION

The use of electron-donating ligands to intercept/stabilize reactive inorganic element centers is a widely explored concept in inorganic chemistry. Recently, *N*-heterocyclic carbenes (NHCs) have received considerable attention in this regard due to their ease of synthesis and ability to tune the steric bulk about the ligating carbon centers.[1] A commonly employed NHC in formally low oxidation state main group element chemistry is IPr (IPr = $[(HCNDipp)_2C:]$, Dipp = $2,6\text{-}{}^{i}Pr_2C_6H_3$), which has been used to access stable complexes of E_2 (E = B, Si, Ge, Sn, P, and As)[2] and related species with unusual/novel bonding environments.[3] Our group has also employed IPr in conjunction with suitable Lewis acidic acceptors (BH_3 and $W(CO)_5$) to prepare various inorganic Group 14 element methylene EH_2 and ethylene $H_2EE'H_2$ complexes (E and E′ = Si, Ge, and/or Sn) via a general donor−acceptor protocol.[4] In addition, we have shown that many of these parent main group hydrides can be accessed using the ylidic *N*-heterocyclic olefin (NHO) donor, $IPr{=}CH_2$ [$IPr{=}CH_2$ = $(HCNDipp)_2C{=}CH_2$] in place of IPr.[4e,f,5] Added interest from this work stems from the implication of EH_2 species, such as the silylene $:SiH_2$, as key intermediates in the growth of semiconducting films from gas phase precursors (e.g., SiH_4).[6]

In this article we detail our attempts to prepare low oxidation state Group 14 element hydride complexes with the aid of common phosphine- and pyridine-based donors. In addition we demonstrate that the Wittig reagent $Ph_3P{=}CMe_2$[7] is an excellent ligand for molecular main group chemistry by virtue of the nucleophilic character of the terminal carbon atom (Scheme 1). Furthermore, the ability to rapidly prepare structural variants of this Wittig reagent from inexpensive reagents makes this system advantageous over many well-known *N*-heterocyclic carbene-based donors. It should be mentioned that, while the use of related Wittig reagents[8] as ligands is known for transition metals and actinides,[9] well-defined coordination chemistry involving R'_3PCR_2 donors within the main group remains a largely untouched area.[10]

Scheme 1. Representative Resonance Forms for Ph_3PCR_2



RESULTS AND DISCUSSION

While carbon-based donors are known to bind/stabilize main group element polyhydrides,[3a,4,5a,11] we desired to test the scope of the donor−acceptor protocol by including phosphine- and pyridine-based Lewis bases (LB) to yield new adducts of the general form $LB{\cdot}EH_2{\cdot}LA$ (LA = Lewis acid). A motivation for such studies would be to later study the controlled thermolysis of these complexes to generate Group 14 metal coatings and/or nanoparticles.[4g] It should be mentioned that nanomaterials are often capped with phosphorus- or nitrogen-containing ligands to engender solubility and to prevent quenching of luminescence by surface reactive sites.[12] Moreover the use of amines and phosphines within the context of low oxidation state Group 14 coordination chemistry has precedence.[13]

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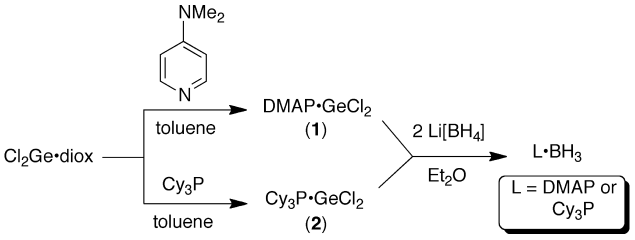
We began this study by preparing Ge(II) dihalide adducts of the widely explored donors, 4-dimethylaminopyridine (DMAP) and tricyclohexylphosphine (Cy_3P). Specifically, these adducts were obtained by combining either DMAP or Cy_3P with Cl_2Ge·dioxane in toluene to afford the respective Ge(II) dichloride complexes DMAP·$GeCl_2$ (**1**) and $Cy_3P·GeCl_2$ (**2**)[14] as air-sensitive (yet thermally stable) colorless solids (Scheme 2).

Scheme 2. Synthesis of DMAP and Cy_3P Adducts of $GeCl_2$ (1 and 2) and Interaction of These Species with Excess $Li[BH_4]$



While the synthesis of the DMAP adduct **1** proceeded in a quantitative fashion, the synthesis of $Cy_3P·GeCl_2$ (**2**) routinely yielded a $[Cy_3PH]^+$-containing byproduct (presumably as a $GeCl_3^-$ salt)[15] which necessitated further purification by fractional crystallization from toluene/hexanes to afford pure **2**. Both compounds **1** and **2** have been structurally authenticated by X-ray crystallography (Figure 1), and as expected, pyramidalized Ge centers are present with an angle sum at Ge ($\sum$Ge) for compound **1** of 280.83(7)° [$\sum$Ge for compound **2** = 284.33(4)°].

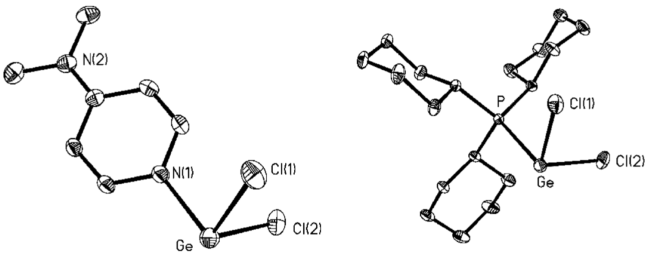
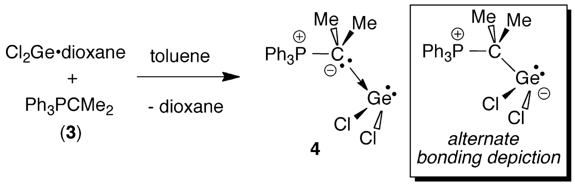


Figure 1. Molecular structures of DMAP·$GeCl_2$ (**1**) (left) and $Cy_3P·GeCl_2$ (**2**) (right) with thermal ellipsoids at the 30% probably level. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: *Compound 1*: Ge–N(1) 2.028(2), Ge–Cl(1) 2.2881(8), Ge–Cl(2) 2.2907(9); N–Ge–Cl(1) 93.03(7), N–Ge–Cl(2) 92.49(7), Cl(1)–Ge–Cl(2) 95.31(3). *Compound 2*: Ge–P 2.5087(7), Ge–Cl(1) 2.2782(7), Ge–Cl(2) 2.2723(7); P–Ge–Cl(1) 93.96(3), P–Ge–Cl(2) 93.21(2), Cl(1)–Ge–Cl(2) 97.16(2).

When DMAP·$GeCl_2$ (**1**) and $Cy_3P·GeCl_2$ (**2**) were each treated with the soluble hydride source, lithium borohydride $Li[BH_4]$, the only spectroscopically identifiable products were the known adducts, DMAP·BH_3 and $Cy_3P·BH_3$, respectively; these reactions also afforded copious amounts of gray precipitate which is assumed to be elemental germanium (Scheme 2). These observations are in contrast to what is found with the strongly donating *N*-heterocyclic carbene IPr, which yields IPr·$GeH_2·BH_3$ under similar reaction conditions as an isolable colorless solid.[4a]

With the goal of expanding the range of suitable donors for stabilizing low oxidation state main group hydrides, our attention shifted to exploring Wittig reagents $R'_3P{=}CR_2$ as Lewis bases.[10] This study was motivated by the structural parallels that exist between Wittig reagents and *N*-heterocyclic olefins (such as IPr=CH_2) due to the mutual presence of ylidic bonding, leading to significant electron density being positioned at a terminal carbon atom (Scheme 1).[5] Prior studies with the donor $Ph_3P{=}CH_2$ revealed a potential ligand degradation pathway wherein deprotonation of a terminal methylene unit occurs in the presence of electron-deficient main group compounds to yield $R_xE\text{-}CH{=}PPh_3$ species.[16] Accordingly, we focused on the phosphorus ylide, $Ph_3P{=}CMe_2$ (**3**),[7] which does not contain acidic hydrogen atoms adjacent to the carbon ligation site. Fortunately the methylated donor $Ph_3P{=}CMe_2$ (**3**) is conveniently prepared in high yield as a moisture-sensitive red solid by treating the commercially available phosphonium salt $[Ph_3P^iPr]I$ with ^nBuLi in toluene, followed by removal of the LiI byproduct by filtration. Crystals of **3** were also analyzed by single-crystal X-ray crystallography, and the resulting molecular structure can be found in the Supporting Information (Figure S1).[17]

The formation of the stable Ge(II) dihalide adduct $Ph_3PCMe_2·GeCl_2$ (**4**) was accomplished by combining equimolar amounts of $Ph_3P{=}CMe_2$ (**3**) and Cl_2Ge·dioxane in toluene solvent (eq 1). Compound **4** can be obtained in analytically pure form via recrystallization from CH_2Cl_2/hexanes, and the crystallographically determined structure of this species is presented as Figure 2. The binding of the Wittig reagent **3** to a $GeCl_2$ unit (to form **4**) is accompanied by a significant ^{31}P NMR shift from 9.8 to 37.0 ppm. The methyl substituents within the Ph_3PCMe_2 donor in **4** appear as a doublet resonance at 1.77 ppm in the ^1H NMR spectrum, and this signal is shifted upfield in comparison to the methyl resonance within the free ligand **3** (2.17 ppm). $Ph_3PCMe_2·GeCl_2$ exhibits a pyramidal geometry about germanium [$\sum$Ge = 287.42(8)°] consistent with the presence of a lone pair at Ge. As will be seen in all complexes of Ph_3PCMe_2 in this study, the binding of the nucleophilic carbon center in Ph_3PCMe_2 to a



(1)

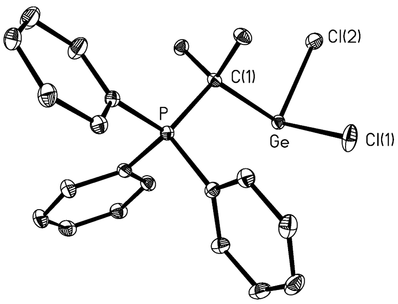
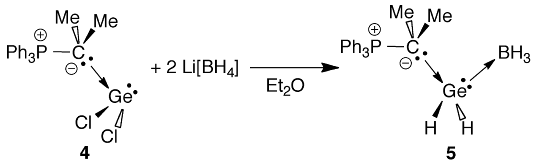


Figure 2. Molecular structure of $Ph_3PCMe_2·GeCl_2$ (**4**) with thermal ellipsoids at the 30% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge–Cl(1) 2.2735(6), Ge–Cl(2) 2.3106(6), Ge–C(1) 2.1535(19), P–C(1) 1.6785(18); C(1)–Ge–Cl(1) 99.07(6), C(1)–Ge–Cl(2) 93.25(5), Cl(1)–Ge–Cl(2) 95.10(2).

$GeCl_2$ unit results in elongation of the intraligand P–C bond from 1.6785(18) Å in free Ph_3PCMe_2 (**3**) to 1.807(2) Å in $Ph_3PCMe_2\cdot GeCl_2$; this effect can be rationalized by a reduction in C(p) → P–C(σ^*) hyperconjugative interactions once **3** participates in adduct formation. The formally dative C–Ge bond length in $Ph_3PCMe_2\cdot GeCl_2$ (**4**) [2.1535(19) Å] is slightly elongated with respect to the corresponding distance in IPr·$GeCl_2$ [2.112(2) Å];[4a] direct structural comparison of **4** with the ylide adduct $IPrCH_2\cdot GeCl_2$ is not possible at the moment due to a lack of suitable X-ray crystallographic data for $IPrCH_2\cdot GeCl_2$.[5a]

When $Ph_3PCMe_2\cdot GeCl_2$ (**4**) was treated with 2 equiv of Li[BH_4] in diethyl ether, clean Cl/H exchange transpired to yield the isolable germanium dihydride–borane adduct $Ph_3PCMe_2\cdot GeH_2\cdot BH_3$ (**5**) (eq 2). The successful installation of hydride functionality at germanium in **5** was evidenced by ^1H NMR spectroscopy, which revealed the presence of a new broad resonance at 4.63 ppm. In addition, IR spectroscopy clearly displayed a Ge–H stretching band at 1975 cm^{-1} which is similar in value to the vibration at 1987 cm^{-1} belonging to a GeH_2 moiety in IPr·$GeH_2\cdot BH_3$.[4a] Compound **5** gave a ^{11}B NMR spectrum with a quartet resonance at −39.4 ppm (in C_6D_6; $^1J_{BH}$ = 95.4 Hz) that was assigned to the terminal BH_3 unit, which is comparable with the ^{11}B NMR resonance observed previously for IPr·$GeH_2\cdot BH_3$ (−40.0 ppm; $^1J_{BH}$ = 99 Hz).[4a] The deutero analogue of **5**, $Ph_3CMe_2\cdot GeD_2\cdot BD_3$ (**5D**) was also synthesized by combining 2 equiv of Li[BD_4] with **4** in Et_2O. As expected, the $^2H\{^1H\}$ NMR spectrum of **5D** consisted of broad peaks positioned at 4.63 and 1.56 ppm, corresponding to GeD_2 and BD_3 units, respectively.



(2)

As shown in Figure 3, $Ph_3PCMe_2\cdot GeH_2\cdot BH_3$ (**5**) exhibits a tetrahedral coordination environment at Ge with crystallographically determined Ge–H bond distances of 1.477(18) and 1.46(2) Å. The adjacent Ge–B and Ge–C bond lengths are 2.0786(17) and 2.0460(13) Å, respectively, which are elongated by ~0.3 Å in comparison to the related distances found in the *N*-heterocyclic carbene adduct IPr·$GeH_2\cdot BH_3$ [Ge–B = 2.053(3) Å; Ge–C = 2.011(2) Å]. Therefore, the metrical data suggest that Ph_3PCMe_2 is a weaker donor than the *N*-heterocyclic carbene, IPr (*vide infra*).

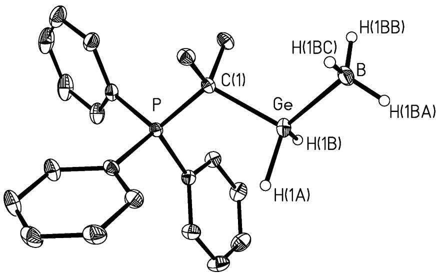


Figure 3. Molecular structure of $Ph_3PCMe_2\cdot GeH_2\cdot BH_3$ (**5**) with thermal ellipsoids at the 30% probability level. All carbon-bound hydrogen atoms and THF solvate have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge–B 2.0786(17), Ge–C (1) 2.0460(13), Ge–H(1A) 1.477(18), Ge–H(1B) 1.46(2); C(1)–Ge–B 111.26(6), C(1)–Ge–H(1A) 103.5(7), C(1)–Ge–H(1B) 100.8(8), H(1A)–Ge–H(1B) 103.4(11), H–B–H 109.1(16) to 113.6(18).

The Wittig reagent-appended germanium(II) dihydride complex $Ph_3PCMe_2\cdot GeH_2\cdot BH_3$ (**5**) showed similar thermal stability in solution in relation to IPr·$GeH_2\cdot BH_3$. For example, we heated a toluene-d_8 solution of $Ph_3PCMe_2\cdot GeH_2\cdot BH_3$ (**5**) in a J-Young NMR tube at 100 °C for 24 h which led to the decomposition of **5** to afford $Ph_3P\cdot BH_3$[18] (>95% conversion according to ^{31}P NMR spectroscopy; δ = 21.7); for comparison, IPr·$GeH_2\cdot BH_3$ decomposes in hot toluene to yield IPr·BH_3.[4a] $^{11}B\{^1H\}$ NMR spectroscopy on the product mixture formed when **5** is heated also confirmed the presence of $Ph_3P\cdot BH_3$ (d, δ = 42.1, $^1J_{BP}$ = 43.7 Hz) with the accompanying formation of a volatile product at ~80 ppm which is tentatively assigned as being the triorganoborane $^iPr_3B$ (literature ^{11}B NMR shift = 83.7 ppm in C_6D_6).[19] One possible route for this decomposition process is hydride transfer[20] from an E–H group (E = Ge or B) to a CMe_2 carbon atom of the Wittig donor, leading to population of a C–P σ^* orbital and release of PPh_3, which is later trapped by liberated BH_3 to form $Ph_3P\cdot BH_3$. The insoluble precipitate which formed during the thermolysis of $Ph_3PCMe_2\cdot GeH_2\cdot BH_3$ (**5**) in toluene was identified as elemental germanium according to EDX analysis (Figure S3 in SI);[17] in addition this solid was imaged by SEM which revealed the formation of a bulk material with a globular morphology (Figure S4 in SI).[17]

It appears that $Ph_3P{=}CMe_2$ is a weaker electron pair donor than the carbene IPr, as $Ph_3PCMe_2\cdot GeH_2\cdot BH_3$ (**5**) rapidly reacts with a stoichiometric amount of IPr to afford IPr·$GeH_2\cdot BH_3$ and free $Ph_3P{=}CMe_2$ as major products via a Lewis base exchange reaction, as determined by NMR spectroscopy. We also attempted to prepare the Ge(II) hydride complex $Ph_3PCMe_2\cdot GeH_2$ by treating the $GeCl_2$ adduct $Ph_3PCMe_2\cdot GeCl_2$ (**4**) with the milder hydride source K[HB^sBu_3]. It was hoped that hydride delivery would occur to yield the less reactive and more hindered borane, $^sBu_3B$, as a byproduct, thus suppressing decomplexation of the Lewis base from Ge via LB–borane adduct formation.[4a] However, $Ph_3PCMe_2\cdot GeCl_2$ (**4**) reacts with 2 equiv of K[HB^sBu_3] to yield free PPh_3 and $^sBu_3B$[21] according to ^{31}P and ^{11}B NMR spectroscopy, along with the formation of gray precipitate (presumably elemental Ge).

Of note, our previous attempts to form $IPrCH_2\cdot GeH_2\cdot BH_3$ led to loss of germanium metal and the isolation of $IPrCH_2\cdot BH_3$ as the sole donor-containing product.[5a] Thus, Ph_3PCMe_2 is likely a stronger donor than the *N*-heterocyclic olefin $IPrCH_2$ and the previously discussed Lewis bases Cy_3P and DMAP. The mechanism by which LB·$GeH_2\cdot BH_3$ complexes (LB = Lewis base) degrade to yield the boranes LB·BH_3 is unknown at this time. Either LB–Ge or Ge–B bond scission (or even hydride transfer from Ge or B[20]) could be involved as the key step in the decomposition process; we are currently exploring possible LB·$GeH_2\cdot BH_3$ degradation pathways by computational methods.

Analogous coordination and hydride transfer chemistry was explored between the Wittig reagent $Ph_3P{=}CMe_2$ and Sn(II) halides. As a start, we prepared the Sn(II) halide adduct $Ph_3PCMe_2\cdot SnCl_2$ (**6**) from the direct reaction of $Ph_3P{=}CMe_2$ and $SnCl_2$ in toluene. This reaction proceeds to high yield if conducted over a short time frame of 3 h. If this reaction is allowed to proceed for longer periods (>24 h), then increasing amounts of the phosphonium salt [Ph_3PCHMe_2]$SnCl_3$

occurs[17] as evidenced by the emergence of a new ^{31}P signal at 30.9 ppm. $Ph_3PCMe_2{\cdot}SnCl_2$ (**6**) was also characterized by single-crystal X-ray crystallography, and the molecular structure of this adduct is found in Figure 4. The most salient metrical parameters of **6** include a Sn−C bond length of 2.3518(14) Å and a sum of the bond angles at Sn of 273.61(6)°; this latter value is substantially smaller than in the Ge congener **4** [287.42(8)°] as is expected for an increase in s-character within the sterochemically active Sn lone pair in $Ph_3PCMe_2{\cdot}SnCl_2$ (**6**).

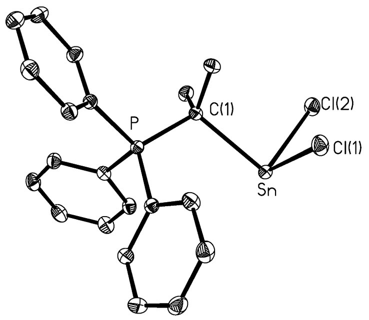
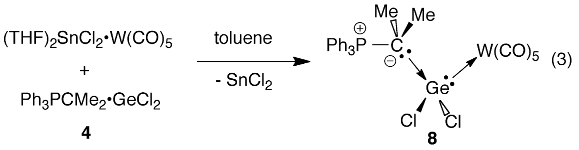


Figure 4. Molecular structure of $Ph_3PCMe_2{\cdot}SnCl_2$ (**6**) with thermal ellipsoids at the 30% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn−C(1) 2.3518(14), Sn−Cl(1) 2.4854(4), Sn−Cl(2) 2.4852(4), P−C(1) 1.8036(15); Cl(1)−Sn−Cl(2) 87.828(15), C(1)−Sn−Cl(1) 94.87(4), C(1)−Sn−Cl(2) 90.91(4).

When $Ph_3PCMe_2{\cdot}SnCl_2$ (**6**) was treated with 2 equiv of $Li[BH_4]$ in Et_2O, the formation of $Ph_3PCMe_2{\cdot}BH_3$ (**7**) along with a black precipitate (presumably metallic tin) was observed. Compound **7** was reported previously by Bestmann and co-workers,[10a] and we independently prepared this species from Ph_3PCMe_2 and $THF{\cdot}BH_3$ in order to obtain structural characterization by X-ray crystallography (Figure S2 in SI).[17]

We also attempted to prepare the germastannene adduct $Ph_3PCMe_2{\cdot}Cl_2Ge\text{-}SnCl_2{\cdot}W(CO)_5$ by combining the nucleophilic Ge(II) adduct $Ph_3PCMe_2{\cdot}GeCl_2$ (**4**) with the known stannylene complex, $(THF)_2{\cdot}SnCl_2{\cdot}W(CO)_5$.[22] However, as noted previously within the IPr adduct series,[4f] $SnCl_2/GeCl_2$ exchange at tungsten transpired to afford the thermally stable germylene complex, $Ph_3PCMe_2{\cdot}GeCl_2{\cdot}W(CO)_5$ (**8**) (eq 3).



Compound **8** was also characterized by a single-crystal X-ray diffraction study (Figure 5), and the geometric parameters about the Ge center in **8** are similar to those found in the NHO adduct $IPrCH_2{\cdot}GeCl_2{\cdot}W(CO)_5$, with a slightly elongated Ge−C dative linkage in **8** [2.0826(15) Å] observed relative to the $IPrCH_2$ adduct [2.053(2) Å].[5a]

It is known from our prior studies, and confirmed above, that the synthesis of Sn(II) dihydride (SnH_2) complexes is a more challenging endeavor than for GeH_2 adducts as a result of decreased Lewis acidic and basic character at Sn, leading to weaker coordinative interactions.[4g] In order to increase the eventual Lewis acidity of a coordinated SnH_2 unit, we decided to use a highly electron-deficient $W(CO)_5$ group as the acceptor moiety within our donor−acceptor protocol; a related approach worked well for the isolation of the formal Sn(II) dihydride adducts, $IPr{\cdot}SnH_2{\cdot}W(CO)_5$ and $IPrCH_2{\cdot}SnH_2{\cdot}W(CO)_5$.[4b,5a] The requisite $SnCl_2$ precursor to a tin hydride−Wittig reagent complex, $Ph_3P{=}CMe_2{\cdot}SnCl_2{\cdot}W(CO)_5$ (**9**), was prepared in nearly quantitative yield as a colorless solid by a THF solvent displacement reaction between the known tin chloride tungsten pentacarbonyl adduct $(THF)_2{\cdot}SnCl_2{\cdot}W(CO)_5$ and the two-electron Wittig donor Ph_3PCMe_2 (**3**) (eq 4). The formation of $Ph_3PCMe_2{\cdot}SnCl_2{\cdot}W(CO)_5$ (**9**) was accompanied by a large change in chemical shift in the ^{31}P NMR spectrum relative to free $Ph_3P{=}CMe_2$ (9.8 ppm) to yield a singlet resonance at 38.2 ppm with flanking tin satellites ($^3J_{PSn}$ = 44.5 Hz). The IR spectrum of **9** shows two resolvable stretching bands at 1930 and 2060 cm^{-1} consistent with a $LB{\cdot}W(CO)_5$ environment (LB = Lewis base), while a ^{119}Sn NMR resonance at 131.3 ppm in C_6D_6 was located which is similar to the resonance observed for $Ph_3PCMe_2{\cdot}SnCl_2$ (**6**) (113.3 ppm), despite the change in coordination number at tin. The related *N*-heterocyclic carbene adduct $IPr{\cdot}SnCl_2{\cdot}W(CO)_5$ has a ^{119}Sn resonance positioned at −71.3 ppm,[4b] while the ylidic *N*-heterocyclic olefin complex $IPrCH_2{\cdot}SnCl_2{\cdot}W(CO)_5$ yields a resonance at −96 ppm.[5a]

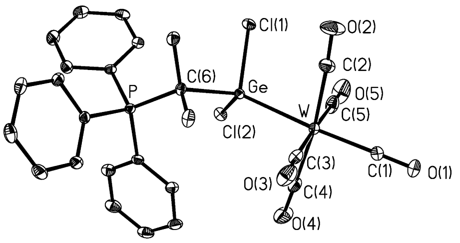
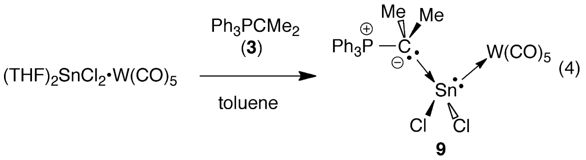


Figure 5. Molecular structure of $Ph_3PCMe_2{\cdot}GeCl_2{\cdot}W(CO)_5$ (**8**) with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(6)−Ge 2.0826(15), P−C(6) 1.8315(16), Ge−Cl(1) 2.2588(4), Ge−Cl(2) 2.2369(4), Ge−W 2.59459(17), W−C(1) 1.982(3), W−C(2−5) 2.019(3) to 2.043(3); C(6)−Ge−W 124.17(4), Cl(1)−Ge−Cl(2) 94.679(17), Ge−W−C(1) 175.25(5), Ge−W−C(2−5) 82.75(6) to 99.11(5).



The molecular structure of $Ph_3PCMe_2{\cdot}SnCl_2{\cdot}W(CO)_5$ (**9**) is presented in Figure 6. As discussed earlier for related adducts, binding of the $Ph_3P{=}CMe_2$ ligand to a $SnCl_2{\cdot}W(CO)_5$ unit leads to considerable elongation of the $Ph_3P\text{-}CMe_2$ P−C bond length from 1.6785(18) Å in the free ligand to 1.8174(18) Å in **9**. The adjacent C−Sn bond length in **9** is 2.2660(18) Å and is similar in value as the C−Sn interaction in the *N*-heterocyclic olefin bound Sn(II) complex $IPrCH_2{\cdot}SnCl_2{\cdot}W(CO)_5$ [2.2435(5) Å *avg.*].[5a] The Sn−W distance in **9** is 2.73047(15) Å and is slightly shorter than the corresponding distances in the structurally authenticated adducts $Cy_3P{\cdot}SnCl_2{\cdot}W(CO)_5$ [2.7438(2) Å][4e] and $IPrCH_2{\cdot}SnCl_2{\cdot}W(CO)_5$ [2.758(4) Å *avg.*].[5a] As expected, a localized C_{4v} coordination environment exists about the tungsten center in **9** with a nearly colinear Sn−W−C(1) array [177.02(7)°] and Sn−W−C(2−5) bond angles involving the remaining CO groups that approach orthogonal geometries [83.98(7) to 96.07(6)°]; a related

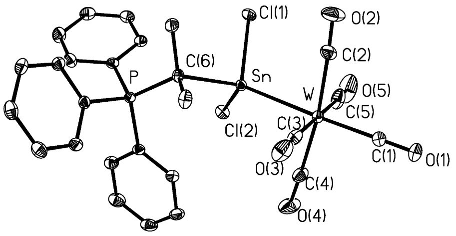
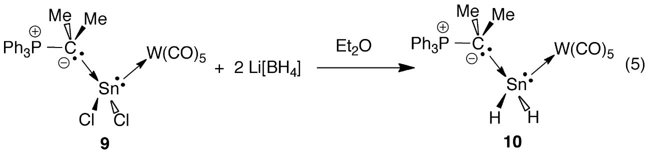


Figure 6. Molecular structure of $Ph_3PCMe_2{\cdot}SnCl_2{\cdot}W(CO)_5$ (**9**) with thermal ellipsoids presented at a 30% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(6)−Sn 2.2660(18), P−C(6) 1.8174(18), Sn−Cl(1) 2.4217(5), Sn−Cl(2) 2.4018(5), Sn−W 2.73047(15), W−C(1) 2.002(2), W−C(2−5) 2.025(2) to 2.038(2); C(6)−Sn−W 123.82(5), Cl(1)−Sn−Cl(2) 93.901(18), Sn−W−C(1) 177.02(7), Sn−W−C(2−5) 83.98(7) to 96.07(6).

coordination environment exists about the W center in $Ph_3PCMe_2{\cdot}GeCl_2{\cdot}W(CO)_5$ (**8**) (Figure 5).

With the successful installation of a Lewis acidic $W(CO)_5$ group and a Wittig electron pair donor at Sn to give $Ph_3PCMe_2{\cdot}SnCl_2{\cdot}W(CO)_5$ (**9**), this compound was then combined with $Li[BH_4]$ in Et_2O (eq 5). In line with prior



(5)

research from our group, the resulting reaction mixture contained the target Sn(II) dihydride adduct $Ph_3PCMe_2{\cdot}SnH_2{\cdot}W(CO)_5$ (**10**) which could be isolated as a brown crystalline solid after crystallization from a diethyl ether/hexanes mixture at −35 °C. Compound **10** was readily identified by the emergence of a new characteristic singlet resonance at 6.66 ppm in the ^1H NMR spectrum which displayed a set of resolvable tin satellites ($^1J_{H-119Sn}$ = 1030 Hz, $^1J_{H-117Sn}$ = 991 Hz) as expected for the formation of a tin(II) hydride with terminally positioned hydrogen atoms.[3a,4b,5a,23] Moreover, a triplet resonance at −49.8 ppm was noted in the ^{119}Sn NMR spectrum of **10** with a $^1J_{Sn-H}$ coupling constant which mirrored the value obtained from ^1H NMR spectroscopy; further coupling to phosphorus could not be resolved due to the gradual decomposition of **10** during the acquisition of the ^{119}Sn NMR data (*vide infra*). Sn−H IR vibrations in **10** were also located at 1740 cm^{-1} with proximal bands from 1891 to 2040 cm^{-1} due to ν(CO) stretches within the $W(CO)_5$ unit. The $A_1{}^1$ ν(CO) stretching band at 2040 cm^{-1} in $Ph_3PCMe_2{\cdot}SnH_2{\cdot}W(CO)_5$ (**10**) is positioned at a lower wavenumber in relation to the $SnCl_2$ adduct $Ph_3PCMe_2{\cdot}SnCl_2{\cdot}W(CO)_5$ (**9**) (2060 cm^{-1}) consistent with a higher degree of electron donation to $W(CO)_5$ from the electron-rich SnH_2 unit in **10**. The analogous complex $IPrCH_2{\cdot}SnH_2{\cdot}W(CO)_5$ affords a ν(Sn−H) band in the IR spectrum at 1758 cm^{-1} with a high frequency CO stretching band at 2043 cm^{-1}, each of which are close in value as the corresponding vibrations in $Ph_3PCMe_2{\cdot}SnH_2{\cdot}W(CO)_5$ (**10**), reflecting the similar donating ability of the Wittig and NHO donors in this system.[5a]

The molecular structure of $Ph_3PCMe_2{\cdot}SnH_2{\cdot}W(CO)_5$ (**10**) is presented in Figure 7 and confirms the successful isolation of a new member of the SnH_2 adduct series. By virtue of the hydridic character of the hydrogen atoms at tin (leading to enhanced electron density and X-ray scattering), these atoms could be located in the electron difference map. Accordingly, Sn−H distances of 1.73(4) and 1.71(3) Å in **10** were determined. The Sn−W distance in $Ph_3PCMe_2{\cdot}SnH_2{\cdot}W(CO)_5$ (**10**) [2.7833(2) Å] is elongated in relation to the Sn−W bond length within the $SnCl_2$ adduct $Ph_3PCMe_2{\cdot}SnCl_2{\cdot}W(CO)_5$ (**9**) [2.73407(15) Å], despite the anticipated increase of electron density at the SnH_2 center in relation to $SnCl_2$ (which bears electron-withdrawing Cl atoms). The Wittig carbon−tin interaction in $Ph_3PCMe_2{\cdot}SnH_2{\cdot}W(CO)_5$ (**10**) is the same within experimental error [2.269(2) Å] as the C−Sn bond length in the halogenated congener **9** [2.2660(18) Å]. The intraligand P−C distance involving the CMe_2 unit in **10** is 1.808(2) Å and matches well the adjacent P−C bond distances within the Ph_3P array [1.802(2) to 1.807(2) Å], indicating the presence of single bonds in each case.

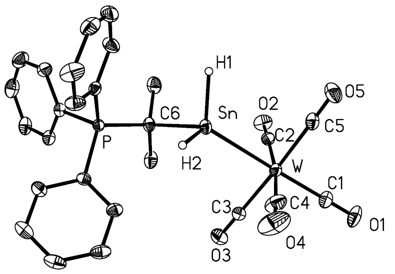


Figure 7. Molecular structure of $Ph_3PCMe_2{\cdot}SnH_2{\cdot}W(CO)_5$ (**10**) with thermal ellipsoids at a 30% probability level. All carbon-bound hydrogen atoms and diethyl ether solvate have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(6)−Sn 2.269(2), P−C(6) 1.808(2), Sn−H(1) 1.73(4), Sn−H(2) 1.71(3), Sn−W 2.7833(2), W−C(1) 2.019(3), W−C(2−5) 2.026(3) to 2.043(3); C(6)−Sn−W 117.03(6), H(1)−Sn−H(2) 100.3(17), Sn−W−C(1) 174.66(8), Sn−W−C(2−5) 82.77(10) to 92.66(8).

Our investigations into the thermal stability of $Ph_3PCMe_2{\cdot}SnH_2{\cdot}W(CO)_5$ (**10**) show that this Wittig complex is less stable than the corresponding carbene-supported adduct $IPr{\cdot}SnH_2{\cdot}W(CO)_5$ reported by our group in 2011.[4b] Compound **10** melts with decomposition to generate black insoluble materials upon heating to 80−81 °C under an atmosphere of nitrogen. In addition, compound **10** is stable for a few hours in C_6D_6 solution at room temperature; however, if solutions of **10** are allowed to stand for greater than 24 h, the complete decomposition of **10** into a black metallic precipitate (containing either Sn metal, Sn/W clusters or both) and free Ph_3P occurs, as determined by ^{31}P NMR spectroscopy; notably, $IPr{\cdot}SnH_2{\cdot}W(CO)_5$ is stable under similar conditions. In order to further evaluate the relative binding affinity of Ph_3PCMe_2, $IPrCH_2$ and IPr, the Wittig analogue $Ph_3PCMe_2{\cdot}SnH_2{\cdot}W(CO)_5$ (**10**) was combined with stoichiometric amounts of IPr or $IPrCH_2$ in toluene at room temperature. These reactions led to the full decomposition of $Ph_3PCMe_2{\cdot}SnH_2{\cdot}W(CO)_5$ before any discernible reactivity (Lewis base exchange) with either IPr or $IPrCH_2$ was detected.

■ CONCLUSIONS

In this paper we highlight the donating ability of the *C*-methylated Wittig reagent $Ph_3P{=}CMe_2$ (**3**) within the context of supporting low oxidation state Group 14 element hydride chemistry. It is shown that reactive targets such as GeH_2 and SnH_2 could be generated/intercepted with the aid of this readily available Wittig donor, while parallel chemistry with the

Table 1. Crystallographic Data for Compounds 1−5

	1	2	3	4	5·THF
formula	$C_7H_{10}Cl_2GeN_2$	$C_{18}H_{33}Cl_2GeP$	$C_{21}H_{21}P$	$C_{21}H_{21}Cl_2GeP$	$C_{25}H_{34}BGeOP$
formula fw	256.66	423.90	304.35	447.84	464.89
cryst. dimens. (mm^3)	0.33 × 0.08 × 0.05	0.42 × 0.31 × 0.28	0.20 × 0.16 × 0.15	0.32 × 0.21 × 0.15	0.19 × 0.17 × 0.12
cryst. syst.	monoclinic	orthorhombic	triclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$Pca2_1$	$P\bar{1}$	$Pna2_1$	$C2/c$
unit cell					
a (Å)	7.3784(2)	15.158(5)	10.0042(2)	12.0720(3)	34.2302(9)
b (Å)	10.6075(3)	9.974(3)	10.1516(2)	9.3272(3)	7.9115(2)
c (Å)	13.2845(3)	13.629(11)	18.8977(4)	17.8199(5)	23.0344(6)
α (deg)	90	90	104.8757(15)	90	90
β (deg)	90.1560(10)	90	93.2352(13)	90	128.5873(3)
γ (deg)	90	90	112.6166(12)	90	90
V (Å^3)	1039.73(5)	2060.5(11)	1686.16(6)	2006.48(10)	4876.0(2)
Z	4	4	4	4	8
ρ (g cm^{-3})	1.697	1.366	1.199	1.482	1.267
μ (mm^{-1})	8.330	1.820	1.372	1.874	1.335
T (K)	173(1)	173(1)	173(1)	173(1)	173(1)
$2\theta_{max}$ (deg)	137.42	54.98	142.50	55.02	56.49
total data	6480	16583	11431	16975	22028
unique data (R_{int})	1889 (0.0366)	4664 (0.0204)	6200 (0.0173)	4572 (0.0159)	5986 (0.0188)
obs data [$I > 2\sigma(I)$]	1664	4527	5443	4472	5317
params.	111	199	401	226	284
R_1 [$I > 2\sigma(I)$]^a	0.0313	0.0189	0.0379	0.0164	0.0264
wR_2 [all data]^a	0.0850	0.0510	0.1020	0.0435	0.0735
max/min $\Delta\rho$ (e$^-$ Å^{-3})	0.497/−0.412	0.530/−0.254	0.423/−0.207	0.287/−0.185	0.858/−0.394
Flack param.		0.015(6)			0.018(2)

$^a R_1 = \sum||F_0| - |F_c||/\sum|F_0|$; $wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^4)]^{1/2}$.

commonly used ligands Cy_3P and DMAP was unsuccessful (presumably due to their weaker donating ability in relation to carbon-based ligands). Given the ability to access a wide scope of Wittig donors of the general form $R_3PCR'_2$ in a rapid fashion from inexpensive precursors, it is anticipated that these Lewis bases will be used more actively in the domain of synthetic inorganic main group chemistry in the future. Thus, one can view Wittig reagents as viable synthetic analogues to ubiquitous *N*-heterocyclic carbene donors, with their potential use to access new bonding inorganic bonding motifs via coordination chemistry and to advance inorganic element-mediated catalysis.

■ 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], ^{n}BuLi (2.5 M solution in hexanes), H_3B·THF (1.0 M solution in THF), K[HB^sBu_3] (1.0 M solution in THF), [Ph_3P^iPr]I, Cl_2Ge·dioxane, DMAP, and Cy_3P were purchased from Aldrich and used as received. $(THF)_2SnCl_2$·W$(CO)_5$ was prepared according to a literature procedure.[22] ^{1}H, ^{2}H{^{1}H}, ^{11}B, ^{13}C{^{1}H}, and ^{119}Sn NMR spectra were recorded on a Varian iNova-400 spectrometer and referenced externally to $SiMe_4$ (^{1}H and ^{13}C{^{1}H}), $Si(CD_3)_4$ (^{2}H{^{1}H}), $F_3B·OEt_2$ (^{11}B), and $SnMe_4$ (^{119}Sn), respectively. 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. Scanning electron microscopy (SEM) images were recorded with a Field Emission Scanning Electron Microscope, JEOL 6301F: each sample was dispersed in toluene and then deposited on an ethanol-cleaned Si(100) wafer (purchased from University Wafer) which was attached to aluminum stubs using double-sided carbon tape. A conductive coating of chrome was then applied to each sample using a Xenosput XE200 sputter coater before the sample was loaded into the SEM holder. Images were recorded using secondary electron imaging with an accelerating voltage of 5.0 kV. Energy dispersive X-ray (EDX) spectra were recorded via a PGT X-ray analysis system on a JEOL 6301F SEM; the samples were placed on carbon tape (purchased from Ted Pella) for EDX analysis.

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 at the University of Alberta using a Bruker APEX II CCD detector/D8 diffractometer using Mo Kα ($Cy_3P·GeCl_2$ (**2**), $Ph_3PCMe_2·GeCl_2$ (**4**), $Ph_3PCMe_2·GeH_2·BH_3$ (**5**), $Ph_3PCMe_2·SnCl_2$ (**6**), $Ph_3PCMe_2·BH_3$ (**7**), $Ph_3PCMe_2·GeCl_2·W(CO)_5$ (**8**), $Ph_3PCMe_2·SnCl_2·W(CO)_5$ (**9**), $Ph_3PCMe_2·SnH_2·W(CO)_5$ (**10**)) or Cu Kα (DMAP·$GeCl_2$ (**1**), Ph_3PCMe_2 (**3**)) 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**, **3**−**6**), Patterson search/structure expansion facilities within the DIRDIF-2008 program suite[28] (compounds **2**, **6**, **8** and **9**), or intrinsic phasing SHELXT[27] (compounds **7** and **10**); structure refinement was accomplished using either SHELXL-97 or SHELXL-2013.[27] All carbon-bound hydrogen atoms were assigned positions on the basis of 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. For compounds **5**, **7**, and **10**, all hydrogen atoms attached to heteroatoms (B, Ge, and Sn) were located from difference Fourier maps, and their coordinates and isotropic displacement parameters

Table 2. Crystallographic Data for Compounds 6−10

	6	7	8	9	10·0.5 Et_2O
formula	$C_{21}H_{21}Cl_2PSn$	$C_{21}H_{24}BP$	$C_{26}H_{21}Cl_2GeO_5PW$	$C_{26}H_{21}Cl_2O_5PSnW$	$C_{28}H_{28}O_{5.5}PSnW$
formula fw	493.94	318.18	771.74	817.84	786.01
cryst. dimens. (mm)	0.28 × 0.26 × 0.03	0.28 × 0.14 × 0.10	0.32 × 0.32 × 0.10	0.32 × 0.32 × 0.07	0.45 × 0.32 × 0.28
cryst. syst.	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$I2/a$	$I2/a$	$P\bar{1}$
unit cell					
a (Å)	12.9507(4)	9.7208(4)	14.2653(4)	14.4711(6)	10.7586(6)
b (Å)	14.5477(4)	9.9807(4)	12.4535(3)	12.6086(5)	11.9138(7)
c (Å)	22.1627(6)	10.0913(4)	31.0261(3)	31.0557(13)	12.7748(8)
α (deg)	90	99.4355(4)	90	90	79.1297(6)
β (deg)	103.1066(3)	92.3567(5)	97.2299(2)	96.8451(4)	89.4825(7)
γ (deg)	90	113.1114(4)	90	90	64.8919(6)
V (Å^3)	4066.7(2)	882.28(6)	5468.1(2)	5626.0(4)	1451.45(15)
Z	8	2	8	8	2
ρ (g cm^{-3})	1.613	1.198	1.875	1.931	1.798
μ (mm^{-1})	1.599	0.153	5.592	5.254	4.911
T (K)	173(1)	173(1)	173(1)	173(1)	173(1)
$2\theta_{max}$ (deg)	54.93	57.87	55.11	56.66	52.79
total data	17697	8248	24150	25310	30449
unique data (R_{int})	4658 (0.0144)	4297 (0.0128)	6334 (0.0122)	6879 (0.0151)	5932 (0.0168)
obs data [$I > 2\sigma(I)$]	4367	3890	6063	6540	5850
params	228	222	325	326	335
R_1 [$I > 2\sigma(I)$]^a	0.0180	0.0348	0.0129	0.0154	0.0167
wR_2 [all data]^a	0.0466	0.0928	0.0311	0.0387	0.0425
max/min $\Delta\rho$ (e$^-$ Å^{-3})	0.438/−0.198	0.426/−0.235	0.518/−0.391	0.876/−0.359	1.019/−0.738

$^aR_1 = \sum||F_0| - |F_c||/\sum|F_0|$; $wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^4)]^{1/2}$.

were allowed to refine freely. A tabular listing of the crystallographic data for compounds **1**−**10** can be found in Tables 1 and 2.

Special Refinement Conditions. *Compound 10.* The O−C and C−C distances within the disordered Et_2O solvent molecule were restrained to be 1.43(1) and 1.50(1) Å, respectively.

Synthetic Details. *Synthesis of DMAP·GeCl$_2$ (1).* To a mixture of DMAP (0.069 g, 0.56 mmol) and Cl_2Ge·dioxane (0.130 g, 0.56 mmol) was added 12 mL of toluene. The reaction mixture was stirred overnight to give a clear, colorless solution. The volatiles were then removed under vacuum to give **1** as a white solid (0.147 g, 98%). Crystals of suitable quality for X-ray crystallography were grown from a toluene/hexanes mixture at −35 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.85 (s, 6H, N(CH_3)$_2$), 5.46 (d, $^3J_{HH}$ = 7.5 Hz, 2H, ArH), 8.05 (d, $^3J_{HH}$ = 7.0 Hz, 2H, ArH). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 38.2 (N(CH$_3$)$_2$), 106.6 (ArC), 143.9 (ArC), 155.6 (ArC). Anal. Calcd for $C_7H_{10}Cl_2GeN_2$: C, 31.64; H, 3.79; N, 10.54. Found: C, 31.90; H, 3.80; N. 10.26. Mp (°C): 132−136.

Preparation of Cy$_3$P·GeCl$_2$ (2).[14] Cy$_3$P (83 mg, 0.29 mmol) and Cl_2Ge·dioxane (69 mg, 0.29 mmol) were combined in 12 mL of toluene. The reaction mixture was stirred overnight to give a white slurry. The mixture was filtered, and the resulting filtrate was concentrated to 7 mL, and 2.5 mL of hexanes was carefully layered on top. This mixture was cooled to −35 °C for 12 h to yield a white microcrystalline solid, containing **2** and a coproduct tentatively identified as a [Cy$_3$PH]GeCl$_3$,[15] which was separated from the mother liquor. The solvent was removed from the mother liquor to yield **2** as a white powder (70 mg, 55%). Crystals of suitable quality for X-ray crystallography were subsequently grown from a toluene/hexanes mixture at −35 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 0.91−1.05 (m, 9H, CyH), 1.37−1.60 (m, 15H, CyH), 1.93−1.96 (m, 6H, CyH), 2.25−2.30 (m, 3H, CyH). ^{13}C{^{1}H) NMR (126 MHz, C_6D_6): δ = 26.3 (s, CyC), 27.4 (d, J_{CP} = 10.0 Hz, CyC), 29.7 (s, CyC), 31.9 (d, J_{CP} = 3.8 Hz, CyC). ^{31}P{^{1}H) NMR (162 MHz, C_6D_6): δ = 1.8 (s). Anal. Calcd for $C_{18}H_{33}Cl_2GeP$: C, 50.99; H, 7.85. Found: C, 51.03; H, 7.99. Mp (°C): 177−180.

Synthesis of Ph$_3$P=CMe$_2$ (3). *n*-BuLi (0.96 mL, 2.5 M solution in hexanes, 2.4 mmol) was added to a 10 mL toluene solution of isopropyltriphenylphosphonium iodide (1.01 g, 2.3 mmol), and the mixture was stirred for overnight to yield a dark-red slurry. The reaction mixture was filtered, and the solvent was then removed from the filtrate under vacuum to give **3** as a red powder (0.58 g, 84%). Crystals suitable for single-crystal X-ray diffraction were grown from a concentrated hexanes solution at −35 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 2.17 (d, $^3J_{HP}$ = 16.4 Hz, 6H, C(CH_3)$_2$), 7.03−7.15 (m, 9H, ArH), 7.60−7.66 (m, 6H, ArH). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ = 9.2 (d, J_{PC} = 123.0 Hz, C(CH$_3$)$_2$), 20.9 (d, J_{CP} = 13.6 Hz, CH$_3$), 130.5 (s, ArC), 133.2 (s, ArC), 133.9 (d, J_{CP} = 8.8 Hz, ArC); the ipso C atoms on the Ph rings could not be located. ^{31}P{^{1}H} NMR (161.8 MHz, C_6D_6): δ = 9.8 (s). Anal. Calcd for $C_{21}H_{21}Cl_2GeP$: C, 82.87; H, 6.95. Found: C, 82.00; H, 6.84. Mp (°C): 115−118.

Synthesis of Ph$_3$PCMe$_2$·GeCl$_2$ (4). To a mixture of Ph$_3$P=CMe$_2$ (0.42 g, 1.4 mmol) and GeCl$_2$·dioxane (0.32 g, 1.4 mmol) was added 5 mL of toluene, and the mixture was stirred for 1 h at room temperature to give an orange slurry. The resulting precipitate was separated from the mother liquor and dried under vacuum. The precipitate was then purified by crystallization from CH_2Cl_2/hexanes at −35 °C to give X-ray quality crystals of **4** (0.29 g, 46%). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.88 (d, $^3J_{HP}$ = 20.9 Hz, 6H, C(CH_3)$_2$), 6.88−6.92 (m, 6H, ArH), 6.98−7.02 (m, 3H, ArH), 7.41−7.46 (m, 6H, ArH). ^{31}P{^{1}H} NMR (161.8 MHz, C_6D_6): δ = 37.5 (s). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.77 (d, $^3J_{HP}$ = 20.4 Hz, 6H, C(CH_3)$_2$), 7.58−7.63 (m, 6H, ArH), 7.68−7.77 (m, 9H, ArH). ^{13}C{^{1}H} NMR (125.3 MHz, CD_2Cl_2): δ = 22.1 (s, CH$_3$), 29.9 (d, J_{PC} = 24.1, C(CH$_3$)$_2$), 120.9 (d, J_{CP} = 80.5 Hz, ArC), 129.9 (d, J_{CP} = 11.3 Hz, ArC), 134.2 (s, ArC), 135.1 (d, J_{CP} = 8.8 Hz, ArC). ^{31}P{^{1}H} NMR (161.8 MHz, CD_2Cl_2): δ = 37.4 (s). Anal. Calcd for $C_{21}H_{21}Cl_2GeP$: C, 56.31; H, 4.73. Found: C, 55.85; H, 4.63. Mp (°C): 103−105.

Synthesis of Ph$_3$PCMe$_2$·GeH$_2$·BH$_3$ (5). To a mixture of Ph$_3$PCMe$_2$·GeCl$_2$ (62 mg, 0.14 mmol) and Li[BH$_4$] (6 mg, 0.3 mmol) was added 5 mL of Et_2O, followed by stirring for 3 h at room temperature to give a white slurry. The volatiles were then removed under vacuum, and the crude product was dissolved in 10 mL of CH_2Cl_2, and the mixture was filtered. The solvent was removed from the filtrate to yield **5** as a white powder (43 mg, 80%). Crystals of X-ray quality were grown from a saturated THF solution at −35 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.73 (br quartet, $^1J_{BH}$ = 3H, 94.8 Hz, BH_3), 1.66 (d, $^3J_{HP}$ = 20.4 Hz, 6H, $C(CH_3)_2$), 4.64 (br, 2H, GeH_2), 6.86−6.93 (m, 6H, Ar*H*), 6.97−7.16 (m, 3H, Ar*H*), 7.48−7.51 (m, 6H, Ar*H*). $^{13}C\{^1H\}$ NMR (125.3 MHz, C_6D_6): δ = 17.4 (d, $^1J_{CP}$ = 23.3 Hz, $C(CH_3)_2$), 26.5 (s, CH_3), 121.9 (d, J_{CP} = 81.0 Hz, ArC), 129.3 (d, J_{CP} = 11.4 Hz, ArC), 133.4 (s, ArC), 134.8 (d, J_{CP} = 8.3 Hz, ArC). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ = 38.8 (s). ^{11}B NMR (159.8 MHz, C_6D_6): δ = −39.4 (quartet, $^1J_{BH}$ = 95.4 Hz, BH_3). IR (cm^{-1}): 1975 (m, υ_{Ge-H}) and 2343 (w, υ_{B-H}). Anal. Calcd for $C_{21}H_{26}BGeP$: C, 64.20; H, 6.67. Found: C, 64.63; H, 6.81. Mp (°C): 110−113.

*Synthesis of $Ph_3PCMe_2\cdot GeD_2\cdot BD_3$ (**5D**).* To a mixture of $Ph_3PCMe_2\cdot GeCl_2$ (68 mg, 0.15 mmol) and Li[BD_4] (9 mg, 0.3 mmol) was added 5 mL of Et_2O, followed by stirring for 3 h at room temperature to give a white slurry. The volatiles were then removed under vacuum, and the crude product was dissolved in 10 mL of CH_2Cl_2, and the mixture was filtered. The solvent was removed from the filtrate to yield **5D** as a white powder (52 mg, 87%). ^{1}H NMR (500 MHz, C_6D_6): Similar to that of $Ph_3PCMe_2\cdot GeH_2\cdot BH_3$ with very low intensity peaks due to residual GeHD and GeH_2 isotopologues (<8%). $^2H\{^1H\}$ NMR (61.39 MHz, C_6H_6) δ = 1.56 (br, BD_3), 4.63 (s, GeD_2). ^{11}B NMR (159.8 MHz, C_6D_6): δ = −39.4 (br). IR (cm^{-1}): 1377 (m, υ_{Ge-D}), 1754 (w, υ_{B-D}) and low intensity peaks for Ge−H and B−H vibrations at 1975 and 2330, respectively.

*Synthesis of $Ph_3PCMe_2\cdot SnCl_2$ (**6**).* $Ph_3P{=}CMe_2$ (113 mg, 0.37 mmol) and $SnCl_2$ (70 mg, 0.37 mmol) were combined in a 5 mL toluene/1 mL THF mixture, followed by stirring for 3 h. The solvent was removed under vacuum to yield **6** as a white powder (153 mg, 83%). Crystals of X-ray quality were grown from CH_2Cl_2/hexanes solution at −35 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.87 (d, $^3J_{HP}$ = 21.2 Hz, 6H, $C(CH_3)_2$), 7.61−7.76 (m, 15H, Ar*H*). $^{13}C\{^1H\}$ NMR (125.3 MHz, CD_2Cl_2): δ = 21.6 (s, CH_3), 32.3 (d, $^1J_{CP}$ = 24.8 Hz, $C(CH_3)_2$), 121.8 (d, J_{CP} = 81.0 Hz, ArC), 130.1 (d, J_{CP} = 11.4 Hz, ArC), 134.2 (s, ArC), 134.7 (d, J_{CP} = 8.5 Hz, ArC). $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_2Cl_2): δ = 36.9 (s, satellites: $^2J_{P-Sn}$ = ~89 Hz). $^{119}Sn\{^1H\}$ NMR (149 MHz, CD_2Cl_2): δ = 113.3 (br). Anal. Calcd for $C_{21}H_{21}Cl_2PSn$: C, 51.06; H, 4.28. Found: C, 49.86; H, 4.28. Mp (°C): 165−167 (turns black 155−157).

*Synthesis of $Ph_3PCMe_2\cdot BH_3$ (**7**).*[10a] To a solution of $Ph_3P{=}CMe_2$ (213 mg, 0.70 mmol) in 5 mL of Et_2O was added a solution of THF·BH_3 (701 μL, 1.0 M solution in THF, 0.70 mmol) dropwise. The reaction mixture was then stirred overnight at room temperature, and the solvent was then removed under vacuum. The resulting solid was washed with hexanes (3 × 5 mL) and dried to afford **7** as a white solid (0.154 g, 69%). Crystals suitable for X-ray crystallography were grown from hexanes/CH_2Cl_2 at −35 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.74 (d, 6H, $^3J_{PH}$ = 21.2 Hz, $C(CH_3)$), 2.33 (q, 3H, $^1J_{BH}$ = 90 Hz, BH_3), 6.89−7.01 (m, 9H, Ar*H*), 7.81−7.85 (m, 6H, Ar*H*). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 30.5 (s, CH_3), 124.7 (d, J_{CP} = 77.0, ArC), 128.7 (d, J_{CP} = 10.8, ArC), 132.4 (d, J_{CP} = 2.3, ArC), 135.4 (d, J_{CP} = 7.8, ArC); the ylidic CMe_2 carbon could not be located. ^{11}B NMR (128 MHz, C_6D_6): δ = −19.4 (q, $^1J_{BH}$ = 85.7 Hz, BH_3). $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6): δ = 39.4 (s).

*Synthesis of $Ph_3PCMe_2\cdot GeCl_2\cdot W(CO)_5$ (**8**).* $Ph_3PCMe_2\cdot GeCl_2$ (43 mg, 0.096 mmol) and $(THF)_2\cdot SnCl_2\cdot W(CO)_5$ (63 mg, 0.096 mmol) were combined in 10 mL of toluene and stirred for 24 h at room temperature to give a pale-yellow slurry. The volatiles were removed from the reaction mixture, and 15 mL of CH_2Cl_2 was added. The resulting solution was filtered, and the solvent was removed from the filtrate to give **8** as a white powder (73 mg, 94%). Crystals of suitable quality for X-ray analysis were grown from CH_2Cl_2/hexanes at −35 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.49 (d, $^3J_{HP}$ = 19.9 Hz, 6H, $C(CH_3)_2$), 6.89−6.94 (m, 6H, Ar*H*), 6.97−7.03 (m, 3H, Ar*H*), 7.38−7.44 (m, 6H, Ar*H*). $^{13}C\{^1H\}$ NMR (125.3 MHz, C_6D_6): δ = 26.2 (s, CH_3), 32.4 (d, J_{CP} = 25.5 Hz, $C(CH_3)_2$), 120.4 (d, J_{CP} = 82.1 Hz, ArC), 129.3 (d, J_{CP} = 6.5 Hz, ArC), 133.8 (s, ArC), 135.5 (d, J_{CP} = 8.8 Hz, ArC), 199.5 (s, eq CO), 202.0 (s, ax. CO). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ = 38.8 (s). IR (Nujol, cm^{-1}): 1924 (br, υ_{CO}) and 2063 (m, υ_{CO}). Anal. Calcd for $C_{26}H_{21}Cl_2O_5PGeW$: C, 40.46; H, 2.74. Found: C, 40.44; H, 2.72. Mp (°C): 188−192.

*Synthesis of $Ph_3PCMe_2\cdot SnCl_2\cdot W(CO)_5$ (**9**).* $Ph_3P{=}CMe_2$ (49 mg, 0.17 mmol) and $(THF)_2SnCl_2\cdot W(CO)_5$ (110 mg, 0.167 mmol) were combined in 10 mL of toluene and stirred for 3 h at room temperature to give a yellow slurry. The volatiles were removed under vacuum to afford **9** as a pale-yellow powder (130 mg, 94%). Crystals of X-ray quality were grown from CH_2Cl_2/hexanes at −35 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.61 (d, $^3J_{HP}$ = 20.4 Hz, 6H, $C(CH_3)_2$; satellites: $^3J_{HSn}$ and/or $^4J_{HW}$ = ~66 Hz), 6.92−7.08 (m, 9H, Ar*H*), 7.32−7.37 (m, 6H, Ar*H*). $^{13}C\{^1H\}$ NMR (125.3 MHz, C_6D_6): δ = 24.6 (s, CH_3), 32.3 (d, J_{CP} = 27.5 Hz, $C(CH_3)_2$), 120.1 (d, J_{CP} = 82.7 Hz, ArC), 129.8 (d, J_{CP} = 11.6 Hz, ArC), 134.2 (s, ArC), 134.8 (d, J_{CP} = 8.8 Hz, ArC), 198.8 (s, satellites: $^1J_{CW}$ = 123.4 Hz, eq CO), 201.2 (s, ax. CO). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ = 38.2 (s, satellites: $^2J_{P-Sn}$ = 44.5 Hz). $^{119}Sn\{^1H\}$ NMR (149.1 MHz, C_6D_6): δ = 131.3 (d, $^2J_{Sn-P}$ = 48.5 Hz). IR (Nujol, cm^{-1}): 1930 (br, υ_{CO}) and 2060 (m, υ_{CO}). Anal. Calcd for $C_{26}H_{21}Cl_2O_5PSnW$: C, 38.18; H, 2.59. Found: C, 38.35; H, 2.65. Mp (°C): 178−180.

*Synthesis of $Ph_3PCMe_2\cdot SnH_2\cdot W(CO)_5$ (**10**).* To a mixture of $Ph_3PCMe_2\cdot SnCl_2\cdot W(CO)_5$ (78 mg, 0.095 mmol) and Li[BH_4] (4.5 mg, 0.21 mmol) was added 5 mL of Et_2O, followed by stirring for 4 h at room temperature to yield a brown slurry. The volatiles were removed under vacuum, and the product was extracted with 10 mL of toluene, and the resulting mixture was filtered. The solvent was then removed under vacuum from the filtrate to yield **10** as a red-brown powder (72 mg, 76%). Crystals of X-ray quality were grown from Et_2O/hexanes at −35 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.61 (d, $^3J_{HP}$ = 20.4 Hz, 6H, $C(CH_3)_2$; satellites: $^3J_{HSn}$ and/or $^4J_{HW}$ = ~60 Hz), 6.66 (s, 2H, SnH_2; satellites: $^1J_{H\text{-}119Sn}$ = 1030 Hz, $^1J_{H\text{-}117Sn}$ = 991 Hz), 6.87−7.06 (m, 9H, Ar*H*), 7.29−7.36 (m, 6H, Ar*H*). $^{13}C\{^1H\}$ NMR (125.3 MHz, C_6D_6): δ = 12.9 (d, J_{CP} = 27.5 Hz, $C(CH_3)_2$), 27.8 (s, CH_3), 121.7 (d, J_{CP} = 81.6 Hz, ArC), 129.4 (d, J_{CP} = 11.5 Hz, ArC), 133.6 (s, ArC), 134.5 (d, J_{CP} = 8.3 Hz, ArC), 202.8 (s, eq CO), 205.1 (s, ax. CO). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ = 38.3 (s; satellites: $^2J_{P-Sn}$ = 36.3 Hz). $^{119}Sn\{^1H\}$ NMR (149.1 MHz, C_6D_6): δ = −49.8 (d, $^2J_{Sn-P}$ = 37.4 Hz). ^{119}Sn NMR (149.1 MHz, C_6D_6): δ = −49.8 (t, $^1J_{Sn-H}$ = ~1075 Hz; the expected t of d pattern was not resolvable due to decomposition of **10** during prolonged time periods in solution). IR (Nujol, cm^{-1}): 1740 (s, υ_{Sn-H}) and 1891 (w, υ_{CO}), 1959 (s, υ_{CO}), 2040 (m, υ_{CO}). Anal. Calcd for $C_{26}H_{23}O_5PSnW$: C, 41.69; H, 3.10. Found: C, 42.72; H, 3.63. Mp (°C): 80−82 (turns black 70−75 °C).

*Synthesis of $Ph_3PCMe_2\cdot SnD_2\cdot W(CO)_5$ (**10D**).* To a mixture of $Ph_3PCMe_2\cdot SnCl_2\cdot W(CO)_5$ (130 mg, 0.16 mmol) and Li[BD_4] (9 mg, 0.3 mmol) was added 5 mL of Et_2O, followed by stirring for 4 h at room temperature to yield a brown slurry. The volatiles were removed under vacuum, and the product was extracted with 10 mL of toluene, and the resulting mixture was filtered. The solvent was then removed under vacuum from the filtrate to yield **10D** as a red-brown powder (73 mg, 61%). ^{1}H NMR (500 MHz, C_6D_6): same as $Ph_3PCMe_2\cdot SnH_2\cdot W(CO)_5$ with very low intensity peaks due to residual SnHD and SnH_2 isotopomers (<9%). $^2H\{^1H\}$ NMR (61.39 MHz, C_6H_6) δ = 6.66 (s, SnD_2). IR (cm^{-1}): 1975 (m, υ_{CO}) and 2343 (w, υ_{CO}), 1254 (υ_{Sn-D}); very low intensity υ_{Sn-H} peak at 1746 cm^{-1}.

Reaction of $DMAP\cdot GeCl_2$ (1) with Li[BH_4]. To a mixture of the $DMAP\cdot GeCl_2$ (126 mg, 0.47 mmol) and Li[BH_4] (22 mg, 0.99 mmol) was added 5 mL of diethyl ether. Upon addition of the solvent a rapid reaction ensued as evidenced by the formation of (presumably) elemental Ge. Analysis of the soluble fraction after 12 h of stirring revealed the clean presence of $DMAP\cdot BH_3$,[27] which was identified by comparison of the ^{11}B NMR spectroscopic data with those found in the literature.[27] In order to isolate $DMAP\cdot BH_3$, the solvent was removed from the reaction mixture, and 6 mL of CH_2Cl_2 was added. The resulting mixture was filtered, and the volatiles were removed from the filtrate to yield $DMAP\cdot BH_3$ as a white powder as $DMAP\cdot BH_3$ (51 mg, 79%).

Reaction of $Cy_3P\cdot GeCl_2$ (2) with Li[BH_4]. Following an identical procedure as listed for the reaction of $DMAP\cdot GeCl_2$ with Li[BH_4], a mixture of the $Cy_3P\cdot GeCl_2$ (38 mg, 0.089 mmol) and Li[BH_4] (5 mg, 0.2 mmol) were combined in 5 mL of Et_2O. The resulting mixture containing (presumably) elemental Ge and $Cy_3P\cdot BH_3$[28] was purified by removing the voltailes, followed by extraction of $Cy_3P{\cdot}BH_3$ with 6 mL of CH_2Cl_2. The isolated white solid from the soluble extract (23 mg, 87%) was identified as $Cy_3P{\cdot}BH_3$ by comparison of the ^{11}B and ^{31}P NMR spectroscopic data with those found in the literature.[28]

*Reaction of $Ph_3PCMe_2{\cdot}SnCl_2$ (**6**) with $Li[BH_4]$.* To a mixture of the $Ph_3PCMe_2{\cdot}SnCl_2$ (99 mg, 0.20 mmol) and $Li[BH_4]$ (10 mg, 0.44 mmol) was added 5 mL of diethyl ether. The resulting slurry was stirred for 2 h to form a shiny black precipitate (presumably metallic tin) with the formation of $Ph_3PCMe_2{\cdot}BH_3$ (**7**) as the sole soluble product, as evidenced by ^1H, ^{11}B, and ^{31}P NMR spectroscopy.

*Reaction of $Ph_3PCMe_2{\cdot}GeH_2{\cdot}BH_3$ (**5**) with IPr.* To a mixture of $Ph_3PCMe_2{\cdot}GeH_2{\cdot}BH_3$ (**5**) (63 mg, 0.16 mmol) and IPr (62 mg, 0.16 mmol) was added 10 mL of toluene, and the reaction mixture was stirred for 12 h. The volatiles were then removed under vacuum to yield a brown powder that was directly analyzed by ^1H, ^{11}B, and ^{31}P NMR spectroscopy. These data revealed the formation of $IPr{\cdot}GeH_2{\cdot}BH_3$ (32%),[4a] Ph_3PCMe_2 (**3**) (24%), PPh_3 (11%), an unidentified product at 31.7 ppm (22%), and unreacted starting material $Ph_3PCMe_2{\cdot}GeH_2{\cdot}BH_3$ (**5**) (11%) according to ^1H, ^{11}B, and ^{31}P NMR spectroscopy.

*Thermolysis of $Ph_3PCMe_2{\cdot}GeH_2{\cdot}BH_3$ (**5**).* Compound **5** (40 mg, 0.10 mmol) was dissolved in 10 mL of toluene, and the solution was heated to reflux. Within 4 h a gray suspension was noted, and continued heating for a total of 24 h afforded a dark-gray slurry. The reaction mixture was filtered, and the solvent was removed from the filtrate to yield a white solid that was identified as $Ph_3P{\cdot}BH_3$[18] (>95% yield) by ^1H, ^{11}B, and ^{31}P NMR spectroscopy. When the same thermolysis was repeated in a closed system in d_8-toluene and the resulting product mixture analyzed *in situ* by ^{11}B NMR spectroscopy, another peak was observed at 80 ppm (16% in relation to 84% of $Ph_3P{\cdot}BH_3$) that was tentatively assigned as the triorganoborane $^{i}Pr_3B$; literature ^{11}B NMR shift for $^{i}Pr_3B$ = 83.7 ppm in C_6D_6.[21] The dark-gray insoluble product formed in the above-mentioned thermolysis was analyzed by EDX spectroscopy and determined to be elemental germanium (Figure S3 in SI).[17]

*Decomposition of $Ph_3PCMe_2{\cdot}SnH_2{\cdot}W(CO)_5$ (**10**).* Compound **10** (45 mg, 0.060 mmol) was dissolved in 10 mL of toluene and stirred at room temperature for 24 h to yield a brown solution over a black precipitate. The volatiles were removed under vacuum, and ^{31}P NMR spectroscopy identified the presence of PPh_3 as the only phosphorus-containing product.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full crystallographic details and the molecular structures of $Ph_3P{=}CMe_2$ (**3**), $Ph_3PCMe_2{\cdot}BH_3$ (**7**), and $[Ph_3PCHMe_2]SnCl_3$. EDX spectrum and SEM image of the precipitate (Ge) formed during the thermolysis of $Ph_3PCMe_2{\cdot}GeH_2{\cdot}BH_3$ (**5**). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561. (c) Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940. (d) Diéz-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874. For related carbene-based donors, see: (e) Martin, D.; Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Organometallics* **2011**, *30*, 5304. (f) Crabtree, R. H. *Coord. Chem. Rev.* **2013**, *257*, 755.

(2) (a) Braunschweig, H.; Dewhurst, R. D.; Hammond, K.; Mies, J.; Radacki, K.; Vargas, A. *Science* **2012**, *336*, 1420. (b) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069. (c) Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 9701. (d) Jones, C.; Sidiropoulos, A.; Holzmann, N.; Frenking, G.; Stasch, A. *Chem. Commun.* **2012**, *48*, 9855. (e) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2008**, *130*, 14970. (f) Abraham, M. Y.; Wang, Y.; Xie, Y.; Wei, P.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *Chem.—Eur. J.* **2010**, *16*, 432.

(3) For recent examples with IPr and related NHC donors, see: (a) Sindlinger, C. P.; Wesemann, L. *Chem. Sci.* **2014**, *5*, 2739. (b) Filippou, A.; Baars, B.; Chernov, O.; Lebedev, Y. N.; Schnakenburg, G. *Angew. Chem., Int. Ed.* **2014**, *53*, 565. (c) Wang, Y.; Xie, Y.; Wei, P.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2013**, *135*, 19139. (d) Xiong, Y.; Yao, S.; Inoue, S.; Epping, J. D.; Driess, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 7147. (e) Mondal, K. C.; Samuel, P. P.; Tretiakov, M.; Sing, A. P.; Roesky, H. W.; Stückl, A. C.; Niepötter, B.; Carl, E.; Wolf, H.; Herbst-Irmer, R.; Stalke, D. *Inorg. Chem.* **2013**, *52*, 4736. (f) Al-Rafia, S. M. I.; Momeni, M. R.; McDonald, R.; Ferguson, M. J.; Brown, A.; Rivard, E. *Angew. Chem., Int. Ed.* **2013**, *52*, 6390. (g) Jana, A.; Huch, V.; Scheschkewitz, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 12179. (h) Shen, C.-T.; Liu, Y.-H.; Peng, S.-M.; Chiu, C.-W. *Angew. Chem., Int. Ed.* **2013**, *52*, 13293.

(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.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 8354. (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.; Shynkaruk, O.; McDonald, S. M.; Liew, S. K.; Ferguson, M. J.; McDonald, R.; Herber, R. H.; Rivard, E. *Inorg. Chem.* **2013**, *52*, 5581. (f) Al-Rafia, S. M.; Momeni, M. R.; Ferguson, M. J.; McDonald, R.; Brown, A.; Rivard, E. *Organometallics* **2013**, *32*, 6658. (g) For a recent review of this field, see: Rivard, E. *Dalton. Trans.* **2014**, *43*, 8577.

(5) (a) Al-Rafia, S. M. I.; Malcolm, A. C.; Liew, S. K.; Ferguson, M. J.; McDonald, R.; Rivard, E. *Chem. Commun.* **2011**, *47*, 6987. For related studies involving NHOs, see: (b) Kuhn, N.; Bohnen, H.; Kreutzberg, J.; Bläser, D.; Boese, R. *J. Chem. Soc., Chem. Commun.* **1993**, 1136. (c) Fürstner, A.; Alcarazo, M.; Goddard, R.; Lehmann, C. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 3210. (d) Dumrath, A.; Wu, X.-F.; Neumann, H.; Spannenberg, A.; Jackstell, R.; Beller, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 8988. (e) Malcolm, A. C.; Sabourin, K. J.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Inorg. Chem.* **2012**, *51*, 12905. (f) Wang, Y.; Abraham, M. Y.; Gilliard, R. J., Jr.; Sexton, D. R.; Wei, P.; Robinson, G. H. *Organometallics* **2013**, *32*, 6639. (g) Berger, C. J.; He, G.; Merten, C.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Inorg. Chem.* **2014**, *53*, 1475.

(6) (a) Jasinski, J. M.; Gates, S. M. *Acc. Chem. Res.* **1991**, *24*, 9. (b) Isobe, C.; Cho, H.-C.; Sewell, J. E. *Surf. Sci.* **1993**, *295*, 117.

(7) Bestmann, H. J.; Kratzer, O. *Chem. Ber.* **1963**, *96*, 1899.

(8) (a) Wittig, G.; Schöllkopf, U. *Chem. Ber./Recl.* **1954**, *87*, 1318. (b) Beedham, I.; Micklefield, J. *Curr. Org. Syn.* **2005**, *2*, 231. (c) Xu, S.; He, Z. *RSC Adv.* **2013**, *3*, 16885.

(9) For selected examples, see: (a) Pörschke, K.-R.; Wilke, G.; Mynott, R. *Chem. Ber.* **1985**, *118*, 298. (b) Fortier, S.; Kaltsoyannis, N.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2011**, *133*, 14224.

(10) (a) Bestmann, H. J.; Sühs, K.; Röder, T. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1038. (b) Borisova, I. V.; Zemlyansky, N. N.; Belsky, V. K.; Kolosova, N. D.; Sobolev, A. N.; Luzikov, Y. N.; Ustynyuk, Y. A.; Beletskaya, I. P. *J. Chem. Soc., Chem. Commun.* **1982**, 1090. (c) Bestmann, H. J.; Röder, T.; Sühs, K. *Chem. Ber.* **1988**, *121*, 1509. (d) Breitsameter, F.; Schrödel, H.-P.; Schmidpeter, A.; Nöth, H.; Rojas-Lima, S. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1293.

(11) (a) Prabusankar, G.; Sathyanarayana, A.; Suresh, P.; Babu, C. N.; Srinivas, K.; Metla, B. P. R. *Coord. Chem. Rev.* **2014**, *269*, 96. (b) Inoue, S.; Eisenhut, C. *J. Am. Chem. Soc.* **2013**, *135*, 18315. (c) 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. (d) Al-Rafia, S. M. I.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Chem.—Eur. J.* **2012**, *18*, 13810. (e) Kinjo, R.; Donnadieu, B.; Celik, M. A.; Frenking, G.; Bertrand, G. *Science* **2011**, *333*, 610. (f) Bonyhady, S. J.; Collis, D.; Frenking, G.; Holzmann, N.; Jones, C.; Stasch, A. *Nat. Chem.* **2010**, *2*, 865.

(12) (a) Chen, M.; Feng, Y.-G.; Wang, X.; Li, T.-C.; Zhang, J.-Y.; Qian, D.-J. *Langmuir* **2007**, *23*, 5296. (b) Nyamen, L. D.; Revaprasadu, N.; Pullabhotla, R. V. S. R.; Nejo, A. A.; Ndifon, P. T.; Malik, M. A.; O'Brien, P. *Polyhedron* **2013**, *56*, 62. (c) Hines, D. A.; Kamat, P. V. *ACS Appl. Mater. Interfaces* **2014**, *6*, 3041.

(13) (a) King, R. B. *Inorg. Chem.* **1963**, *2*, 199. (b) Jutzi, P.; Hoffman, J.; Brauner, D. J.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 1002. (c) du Mont, W.-W.; Neudert, B.; Rudolph, C.; Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 308. (d) Ando, W.; Sekiguchi, A.; Hagiwara, K.; Sakakibara, A.; Yoshida, H. *Organometallics* **1988**, *7*, 558. (e) Pu, L.; Twamley, B.; Power, P. P. *Organometallics* **2000**, *19*, 2874. (f) Hadlington, T. J.; Hermann, M.; Li, J.; Frenking, G.; Jones, C. *Angew. Chem., Int. Ed.* **2013**, *52*, 10199. (g) See also: Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479.

(14) For a prior report involving the preparation of $Cy_3P{\cdot}GeCl_2$, see: Doddi, A.; Gemel, C.; Winter, M.; Fischer, R. A.; Goedecke, C.; Rzepa, H. S.; Frenking, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 450.

(15) The identification of the $[HPCy_3]^+$ salt byproduct formed in the reaction of Cy_3P with $Cl_2Ge{\cdot}$dioxane was accomplished by ^{31}P NMR spectroscopy (δ = 20.2 ppm) and the detection of a characteristic doublet ^1H NMR resonance for the P-H residue at 7.12 ($^1J_{PH}$ = 488 Hz) in C_6D_6; this latter resonance collapsed into a singlet resonance in the $^1H\{^{31}P\}$ spectrum. Phosphonium salts of $GeCl_3^-$ ($[HPR_3]GeCl_3$) have been reported: (a) du Mont, W.-W.; Rudolph, G. *Chem. Ber.* **1976**, *109*, 3419. (b) Dal Canto, R. A.; Roskamp, E. J. *J. Org. Chem.* **1992**, *57*, 406. (c) Davis, M. F.; Levason, W.; Reid, G.; Webster, M. *Dalton Trans.* **2008**, 2261.

(16) (a) Kolodiazhnyi, O. I. *Tetrahedron* **1996**, *52*, 1855. (b) Cristau, H.-J. *Chem. Rev.* **1994**, *94*, 1299. (c) Bestmann, H. J.; Arenz, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 559.

(17) See the Supporting Information for full details.

(18) Rajendran, K. V.; Gilheany, D. G. *Chem. Commun.* **2012**, *48*, 817.

(19) Papp, R.; Somoza, F. B., Jr.; Sieler, J.; Blaurock, S.; Hey-Hawkins, E. *J. Organomet. Chem.* **1999**, *585*, 127.

(20) For related studies involving hydride transfer to carbene donor sites (followed by ring-expansion), see: (a) Arrowsmith, M.; Hill, M. S.; Kociok-Köhn, G.; MacDougall, D. J.; Mahon, M. F. *Angew. Chem., Int. Ed.* **2012**, *51*, 2098. (b) Schmidt, D.; Berthel, J. H. J.; Pietsch, S.; Radius, U. *Angew. Chem., Int. Ed.* **2012**, *51*, 8881. (c) Reference 11d.. (d) Momeni, M. R.; Rivard, E.; Brown, A. *Organometallics* **2013**, *32*, 6201. (e) Iversen, K. J.; Wilson, D. J. D.; Dutton, J. L. *Organometallics* **2013**, *32*, 6209. (f) Fang, R.; Yang, L.; Wang, Q. *Organometallics* **2014**, 33, 53.

(21) Brown, H. C.; Krishnamurthy, S.; Hubbard, J. L.; Coleman, R. A. *J. Organomet. Chem.* **1979**, *166*, 281.

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

(23) For related low oxidation state Sn(II) hydrides, see: (a) Eichler, B. E.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 8785. (b) Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 4806. (c) Rivard, E.; Fischer, R. C.; Wolf, R.; Peng, Y.; Merrill, W. A.; Schley, N. D.; Zhu, Z.; Pu, L.; Fettinger, J. C.; Teat, S. J.; Nowik, I.; Herber, R. H.; Takagi, N.; Nagase, S.; Power, P. P. *J. Am. Chem. Soc.* **2007**, *129*, 16197.

(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) Lesley, M. J. G.; Woodward, A.; Taylor, N. J.; Marder, T. B.; Cazenobe, I.; Ledoux, I.; Zyss, J.; Thornton, A.; Bruce, D. W.; Kakkar, A. K. *Chem. Mater.* **1998**, *10*, 1355.

(30) Blumenthal, A.; Bissinger, P.; Schmidbaur, H. J. *J. Organomet. Chem.* **1993**, *462*, 107.