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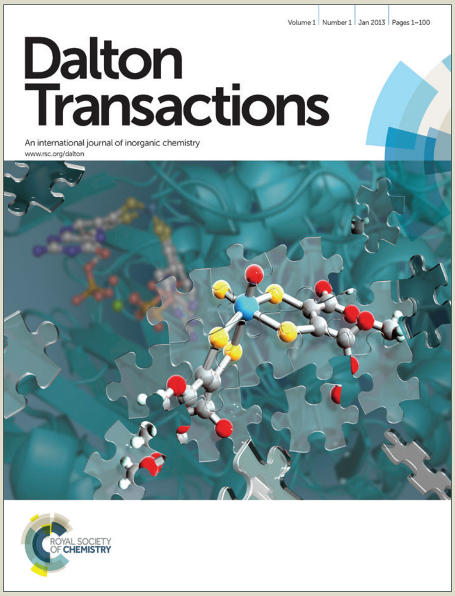

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**Perspective**

# Donor-acceptor Chemistry in the Main Group

Eric Rivard*

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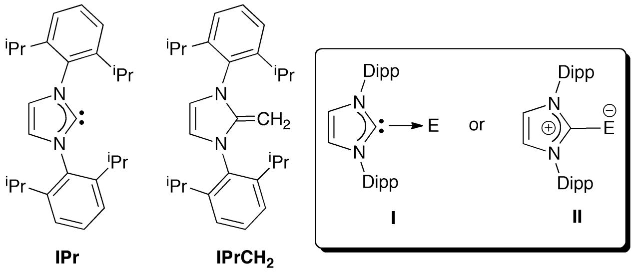
This Perspective article summarizes recent progress from our laboratory in the isolation of reactive main group species using a general *donor-acceptor* protocol. A highlight of this program is the use of carbon-based donors in combination with suitable Lewis acidic acceptors to yield stable complexes of parent Group 14 element hydrides (*e.g*. $GeH_2$ and $H_2SiGeH_2$). It is anticipated that this strategy could be extended to include new synthetic targets from throughout the Periodic Table with possible applications in bottom-up materials synthesis and main group element catalysis envisioned.

## 1. Introduction

The chemistry of the simplest members of a molecular family continues to attract considerable attention since the early attempts to prepare methylene $CH_2$ as an isolable species.[1] While $CH_2$ has resisted isolation in the bulk phase,[2] the delivery of methylene functionality to substrates has been elegantly accomplished via phosphorus- ($R_3P{=}CH_2$) and metal-based ($L_xM{=}CH_2$; L = ligands) reagents.[3] Keeping focus on the Group 14 (tetrel) element series, the heavier congeners of methylene, $EH_2$ (E = Si-Pb) have been studied in detail by computational methods[4] and intercepted within an Ar or Ne matrix under cryogenic conditions.[5] An impetus for studying these "heavy methylene" analogues stems from the demonstrated role of transient $SiH_2$ in the thermal decomposition of silane gas ($SiH_4$) *en route* to clean surfaces of silicon for electronic device applications.[6] The research program described in this Perspective article began with the questions: Can inorganic methylenes such as $GeH_2$ be generated and stabilized at room temperature in the form of a coordination complex? If so, can these species be used as reactive synthons for chemical synthesis? As will be shown, the associated research activities in our group has led to the stabilization of a variety of inorganic species using a general *donor-acceptor* approach and the discovery of some novel chemical transformations from this pursuit.

A great deal of the studies described in this article involve the use of *N*-heterocyclic carbene (NHC) and *N*-heterocyclic olefin (NHO) donors (Scheme 1) to bind/stabilize electron deficient main group element moieties. Due to their strong electron donating abilities, NHCs are now routinely used as ligands in metal-mediated catalysis[7] and to isolate intriguing main group element species in the form of stable adducts, *e.g*. IPr•Si=Si•IPr, **1** (IPr = $[(HCNDipp)_2C{:}]$; Dipp = 2,6-$^iPr_2C_6H_3$).[8,9] It is also important to mention that both the groups of Arduengo[10] and Kuhn[11] played pioneering roles in the development of NHCs and NHOs as isolable ligands.



**Scheme 1.** *N*-Heterocyclic carbene (IPr) and *N*-heterocyclic olefin ($IPrCH_2$) donors used in advancing main group hydride coordination chemistry. Common ways of depicting carbene adduct formation in the literature are presented to the right. For clarity the adducts in this article will be presented as form **II** with formal charges omitted.

## 2. Prior Examples of Donor-acceptor Stabilization

As shown in Scheme 2, molecular entities with small HOMO-LUMO gaps and concomitantly dual nucleophilic and electrophilic character (*e.g*. $GeH_2$) are amenable to simultaneous coordination by both a Lewis acid (LA) and a Lewis base (LB). The binding of suitable LA/LB combinations shut down the once readily available pathways for substrate decomposition/oligomerization, enabling stable complexes to be formed. The following section represents provides examples of donor-acceptor stabilization as they pertain to motivating our later studies in this field.

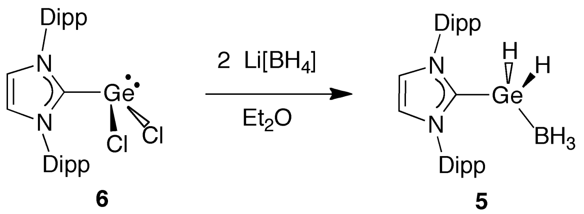
The Marks group were early participants in this area through their studies of organogermylene and stannylene complexes.[12] In the representative compound THF•$SnMe_2$•$Fe(CO)_4$ (**2**), the $SnMe_2$ unit can be regarded as both a Lewis base (electron pair donor) and a Lewis acid (electron pair acceptor) which supports the formally dative bonding modes: THF:→Sn and Sn:→Fe.[13] It should be noted that free stannylene $SnMe_2$ is not stable[14] and spontaneously forms oligomeric species $[SnMe_2]_x$ joined by intrachain Sn-Sn σ-bonds.[15]

The extensive work by Scheer and coworkers concerning the isolation of reactive Group 13/15 hydrides also had a vital role in spurring the current Group 14 element chemistry ongoing in our laboratory. In a landmark discovery, the Scheer group showed that the parent hydrides $H_2P$-$AlH_2$ and $H_2P$-$GaH_2$ could be intercepted when partnered with suitable Lewis acid/base pairs (*e.g.* $Me_3N$•$H_2Al$-$PH_2$•$W(CO)_5$ (**3**)).[16a] A series of reports followed[16] describing the chemistry of these encapsulated species and a recent addition to this field is the surprisingly stable arsanylborane adduct $Me_3N$•$H_2B$-$AsH_2$ (**4**).[16d,17] In the absence of a donor group, monomeric species such as the phosphinoborane $H_2P$-$BH_2$ readily polymerize.[18]

## 3. Donor-acceptor Stabilization: Main Group Hydrides

Our contributions to this field began in 2009 with the preparation of the $GeH_2$ complex IPr•$GeH_2$•$BH_3$ (**5**).[19] The original intention was to form the germanium(II) dihydride complex IPr•$GeH_2$ by treatment of the newly prepared $GeCl_2$ adduct IPr•$GeCl_2$ (**6**) with various hydride sources such as NaH, KH and Li[$HBEt_3$] to effect Cl/H exchange at germanium. However in the case of the alkali metal hydrides NaH and KH, the formation of Ge metal and free carbene IPr occurred. When **6** was combined with two equivalents of Li[$HBEt_3$], the sole carbene-containing product isolated was the borane adduct IPr•$BEt_3$. These results suggested that the $C_{IPr}$-Ge linkage in the target species IPr•$GeH_2$ is weak (likely due to a reduction of Lewis acidity in $GeH_2$ relative to $GeCl_2$) leading to the unintended liberation of $GeH_2$ followed by the rapid decomposition[20] of this metastable entity into Ge and $H_2$.

Fortunately the road to a $GeH_2$ adduct opened when IPr•$GeCl_2$ (**6**)[21] was mixed with two equivalents of Li[$BH_4$] in $Et_2O$. This reaction cleanly affords IPr•$GeH_2$•$BH_3$ (**5**) as a colorless solid (eqn (1)) that is stable to *ca.* 130 °C in the solid state, and this main group hydride persists for days at room temperature in organic solvents. The hydrides bound to Ge and B in IPr•$GeH_2$•$BH_3$ (**5**) can be readily located by X-ray crystallography (Fig. 1) due to the increased electron density that is found about these hydrides ($H^{\delta-}$) in comparison to commonly encountered C-H residues. As will be seen, this property enables us to locate many of the hydride substituents in our products in the electron difference map during structure refinement. The stability of **5** can be attributed to the presence of both a Lewis base and a Lewis acid at Ge which leads to *push-pull* stabilization. In other words, the coordination of $BH_3$ to the lone pair of the $GeH_2$ unit lowers the energy of the proximal empty p-orbital at Ge, enabling a stronger dative $C_{IPr}$-Ge bond to form; this interaction is depicted diagrammatically in Scheme 2. Attempts to directly apply this protocol to prepare the $SnH_2$ complex IPr•$SnH_2$•$BH_3$, by allowing IPr•$SnCl_2$ (**7**) to react with excess Li[$BH_4$], gave only IPr•$BH_3$ and tin metal as non-volatile products. In order to counteract the lower Lewis acidity and basicity of the :$SnH_2$ unit relative to :$GeH_2$ (leading to more labile/unstable bonds to Sn) an alternate route to a $SnH_2$ adduct had to be devised.



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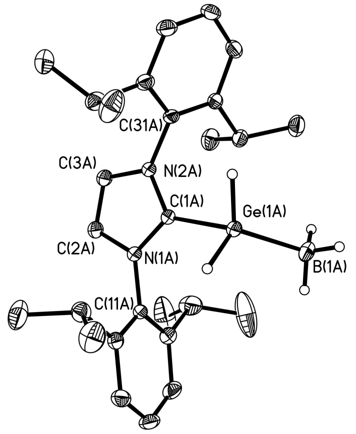
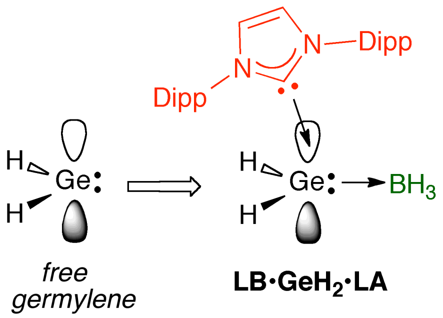
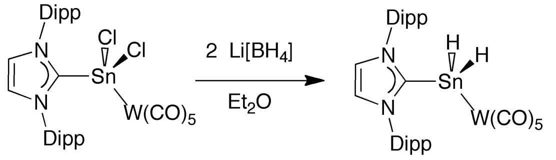


**Fig 1.** Molecular structure of IPr•$GeH_2$•$BH_3$ (**5**) with thermal ellipsoids at the 30 % probability level.[19]



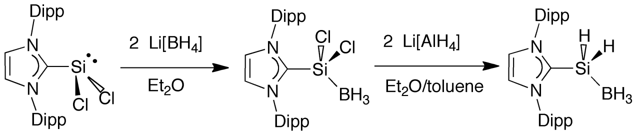
**Scheme 2.** Donor-acceptor (or push-pull) stabilization of the singlet germylene, $GeH_2$. Dipp = 2,6-$^iPr_2C_6H_3$; LB = Lewis base; LA = Lewis acid.

The chemistry of Sn(II) hydrides is relatively new with the first example of a stable member of this molecular class being the terphenyl-susbtituted centrosymmetric dimer $[Ar^{Trip}Sn(\mu\text{-}H)]_2$ ($Ar^{Trip}$ = 2,6-$Trip_2C_6H_3$; Trip = 2,4,6-$^iPr_3C_6H_2$) reported by Power in 2000.[22] In 2011, we were able to intercept $SnH_2$ in the form of the donor-acceptor complex IPr•$SnH_2$•$W(CO)_5$ (**8**) by taking advantage of the highly Lewis acidic nature of the 16-electron $W(CO)_5$ fragment.[23] Compound **8** was prepared in a multi-step procedure starting from $(THF)_2SnCl_2$•$W(CO)_5$ (**9**)[24] which was combined with the strong electron pair donor IPr to give the metal carbonyl adduct IPr•$SnCl_2$•$W(CO)_5$ (**10**) as a stable yellow solid. Once the Sn(II) center is nestled between an IPr donor and $W(CO)_5$ acceptor, halide-hydride metathesis chemistry readily occurs between **10** and Li[$BH_4$] (eqn (2)) to give IPr•$SnH_2$•$W(CO)_5$ (**8**) in high yield (Fig. 2).



**10** **8** (2)

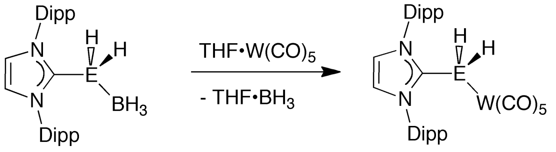
NMR spectroscopy is a particularly useful tool in analyzing **8** given that the $^{119}$Sn NMR resonance shows well-defined coupling to the adjacent hydrides (t, $^1J_{\text{Sn-H}} = 1158$ Hz) while resolvable Sn-W coupling was also noted involving the $^{183}$W nuclei within the W(CO)$_5$ units ($I = ½$; 14 % abundance; $^1J_{\text{Sn-W}} = 828$ Hz).[23] Later we expanded the homologous series EH$_2$ to include an adduct of SiH$_2$, IPr•SiH$_2$•BH$_3$ (**11**), which can be prepared according to the reaction sequence outlined in Scheme 3.[25,26] Thus far our attempts to prepare stable adducts containing a Pb(II) dihydride unit, *e.g.* IPr•PbH$_2$•W(CO)$_5$, have been unsuccessful. The anticipatedly low nucleophilicity of the lone pair within PbH$_2$ due to the inert pair effect, coupled with the thermodynamic instability of Pb-H linkages are likely culprits behind the observed synthetic difficulties. In this context, the formation of Pb(II) hydride intermediates (RSnH; R = sterically encumbered group) have been implicated in the synthesis of low-oxidation state diplumbylynes (RPbPbR) and lead clusters (R$_6$Pb$_{10}$ and R$_6$Pb$_{12}$).[27]



**12** **13** **11**

**Scheme 3.** Synthesis of IPr•SiH$_2$•BH$_3$ (**11**)[25] from the interaction of Li[AlH$_4$] with IPr•SiCl$_2$•BH$_3$ (**13**).[28]

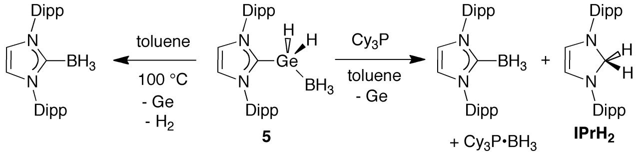
The C$_{\text{IPr}}$-E and E-B bonds in IPr•EH$_2$•BH$_3$ (E = Si and Ge; **11** and **5**) can be described as being labile and dative in nature, and some experimental observations support this notion. For example, efficient BH$_3$/W(CO)$_5$ group exchange transpires when IPr•GeH$_2$•BH$_3$ (**5**) and IPr•SiH$_2$•BH$_3$ (**11**) are each treated with THF•W(CO)$_5$, leading to the isolation of the new complexes IPr•EH$_2$•W(CO)$_5$ (E = Ge and Sn; **14** and **15**) in nearly quantitative yields (eqn (3)).[23,25] Moreover, heating IPr•GeH$_2$•BH$_3$ (**5**) to either 60 °C in THF or 100 °C in toluene causes the complete decomposition of this species into IPr•BH$_3$, germanium metal and hydrogen gas.[19] In addition, compound **5** reacts with Cy$_3$P at room temperature to yield IPr•BH$_3$, Cy$_3$P•BH$_3$, germanium metal and the dihydroaminal IPrH$_2$ (Scheme 4).[25] For comparison, the silylene adduct IPr•SiH$_2$•BH$_3$ (**11**) is much more stable than its Ge counterpart **5**, as it remains unchanged in hot toluene (100 °C) for 24 hrs and only reacts sluggishly with Cy$_3$P.[25] In a recent development, we have taken advantage of the ability of our GeH$_2$ adducts to release Ge metal under mild heating to prepare luminescent germanium nanoparticles in a controlled fashion when appropriate capping agents are present during the thermolysis.[29]



E = Si and Ge
**11** and **5**

E = Si and Ge
**14** and **15**

(3)



**Scheme 4.** Thermal and phosphine-induced release of germanium metal from IPr•GeH$_2$•BH$_3$ (**5**).

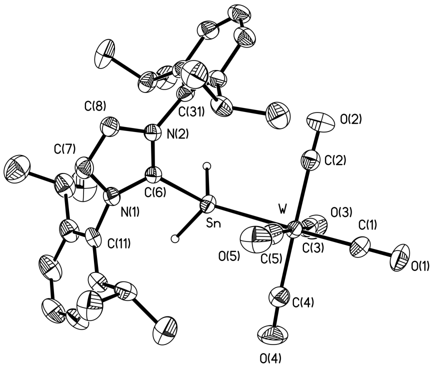
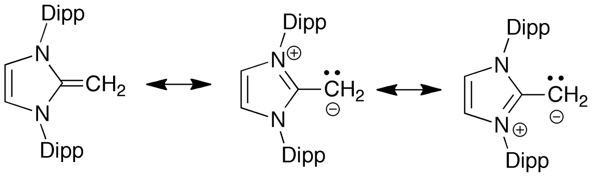


**Fig 2.** Molecular structure of IPr•SnH$_2$•W(CO)$_5$ (**8**) with thermal ellipsoids at the 30 % probability level.[23]

It is also instructive to detail our efforts to replace the carbene donor IPr in the donor-acceptor protocol with other widely used Lewis bases. For a point of comparison, we have prepared a series of adducts LB•GeCl$_2$ and LB•SnCl$_2$ (LB = phosphine and pyridine donors) and attempted to transform these species into the donor-acceptor complexes LB•EH$_2$•BH$_3$ and LB•EH$_2$•W(CO)$_5$ (E = Ge and Sn).[30] Somewhat to our surprise, we found that 4-dimethylaminopyridine (DMAP) and Cy$_3$P adducts of ECl$_2$, when treated with Li[BH$_4$], gave either DMAP•BH$_3$ or Cy$_3$P•BH$_3$ as isolable/identifiable products with no sign of compounds with encapsulated EH$_2$ moieties; similar difficulties were encountered when the donor-acceptor complexes Cy$_3$P•ECl$_2$•W(CO)$_5$ (E = Ge and Sn; **16** and **17**) were combined with various hydride sources. Thus the commonly employed donors DMAP and Cy$_3$P are not able to bind/stabilize EH$_2$ fragments under the conditions explored. Notably, we have found that a rarely explored ligand class, termed *N*-heterocyclic olefins (NHOs),[10c,11] are excellent donors for low oxidation state main group hydride chemistry. As shown in Scheme 5, the hindered NHO, IPr=CH$_2$ has ylidic-type reactivity by virtue of significant polarization of the *exocyclic* C=C double bond, leading to nucleophilic character at the terminal carbon atom. Using this property to our advantage, the stable complexes IPrCH$_2$•GeH$_2$•W(CO)$_5$ (**18**) and IPrCH$_2$•SnH$_2$•W(CO)$_5$ (**19**) (Fig. 3) were prepared using parallel synthetic strategies as outlined for the IPr adducts described above.[31] Moreover, clean Lewis base exchange between the NHO adducts $IPrCH_2•EH_2•W(CO)_5$ and IPr occurs to generate free $IPr=CH_2$ and the carbene-bound adducts $IPr•EH_2•W(CO)_5$ (E = Ge and Sn; **15** and **8**; eqn (4)).[31] This Lewis base exchange reaction has been observed in related studies from our group[32] and points to the carbene IPr being a stronger donor than its *N*-heterocyclic olefin counterpart $IPr=CH_2$. Furthermore, the ability to readily exchange Lewis bases at an electron deficient $EH_2$ site is consistent with the presence of dative/coordinative C(donor)-E bonds.



**$IPrCH_2$**

**Scheme 5.** Representative canonical forms for $IPrCH_2$ illustrating the nucleophilic character of the terminal $CH_2$ group.

Recently, the Ghadwal group has explored the reactivity between $IPr=CH_2$ and $HSiCl_3$ with the goal of preparing the Si(II) adduct $IPrCH_2•SiCl_2$; for reference, a reaction mixture containing IPr and $HSiCl_3$ was previously shown to give the novel Si(II) adduct $IPr•SiCl_2$ (**12**) in high yield.[33a] However in place of forming a Si(II) adduct, nucleophilic substitution between $IPrCH_2$ and a Si-Cl bond in $HSiCl_3$ transpired, followed by deprotonation of a C-H group in $IPrCH_2$ to yield $IPr=CH-SiCl_2H$ (**20**).[33b] A related transformation involving the perhalogenated cyclophosphazene $[Cl_2PN]_3$ and $IPr=CH_2$ has been reported in our group to give the stable $P_3N_3$ heterocycle $[(IPr=CH)PClN(PCl_2N)_2]$ (**21**) with [IPrMe]Cl (**22**) as a byproduct.[34]

$IPr•GeH_2•BH_3$ (**5**) can also be prepared in high yield by combining the Ge(IV) adduct $IPr•GeCl_4$ (**23**) with excess lithium borohydride in diethyl ether solvent (eqn (5)).[35] This process likely involves the generation of an unstable $HGeCl_3$ adduct (via H/Cl exchange) that later reductively eliminates a formal equivalent of HCl to yield $IPr•GeCl_2$ (**6**), which is then converted into $IPr•GeH_2•BH_3$ (**5**) by interaction with $Li[BH_4]$. A similar pathway is proposed to occur during the synthesis of $GeCl_2•dioxane$, where $GeCl_4$ is treated with the hydride source $^nBu_3SnH$ in the presence of dioxane as a Lewis base.[36]

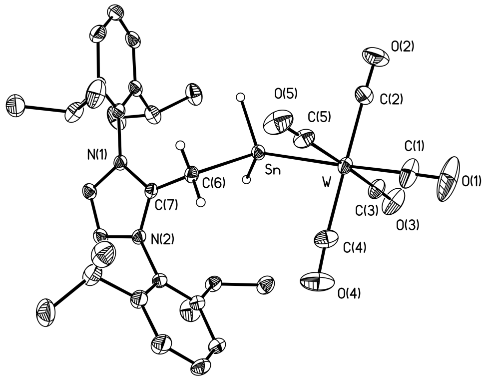
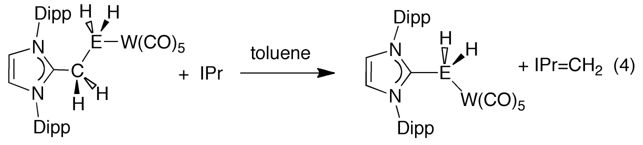
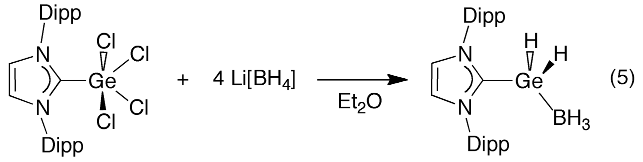


**Fig. 3.** Molecular structure of $IPrCH_2•SnH_2•W(CO)_5$ (**19**) with thermal ellipsoids at the 30 % probability level.[31]



E = Ge and Sn
**18** and **19**

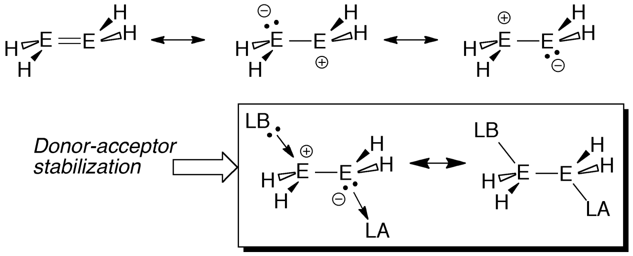
E = Ge and Sn
**15** and **8**



**23**

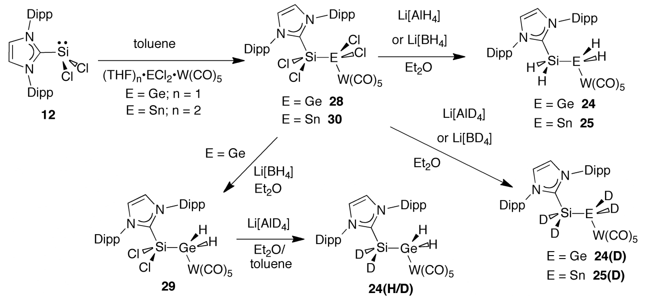
**5**

We have also applied donor-acceptor stabilization in the realm of inorganic ethylene chemistry ($H_2EE'H_2$; E and E′ = Si, Ge or Sn). These studies were largely motivated by detailed computational studies which revealed that inorganic ethylenes possess dual Lewis acid and basic behavior as a result of smaller HOMO-LUMO energy gaps in relation to ethylene $H_2C=CH_2$. In addition, the closer energies of the frontier orbitals in the heavier element ethylenes allow for energetically favourable mixing between E-E π and E-E σ* states (with some E-E σ/E-E π* mixing) when the substituents are arranged in a *trans bent* geometry; this bonding situation effectively shuttles π-electron density into non-bonding regions at each tetrel element.[37,38] This feature can be illustrated using the canonical forms listed in Scheme 6, and accordingly we reasoned that in the presence of suitable LB/LA combinations that such species could be trapped in the form of stable complexes.



**Scheme 6.** Resonance forms for the *trans bent* inorganic ethylenes, $H_2EEH_2$ (E = Si, Ge, Sn and Pb) and their complexation via donor-acceptor stabilization.

After considerable effort we devised a general pathway to the parent inorganic ethylene complexes $IPr•H_2SiGeH_2•W(CO)_5$ (**24**) and $IPr•H_2SiSnH_2•W(CO)_5$ (**25**).[39] In order to gain access to the requisite perhalogenato adducts, $IPr•Cl_2SiE'Cl_2•W(CO)_5$, it was noted that bound THF within the tungsten carbonyl complexes $(THF)GeCl_2•W(CO)_5$ (**26**) and $(THF)_2SnCl_2•W(CO)_5$ (**9**) could be easily displaced with the two-electron donor IPr to yield stable adducts $IPr•E'Cl_2•W(CO)_5$ (E′ = Ge and Sn; **27** and **10**).[23] Thus following a parallel strategy, Roesky's Si(II) complex $IPr•SiCl_2$ (**12**), which features a nucleophilic lone pair at Si,[40] was allowed to react with $(THF)GeCl_2•W(CO)_5$ (**26**) to yield a formal donor-acceptor adduct of tetrachlorosilagermene $IPr•Cl_2SiGeCl_2•W(CO)_5$ (**28**). Interestingly, the Ge-Cl residues in **28** proved to be more reactive towards hydride reagents in comparison to Si-Cl bonds, and selective installation of hydride functionality at Ge to form $IPr•Cl_2SiGeH_2•W(CO)_5$ (**29**) was accomplished by treating **28** with $Li[BH_4]$.[39] The increased reactivity of the Ge-Cl units can be rationalized by noting that $W(CO)_5$ is highly electron withdrawing in nature, which causes an increase in the electrophilic character of the proximal Ge center. In order to synthesize Si-H linkages, the stronger $H^-$ donor $Li[AlH_4]$ was required (Scheme 7); however great care was needed to ensure that the Lewis acidic $AlH_3$ by-product was rapidly removed (*i.e.* work-up 10 min. after the reaction was initiated), otherwise the target donor-acceptor ethylene complexes would degrade to yield the carbene-alane $IPr•AlH_3$. The analogous silastannene adduct $IPr•H_2SiSnH_2•W(CO)_5$ (**25**) (Fig. 4) was prepared according to a similar procedure used to obtain **24** with the use of $Li[BH_4]$ as a hydride source (Scheme 7). Compound **25** is less stable than its silagermene congener **24**, and spontaneous elimination of a formal equivalent of $SiH_2$ occurs in solution at room temperature to give the known Sn(II) dihydride adduct $IPr•SnH_2•W(CO)_5$ (**8**)[23] as a soluble product. Perhaps under judicious conditions we will be able to initiate the release of $H_2SiGeH_2$ or $H_2SiSnH_2$ to later generate bulk or nanomaterials with the tailored binary compositions SiGe or SiSn.[41] It should be mentioned that deuterium isotopologues of all the reported hydride adducts were made (**24(H/D)**, **24(D)**, and **25(D)**; Scheme 7). These synthetic efforts were useful in tracking reactivity pathways (*vide infra*) and for detangling IR assignments in the $W(CO)_5$ adducts as the Ge-H stretches often appear in the same region as the metal carbonyl ν(CO) vibrations. The Si-Ge and Si-Sn distances within compounds **24** and **25** [2.3717(14) and 2.5808(5) Å, respectively] are each within the range expected for single bonds, indicating the loss of E-E′ π-bonding character within the $H_2EE'H_2$ arrays upon complexation.[39]



**Scheme 7.** Synthesis of the silagermene and silastannene adducts $IPr•H_2SiGeH_2•W(CO)_5$ (**24**) and $IPr•H_2SiSnH_2•W(CO)_5$ (**25**) along with their deuterium isotopologues.[39]

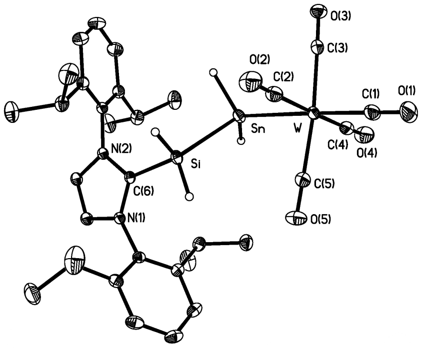
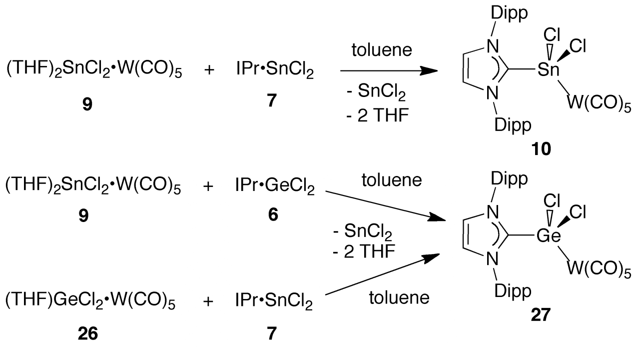


**Fig. 4.** Molecular structure of $IPr•H_2SiSnH_2•W(CO)_5$ (**25**) with thermal ellipsoids at the 30 % probability level.[39]

We also investigated the possible synthesis of related mixed element ethylene analogues by replacing $IPr•SiCl_2$ (**12**) with $IPr•GeCl_2$ (**6**) and $IPr•SnCl_2$ (**7**) in the reaction sequence outlined in Scheme 7. However in place of isolating stable dimetallene adducts, $ECl_2$ group metathesis transpired (Scheme 8).[42] We did succeed in eventually preparing the digermene adducts $IPr•H_2GeGeH_2•W(CO)_5$ (**31**) and $IPrCH_2•H_2GeGeH_2•W(CO)_5$ (**32**), and eqn (6) illustrates a low yielding (20 %) but reproducible route to the digermene complex **31** (Fig. 5) via a three-component, one pot, reaction between $IPr•GeCl_2$ (**6**) $GeCl_2•$dioxane and $Li[BH_4]$, followed by fractional crystallization.



**Scheme 8.** Attempted formation of mixed element dimetallene adducts ($Cl_2EE'Cl_2$) and the resulting $ECl_2$ metathesis chemistry (E = Ge and Sn).[42]

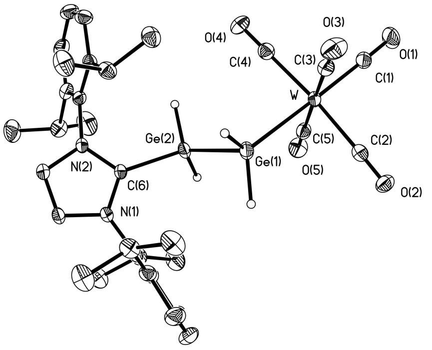
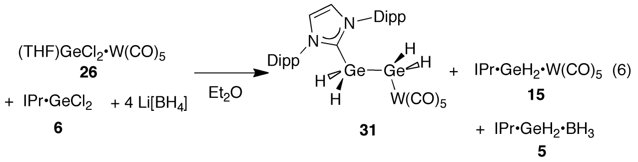
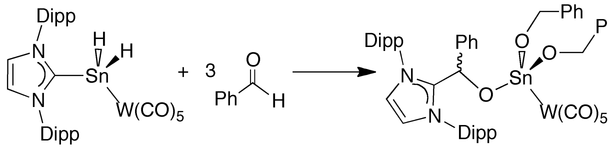


**Fig. 5.** Molecular structure of $IPr•H_2GeGeH_2•W(CO)_5$ (**31**) with thermal ellipsoids at the 30 % probability level.[42]



One area that remains ripe for exploration is the general reactivity of our donor-acceptor encapsulated methylene $EH_2$ and ethylenes $H_2EE'H_2$. Due to the presence of polarized E-H bonds and concomitant hydridic character, one would expect these species to be possible reducing agents in organic chemistry (*e.g.* in the hydrosilylation of ketones).[43] Moreover, the potentially labile nature of the coordinative bonds to these main group hydrides should enable for the opening of coordination sites for substrate binding/activation. We have documented two salient reduction processes involving a $SnH_2$ and $H_2SiGeH_2$ adduct, respectively, and these examples serve to illustrate the possible utility of these complexes in further chemical transformations. When the carbene adduct IPr•SnH$_2$•W(CO)$_5$ (**8**) was treated with benzophenone, hydrostannylation to form Sn-appended benzyloxy groups occurred along with the insertion of an additional PhC(O)H unit into a C$_{\text{IPr}}$-Sn linkage (eqn (7)).[23] Our attempts to achieve turn-over (*i.e.* release of HOBz) and render this system catalytic were not successful but this early reaction does illustrate that the inherent reactivity of the SnH$_2$ unit in **8** was not quenched despite the presence of capping IPr and W(CO)$_5$ groups. In a related transformation, delivery of a hydride to an equivalent of acetylacetone H$_3$CC(O)CH$_2$C(O)CH$_3$ was demonstrated using the inorganic ethylene adduct IPr•H$_2$SiGeH$_2$•W(CO)$_5$ (**24**); by conducting selective deuterium labelling studies, it was shown that the Si-H unit participated in hydride transfer to one of the ketonic carbons of acetylacetone.[39]



(7)

**8** **33**

In a collaboration with Prof. Rolfe Herber at the Racah Institute of Physics, the electron density and bonding properties within a series of Sn(II) halide and hydride adducts were interrogated via $^{119}$Sn Mössbauer effect spectroscopy.[30] This technique provides a measure of the degree of s-electron density about a tin atom as this parameter can be directly correlated to the isomer shift (IS) value obtained (equal to the center of the doublet resonance); see Fig. 6 for a typical Mössbauer spectrum for one of our adducts, IPr•SnCl$_2$ (**7**).[44] In addition, the degree of asymmetry in the electronic environment around tin can be discerned via changes in the magnitude of the quadrupolar splitting (QS) between the two peaks that make up the doublet resonances. Numerous compounds in the series LB•SnCl$_2$ and LB•SnX$_2$•W(CO)$_5$ (LB = IPr, IPrCH$_2$, IPr•SiCl$_2$ and PCy$_3$; X = Cl or H) were investigated and some interesting trends emerged. First of all, the IS values noted were in the range often observed for Sn(II) complexes while coordination of a W(CO)$_5$ group at tin afforded a decrease in IS value, consistent with some s-electron density at tin being transferred to the W(CO)$_5$ acceptor. Furthermore, within the series LB•SnCl$_2$•W(CO)$_5$ the IS values remained remarkably invariant to the nature of the donor (LB) bound at tin. This observation, when taken with supporting computational investigations, indicate that the LB-Sn interactions are made with tin based orbitals that are largely of p-character; thus the bonding descriptor outlined in Scheme 2 appears to be quite valid for the LB-Sn interactions in these adducts.[30]

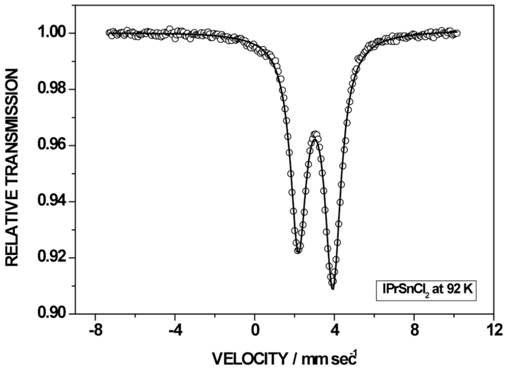


**Fig. 6.** Mössbauer spectrum for IPr•SnCl$_2$ (**7**).[30]

More recently we became interested in the notion of generating extended oligomeric [ER$_2$]$_x$ arrays sandwiched between Lewis acidic and basic entities, in order to directly observe the role of catenation (*i.e.* forming extended E-E σ-bonded networks) on the conjugation and optical properties of the resulting materials.[45] Drawing inspiration from polymer chemistry,[46] it was expected that a narrowing of the optical band gap would transpire upon chain growth leading to the possible use of the resulting materials as low energy photoresists. Our first approach involved directly combining IPr•GeCl$_2$•W(CO)$_5$ (**27**) with GeCl$_2$•dioxane with the hope that a GeCl$_2$ unit would insert into the dative C$_{\text{IPr}}$-Ge bond; however this strategy did not yield any discernable reaction. We were eventually able to construct new carbene-supported Ge chains by the sequential reaction of IPr•GeCl$_2$ (**6**) with increasing equivalents of GeCl$_2$•dioxane.[47] The formation of the first addition product IPr•GeCl$_2$GeCl$_2$ (**34**) was surprisingly challenging as the terminal Ge-Ge bond in this complex is quite labile; one can view this linkage as being formally derived from the donation of a lone pair at Ge in IPr•GeCl$_2$ (**6**) into an empty p-orbital on a GeCl$_2$ unit. Accordingly the synthesis of **34** has to be conducted in CH$_2$Cl$_2$ as more strongly coordinating solvents such as THF resulted in Ge-Ge bond scission and the regeneration of IPr•GeCl$_2$ (**6**) (Scheme 9). Not only is the crystallographically determined Ge-Ge bond in IPr•GeCl$_2$GeCl$_2$ (**34**) very long [2.6304(9) Å] (Fig. 7), our computational studies revealed that the electron density along the bond critical point by the atoms-in-molecules (AIM) method was small, suggesting the presence of a weak bonding interaction.

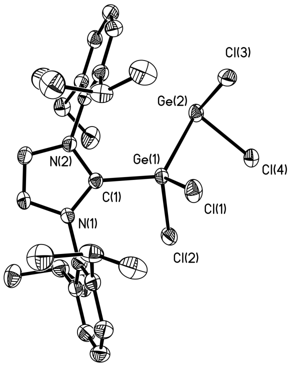
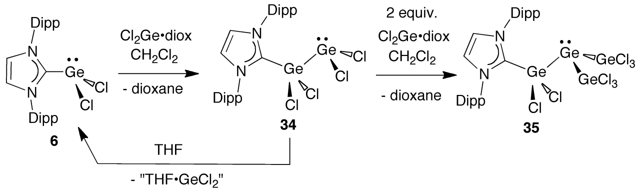


**Fig. 7.** Molecular structure of IPr•GeCl$_2$GeCl$_2$ (**34**) with thermal ellipsoids at the 30 % probability level.[47]

When additional equivalents of germanium(II) dichloride were added to **34**, the formation of a new branched product IPr•$GeCl_2(GeCl_3)_2$ (**35**) transpired (Scheme 9; Fig. 8). This product is more stable in solution than its digermene counterpart **34**, and an accompanying computational study uncovered a preference for branched structures over linear $(GeCl_2)_x$ arrangements as the number of joined Ge atoms is increased beyond 2.[47] Branching of the oligogermanium arrays leads to shortening of the Ge-Ge bond distances to nearly equivalent single-bond lengths of 2.4870(8) to 2.4987(8) Å in **35** along with an increase in both the bonding electron density and covalent character according to computational analyses. This result demonstrates a parallel between the chemistry of Ge and C as branched hydrocarbons are also more thermodynamically stable than their linear counterparts.[48] Thus far our attempts to convert these oligohalogermane adducts to either germanium hydrides or extended Ge metal clusters have not been successful; for example the formation of IPr•$GeH_2$•$BH_3$ (**5**) was observed when either **34** and **35** were allowed to react with Li[$BH_4$]. As a final point, it is known that oligogermanes such as $H_2GeGeH_2$ can have various isomer forms that lie close in energy[37] (*e.g.* the germyl-germylene HGe-$GeH_3$), thus it would be interesting to see if the introduction of new donors types at Ge could enable the stabilization of one isomer form over another.[49]



**Scheme 9.** Donor-supported growth of perhalogermanium chains.[47]

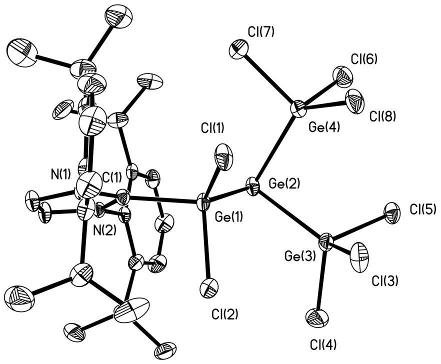
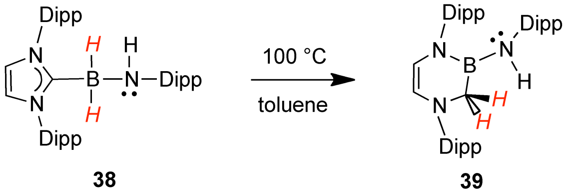


**Fig. 8.** Molecular structure of IPr•$GeCl_2(GeCl_3)_2$ (**35**) with thermal ellipsoids at the 30 % probability level.[47]

Our forays into molecular main group chemistry has led to the discovery of a potentially general degradation/ligand activation process involving the widely used carbene donor IPr and boron hydrides. As part of our studies involving the preparation of the stable Si(II) and Ge(II) hydridoamide adducts IPr•EH(NHDipp)•$BH_3$ (E = Si and Ge; **36** and **37**), it was noted that the byproduct IPr•$BH_2$NHDipp (**38**) was routinely formed during the syntheses.[50] An attempt to convert this amidoborane adduct[51] into the carbene-bound iminoborane IPr•HB=NDipp via thermal dehydrogenation led to an unexpected result. In place of $H_2$ elimination, we observed a formal hydride-migration/ring-expansion reaction to yield the C-N activated heterocycle, [$(HCNDipp)_2CH_2BNHDipp$] (**39**) (eqn (8); Fig. 9). The mechanism of this transformation has been investigated in detail computationally and experimentally via deuterium labelling studies, which show two consecutive B to C hydride migration events transpiring *en route* to the observed ring-expanded product.[52] It should be mentioned that similar activation processes have been reported for Be and Si hydrides,[53] and the potential for the carbene donor to participate in ring-expansion has to be kept in mind when exploring the chemistry of main group hydride-carbene adducts in catalysis.[54]



(8)

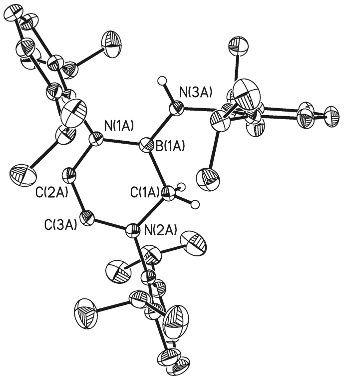


**Fig. 9.** Molecular structure of the ring-expanded product [$(HCNDipp)_2CH_2BNHDipp$] (**39**) with thermal ellipsoids at the 30 % probability level.[50]

## 4. Conclusions

The goal of this Perspective was to provide a brief historical account of the development of *donor-acceptor* stabilization method to intercept Group 14 hydride species that resisted isolation using pre-existing methods. Not only are these main group element complexes of fundamental interest in terms advancing our view of chemical bonding, we have shown early glimpses of potential applications of these metastable complexes, including their use as reducing agents in organic chemistry and the clean generation of metal nanoparticles upon mild thermolysis.[29] It should be noted that this approach is likely quite general in nature and increasingly challenging/exotic targets (*e.g.* a molecular adduct of B≡N) should be rendered isolable in the condensed phase with an appropriate choice of synthetic conditions and Lewis acid/base capping agents. In addition, *N*-heterocyclic olefins (NHOs) such as IPr=$CH_2$ have been found to be excellent ligands for p-block chemistry, and investigations towards using these donors to support transition metal-mediated catalysis are underway. Lastly, in our search for new molecular main group hydride adducts, we found that boron hydride adducts can participate in carbene activation/degradation processes. As a result, such decomposition pathways need to be considered when exploring future applications involving these complexes.[55]

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*Department of Chemistry, University of Alberta, 11227 Saskatchewan Dr., Edmonton, AB, Canada, T6G 2G2. E-mail: erivard@ualberta.ca; Fax: +1 780 492 8231; Tel: +1 780 492 4255*

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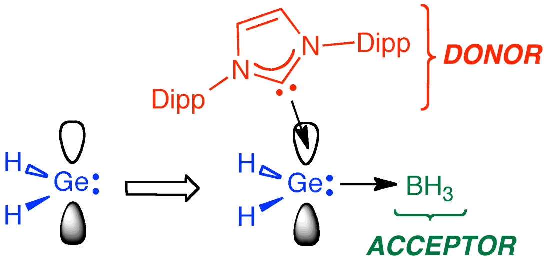
## Table of Contents Graphic/Synopsis

This Perspective article describes the preparation of low-oxidation state main group hydrides using a general donor-acceptor strategy.



## Biographical Sketch and Author Image

*Eric Rivard completed his B.Sc. (Honors) degree at the University of New Brunswick and later obtained a Ph.D. degree at the University of Toronto under the supervision of Professor Ian Manners FRS. He then conducted NSERC sponsored postdoctoral work with Professors Jonas Peters (Caltech) and Philip Power FRS (University of California, Davis), followed by research with Professor Cameron Jones. In 2008 he began his independent career as an Assistant Professor at the University of Alberta and was recently promoted to the rank of Associate Professor. He has been the recipient of an Alberta Innovates New Faculty Award, a Petro-Canada Young Innovator Award and various teaching awards. His current research interests involve the stabilization of low oxidation main group hydrides and the development of new light-emitting systems via zirconium-mediated syntheses; he has published over 60 papers thus far.*