

## Preparation and Structures of Group 12 and 14 Element Halide–Carbene Complexes

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The synthesis of a series of *N*-heterocyclic carbene (NHC) complexes involving zinc, cadmium, and the heavy Group 14 elements germanium, tin, and lead is reported. The direct reaction between the bulky carbene IPr (IPr = (HCNDipp)<sub>2</sub>C:, Dipp = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and the Group 14 halide reagents GeCl<sub>4</sub> and SnCl<sub>4</sub> afforded the 1 : 1 complexes IPr·ECl<sub>4</sub> (E = Ge and Sn) in high yield; similarly, ZnI<sub>2</sub> interacted with IPr in THF to give the THF-bound complex IPr·ZnI<sub>2</sub>·THF. CdCl<sub>2</sub> underwent divergent chemistry with IPr and the major product isolated was the imidazolium salt [IPrH][IPr·CdCl<sub>3</sub>], which could be converted into IPr·CdCl<sub>2</sub>·THF upon treatment with Tl[OTf]. In addition, the stable Pb<sup>II</sup> amide adduct, IPr·PbBr (NHDipp), was prepared. Each of the new carbene–element halide adducts was treated with the hydride sources Li[BH<sub>4</sub>] and Li[HBt<sub>3</sub>] in order to potentially access new element hydride adducts and/or clusters. In most instances scission of the element–carbene bonds transpired, except in the case of IPr·ZnI<sub>2</sub>·THF, which reacted with two equivalents of Li[BH<sub>4</sub>] to yield the thermally stable bis(borohydride) zinc complex IPr·Zn(BH<sub>4</sub>)<sub>2</sub>.

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### Introduction

Since the discovery that *N*-heterocyclic carbenes (NHC) could be synthesised in large quantities as thermally stable materials,<sup>[1]</sup> researchers have sought to explore this versatile ligand class within the context of catalysis<sup>[2]</sup> and to intercept novel bonding environments within the main group.<sup>[3]</sup> In relation to the latter concept, the generation/stabilisation of reactive main group element allotropes such as the tetrylone dimers E<sub>2</sub> (E = Si, Ge, and Sn),<sup>[4–6]</sup> the diboron species B<sub>2</sub>,<sup>[7]</sup> and the parent methylene and ethylene analogues (EH<sub>2</sub> and H<sub>2</sub>EEH<sub>2</sub>)<sup>[8–11]</sup> in the form of stable NHC adducts, represent interesting additions to the chemical literature.<sup>[12]</sup>

In general, the preparation of the above-mentioned reactive species necessitates the use of main group element halide adducts of NHCs as starting reagents. In line with this concept, we report the synthesis of new Group 12 and 14 element halide adducts containing the readily prepared hindered carbene IPr (IPr = (HCNDipp)<sub>2</sub>C:, Dipp = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) as a donor.<sup>[13]</sup> Added interest for this research endeavour stems from the reports that various NHC–zinc adducts (including those of ZnBr<sub>2</sub>) can act as catalysts for a variety of transformations ranging from the ring-opening polymerization of lactides, to the synthesis of value added products from CO<sub>2</sub>.<sup>[14]</sup> Our ultimate goal for preparing Group 12 and 14 element halide complexes is to convert these species into new hydride analogues using productive halide/hydride substitution chemistry; such species could yield novel chemistry with CO<sub>2</sub><sup>[14]</sup> and might be useful

precursors to new clusters and/or nanomaterials by thermolysis chemistry.<sup>[15]</sup>

### Results and Discussion

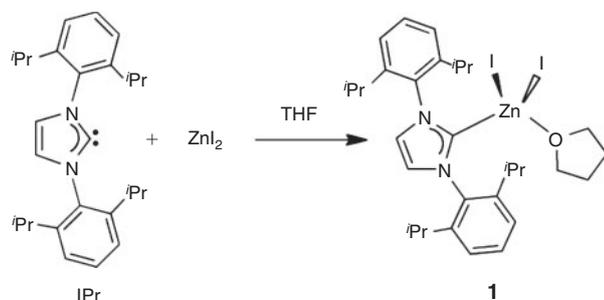
#### Carbene Complexes of Group 12 Element Dihalides

The use of NHC as ligands with Group 12 elements is not a new concept, as illustrated by the report of a stable NHC–mercury complex by Wanzlick in 1970.<sup>[16,17]</sup> The primary motivation for our exploration of carbene coordination chemistry involving Group 12 element halides is the future synthesis of novel hydride species by halide metathesis chemistry;<sup>[18]</sup> it should be mentioned that one of our original synthetic targets from this study, [IPr·ZnH(μ-H)]<sub>2</sub>, was recently prepared by Okuda and coworkers.<sup>[18c]</sup>

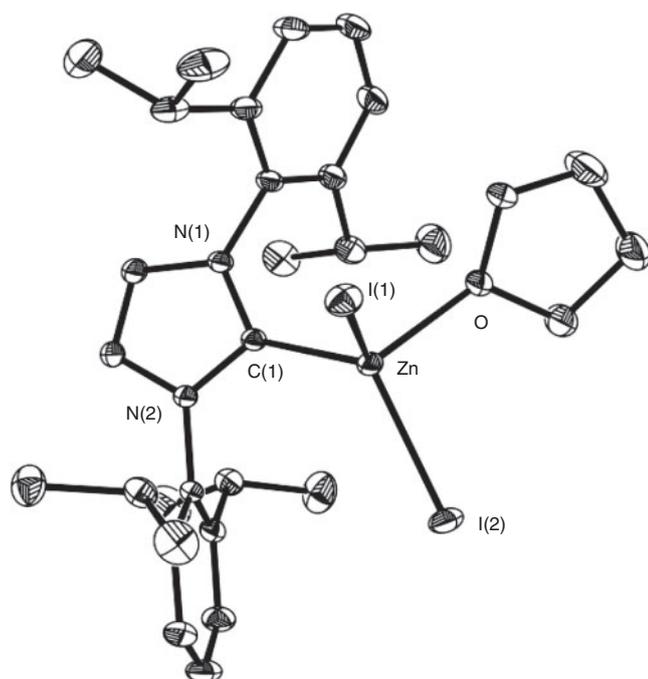
As depicted in Scheme 1, the thermally stable zinc iodide adduct IPr·ZnI<sub>2</sub>·THF (**1**) (mp = 150–152°C) was prepared in high yield by combining IPr with ZnI<sub>2</sub> in THF. The <sup>1</sup>H NMR spectrum of **1** gave expected features for a mono-adduct of IPr including a diagnostic pair of doublet resonances due to the presence of diastereotopically inequivalent Me groups within the peripheral isopropyl groups of the carbene donor. Additional structural authentication of **1** was achieved by single-crystal X-ray crystallography and the refined structure of **1** is shown in Fig. 1.

As expected, the Zn centre in **1** adopts a slightly distorted tetrahedral geometry with a C<sub>IPr</sub>–Zn bond length of 2.0419(19) Å.

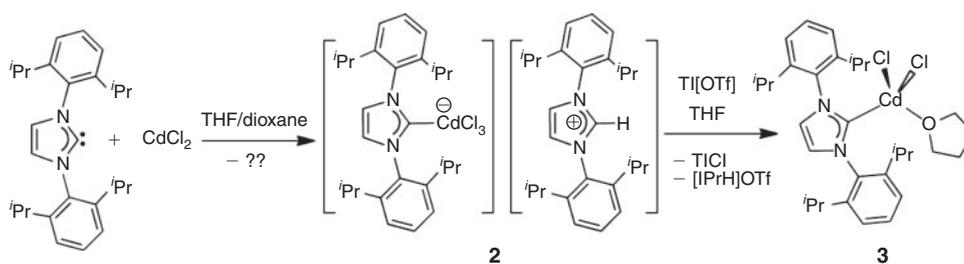
For comparison, the  $C_{\text{IPr}}\text{-Zn}$  distances in the recently reported zinc dichloride adduct  $\text{IPr}\cdot\text{ZnCl}_2\cdot\text{THF}$  (2.045(6) Å average) has the same value within experimental error as **1**,<sup>[19]</sup> while the  $\text{Zn-O}$  distance in **1** (2.1252(16) Å) is lengthened in relation to the  $\text{Zn-O}$  bond length in  $\text{IPr}\cdot\text{ZnCl}_2\cdot\text{THF}$  (2.093(4) Å average).<sup>[19,20]</sup> Attempts to bind an additional equivalent of IPr to the Zn centre in **1** (to form  $\text{IPr}\cdot\text{ZnI}_2\cdot\text{IPr}$ ) did not yield any appreciable coordination chemistry, but rather crystals of



Scheme 1.



**Fig. 1.** Thermal ellipsoid plot (30% probability level) for  $\text{IPr}\cdot\text{ZnI}_2\cdot\text{THF}$  (**1**). All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg.]:  $\text{Zn-C}(1)$  2.0419(19),  $\text{Zn-I}(1)$  2.6120(3),  $\text{Zn-I}(2)$  2.5580(3),  $\text{Zn-O}$  2.1252(16);  $\text{I}(1)\text{-Zn-I}(2)$  112.701(10),  $\text{C}(1)\text{-Zn-I}(1)$  108.10(6),  $\text{C}(1)\text{-Zn-I}(2)$  120.21(5),  $\text{C}(1)\text{-Zn-O}$  110.49(7).



Scheme 2.

the monomeric THF-free adduct  $\text{IPr}\cdot\text{ZnI}_2$  were obtained.<sup>[21]</sup> Of particular note, Jones and coworkers have recently reported the analogous bromide adduct  $[\text{IPr}\cdot\text{ZnBr}(\mu\text{-Br})_2]$  whereby the replacement of iodide with bromide groups at zinc led to the formation of a centrosymmetric dimer.<sup>[22]</sup>

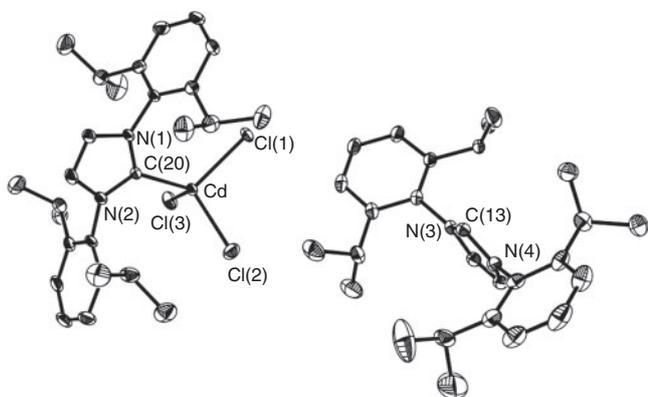
Our attempts to extend carbene complexation to cadmium dichloride proved to be more of a challenge.<sup>[22,23]</sup> When IPr was directly combined with  $\text{CdCl}_2$  in a THF/dioxane solvent mixture, a new Cd-containing product was obtained after crystallizing the resulting crude material from THF/hexanes at  $-35^\circ\text{C}$ . Interestingly, this product contained  $^1\text{H}$  NMR spectroscopic resonances consistent with the presence of two distinct IPr environments. For example, a singlet resonance was present at 6.57 ppm (in  $\text{C}_6\text{D}_6$ ) due to backbone-positioned C-H groups of the central five-membered ring in IPr; this signal was also accompanied by adjoining satellites resonances resulting from long-range coupling ( $\sim^4J = 5.6$  Hz) to NMR active  $^{111}\text{Cd}$  and  $^{113}\text{Cd}$  nuclei ( $I = 1/2$ ; 12.8 and 12.2% abundances, respectively).<sup>[24]</sup> Thus it appeared that one of the IPr units was bound to a Cd centre. A second set of IPr resonances was also detected and gave diagnostic resonances for the known imidazolium cation  $[\text{IPrH}]^+$  (e.g. the backbone C-H groups of the imidazolium heterocycle were located at 9.21 ppm). The composition of the isolated Cd product was corroborated by X-ray crystallography, which identified the product as  $[\text{IPrH}][\text{IPr}\cdot\text{CdCl}_3]$  (**2**) (Scheme 2, Fig. 2).

The formation of **2** suggests that C-H bond activation of one equivalent of carbene likely transpired<sup>[25]</sup> to form the imidazolium salt **2**; at this time we are unsure about the fate of the other product(s) generated in this transformation. In chemistry reported by the Jones group, IPr and  $\text{Cl}_2\text{Ge}\cdot\text{dioxane}$  combine in THF to give crystals of  $[\text{IPrH}]\text{GeCl}_3$ ,<sup>[5a,26]</sup> whereas when the same reaction is conducted in either  $\text{Et}_2\text{O}$ <sup>[5a]</sup> or toluene<sup>[8]</sup> the production of  $\text{IPr}\cdot\text{GeCl}_2$  occurs in high yield. Therefore the stronger donating ability of the THF and dioxane appear to assist in the C-H activation/deprotonation chemistry leading to HCl production and the subsequent formation of **2**. Unfortunately, our attempts to react  $\text{CdCl}_2$  with IPr in less polar solvents ( $\text{Et}_2\text{O}$  and toluene) gave no reaction, presumably due to the low solubility of  $\text{CdCl}_2$  in these solvents. In contrast to our studies, the Jones group reports clean adduct formation between  $\text{CdI}_2$  and IPr in toluene, to form  $[\text{IPr}\cdot\text{CdI}(\mu\text{-I})_2]$ , adding support to the notion that polar solvents accelerate the production of HCl in the reaction between  $\text{CdCl}_2$  and IPr.<sup>[22]</sup>

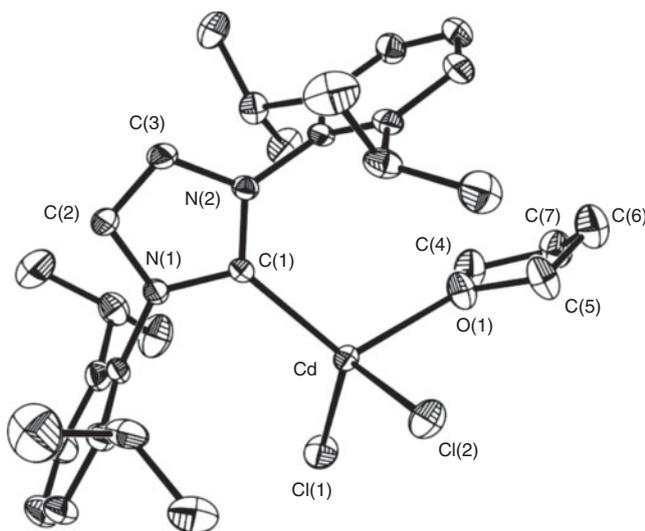
As depicted in Fig. 2, compound **2** consists of discrete cationic  $[\text{IPrH}]^+$  and anionic  $[\text{IPr}\cdot\text{CdCl}_3]^-$  units in the solid state. The  $C_{\text{IPr}}\text{-Cd}$  interaction in **2** is 2.246(3) Å and is considerably shorter than the  $C_{\text{NHC}}\text{-Cd}$  distances noted within various NHC adducts of  $\text{CdMe}_2$  (2.327(2) to 2.406(4) Å).<sup>[23]</sup> The Cd centre within the  $[\text{IPr}\cdot\text{CdCl}_3]^-$  anion has a distorted tetrahedral geometry with bond angles at Cd in the range of  $103.59(3)^\circ$  to

114.76(7)°, while the metrical parameters for the remaining [IPrH]<sup>+</sup> cation match those found in related imidazolium salts present in the literature.<sup>[5a,27]</sup>

As part of our attempts to induce HCl elimination from [IPrH][IPr·CdCl<sub>3</sub>] (**2**) and generate a well defined neutral cadmium dihalide adduct, we treated **2** with thallium triflate, Tl[OTf], in THF. Upon adding Tl[OTf] to **2**, the immediate formation of a white precipitate (presumably TlCl) was observed; analysis of the resulting filtrate confirmed the presence of [IPrH]OTf and a new carbene containing product (**Scheme 2**). The latter species exhibited diagnostic coupling between the IPr unit and Cd in the form of <sup>111</sup>Cd and <sup>113</sup>Cd satellites. Fortunately the cadmium–carbene complex could be selectively separated from [IPrH]OTf by extraction with benzene, and crystals of this species could be obtained from THF/hexanes which identified the product as the target adduct IPr·CdCl<sub>2</sub>·THF (**3**) (**Fig. 3**). Notably, IPr·CdCl<sub>2</sub>·THF readily



**Fig. 2.** Thermal ellipsoid plot (30% probability level) for [IPrH][IPr·CdCl<sub>3</sub>] (**2**). All hydrogen atoms and toluene solvate have been omitted for clarity. Selected bond lengths [Å] and angles [deg.]: Cd–C(1) 2.246(3), Cd–Cl(1) 2.4790(8), Cd–Cl(2) 2.4650(10), Cd–Cl(3) 2.4573(9); C(1)–Cd–Cl(1) 114.76(7), Cl(1)–Cd–Cl(2) 103.59(3), Cl(2)–Cd–Cl(3) 112.24(4).



**Fig. 3.** Thermal ellipsoid plot (30% probability level) for IPr·CdCl<sub>2</sub>·THF (**3**). All hydrogen atoms and THF solvate have been omitted for clarity. Selected bond lengths [Å] and angles [deg.]: Cd–C(1) 2.218(2), Cd–Cl(1) 2.4029(6), Cd–Cl(2) 2.4338(6), Cd–O(1) 2.3413(17); Cl(1)–Cd–Cl(2) 114.08(3), C(1)–Cd–Cl(1) 119.97(6), C(1)–Cd–Cl(2) 111.26(6), C(1)–Cd–O(1) 112.14(8).

underwent loss of THF under vacuum to yield IPr·CdCl<sub>2</sub>, which was characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy and elemental analysis (C, H, and N).

Compound **3** adopts a similar coordination motif as its lighter Group 12 element congener IPr·ZnCl<sub>2</sub>·THF<sup>[19]</sup> with Cd–Cl bonds (2.4184(8) Å average) which are longer than the reported Zn–Cl distances in IPr·ZnCl<sub>2</sub>·THF (2.257(4) Å average) due to the larger covalent radius of Cd. A C<sub>IPr</sub>–Cd bond length of 2.218(2) Å was determined in **3** which is contracted in relation to the C<sub>IPr</sub>–Cd distance within the anionic [IPr·CdCl<sub>3</sub>]<sup>−</sup> unit in **2** (2.246(3) Å), however, a similar C<sub>IPr</sub>–Cd bond length of 2.249(5) Å was noted in [IPr·CdI(μ-I)]<sub>2</sub>.<sup>[22]</sup> We did not extend our synthetic investigations to include the Hg<sup>II</sup> adducts IPr·HgX<sub>2</sub> (X = halide) as efficient routes to these species are already known.<sup>[28]</sup>

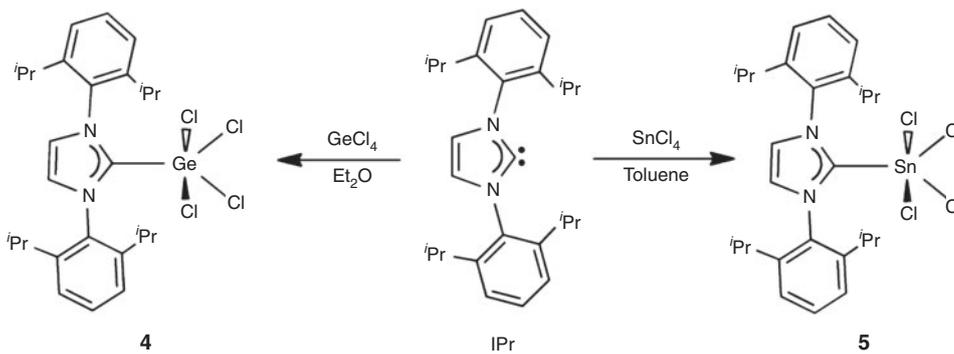
### Carbene Complexes of Group 14 Element Halides

As discussed in the Introduction, the synthesis of many novel carbene-supported main group species (such as Si<sub>2</sub>)<sup>[4]</sup> depends upon the availability of suitable element halide adducts as precursors. Despite the availability of several IPr-capped species such as IPr·EX<sub>2</sub> (E = Si, Ge, and Pb; X = Cl or Br)<sup>[5,8,29]</sup> and IPr·SiX<sub>4</sub> (X = F, Cl, or Br),<sup>[4,29b,30]</sup> the Ge<sup>IV</sup> and Sn<sup>IV</sup> adducts IPr·GeCl<sub>4</sub> and IPr·SnCl<sub>4</sub> remained conspicuously absent from the literature. We now report that these complexes are readily prepared in high yield as moisture-sensitive white solids (86% yield each) by combining IPr with GeCl<sub>4</sub> and SnCl<sub>4</sub>, respectively (**Scheme 3**).

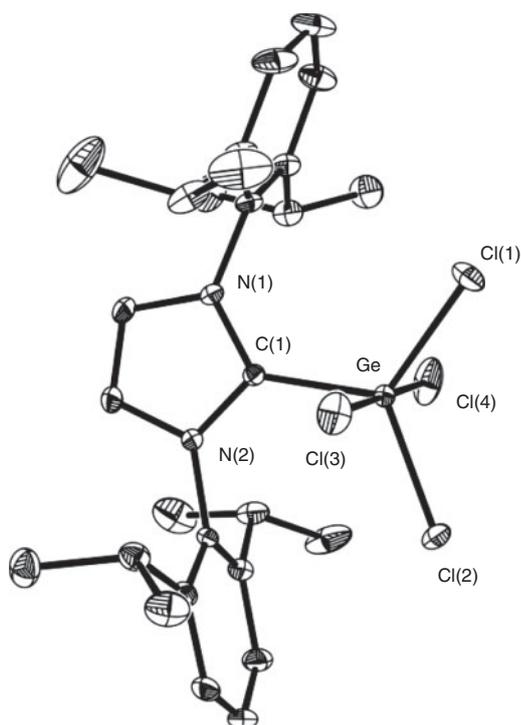
Both IPr·GeCl<sub>4</sub> (**4**) and IPr·SnCl<sub>4</sub> (**5**) crystallised in nearly isostructural arrangements (**Figs 4 and 5**, respectively) with the carbene ligands occupying equatorial sites about the trigonal bipyramidal Ge and Sn centres. Another interesting aspect of these structures is that the central ring of each IPr donor aligns in such a fashion as to keep its constituent atoms nearly co-planar with the two adjacent equatorial Cl atoms (e.g. N(1)–C(1)–Ge–Cl(1) torsion angle = 6.81(14)°, thus minimising repulsive steric interactions between the flanking Dipp groups and the axially disposed Cl atoms. A similar geometric arrangement of the IPr and equatorial chloro ligands exists in Robinson's Si<sup>IV</sup> complex IPr·SiCl<sub>4</sub>.<sup>[4]</sup> In line with the presence of trigonal bipyramidal geometries in **4** and **5**, nearly linear Cl<sub>ax</sub>–E–Cl<sub>ax</sub> angles were found (Cl(3)–Ge–Cl(4) = 179.66(4)° in **4**; Cl(2)–Sn–Cl(3) = 177.51(3)° in **5**) which match closely with the corresponding Cl<sub>ax</sub>–Si–Cl<sub>ax</sub> angle of 176.94(4)° in IPr·SiCl<sub>4</sub>. The C<sub>IPr</sub>–Ge bond length in **4** is 1.9921(14) Å and is significantly shorter than the C<sub>IPr</sub>–Ge distance in the Ge<sup>II</sup> adduct IPr·GeCl<sub>2</sub> (2.112(2) Å).<sup>[8]</sup> The C<sub>IPr</sub>–Ge bond contraction in **4** relative to in IPr·GeCl<sub>2</sub> can be explained by both the smaller effective size of Ge<sup>IV</sup> versus Ge<sup>II</sup><sup>[31]</sup> and the greater Lewis acidity of the GeCl<sub>4</sub> unit in comparison to GeCl<sub>2</sub>; a similar trend is found when the C<sub>IPr</sub>–Sn bond lengths in **5** (2.186(2) Å) and IPr·SnCl<sub>2</sub> (2.341(8) Å)<sup>[8]</sup> are compared.

The last element halide complex prepared in this study was the Pb<sup>II</sup> amide adduct, IPr·PbBr(NHDipp) (**6**). This species was targeted as previous work in our laboratory showed that the lighter congeners IPr·ECl(NHDipp) (E = Si, Ge, and Sn) can undergo unusual transmetalation chemistry in the presence of the hydride source Li[BH<sub>4</sub>].<sup>[32]</sup> The synthesis of **6** is outlined in **Scheme 4** and relies upon the use of Jones' soluble Pb<sup>II</sup> precursor IPr·PbBr<sub>2</sub> as a reagent.<sup>[5b]</sup>

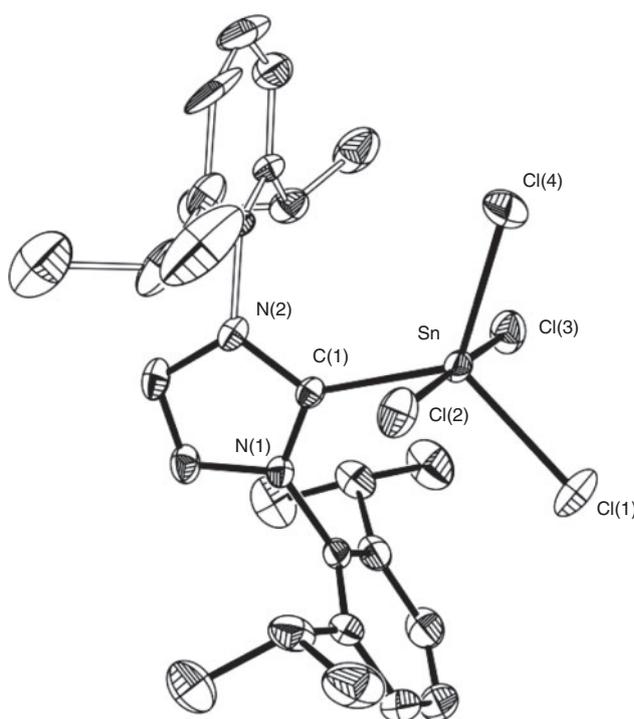
Compound **6** is a thermally stable (up to 260°C) yellow solid that is soluble in organic solvents. In contrast to the known amido-tetrelene adducts IPr·ECl(NHDipp) (E = Si, Ge, and



Scheme 3.



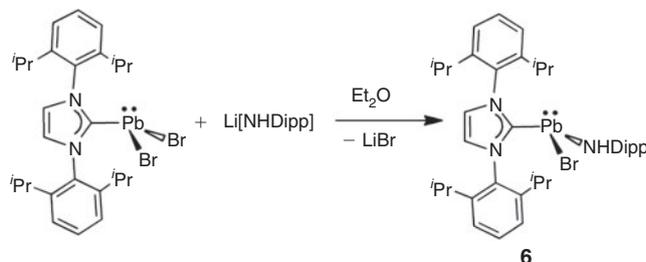
**Fig. 4.** Thermal ellipsoid plot (30% probability level) for IPr-GeCl<sub>4</sub> (**4**). All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg.]: C(1)–Ge 1.9921(14), Ge–Cl(1) 2.1428(5), Ge–Cl(2) 2.1455(4), Ge–Cl(3) 2.3206(5), Ge–Cl(4) 2.2516(5); C(1)–Ge–Cl(1) 118.46(4), C(1)–Ge–Cl(2) 118.93(4), C(1)–Ge–Cl(3) 88.07(4), C(1)–Ge–Cl(4) 92.24(4), Cl(3)–Ge–Cl(4) 179.66(2); N(1)–C(1)–Ge–Cl(1) torsion angle = 6.81(14)°.



**Fig. 5.** Thermal ellipsoid plot (30% probability level) for IPr-SnCl<sub>4</sub> (**5**). All hydrogen atoms and the minor orientation of a disordered Dipp group (40/60 ratio) have been omitted for clarity. Selected bond lengths [Å] and angles [deg.]: Sn–C(1) 2.186(2), Sn–Cl(1) 2.3329(7), Sn–Cl(2) 2.4229(8), Sn–Cl(3) 2.3941(8), Sn–Cl(4) 2.3093(8); C(1)–Sn–Cl(1) 121.39(7), C(1)–Sn–Cl(4) 118.00(3), Cl(1)–Sn–Cl(4) 120.56(7), Cl(2)–Sn–Cl(3) 177.51(3); N(1)–C(1)–Sn–Cl(1) torsion angle = –7.9(2)°.

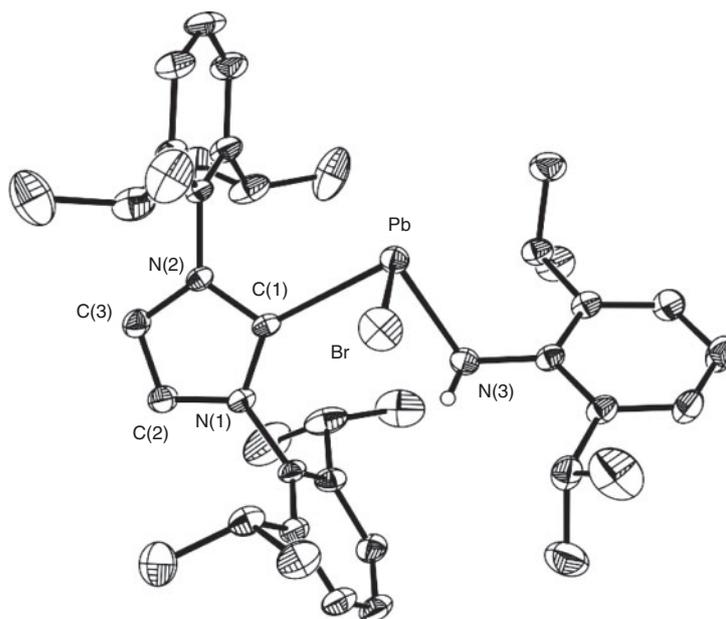
Sn) which have up to six spectroscopically inequivalent methyl environments by <sup>1</sup>H NMR spectroscopy,<sup>[32]</sup> compound **6** displays four broad peaks for the methyl environments in IPr and one sharp doublet resonance for the methyl groups in the NHDipp fragment. Thus it appears that the large size of the Pb centre leads to the formation of a long C<sub>IPr</sub>–Pb bond (see below) that enables the IPr group to rotate more freely in comparison to its Si, Ge, and Sn analogues; moreover attempts to freeze out the IPr motion by cooling to –90°C (in *d*<sub>8</sub>-toluene) did not result in any change in the above-mentioned broad spectroscopic features from the IPr unit.

Crystals of IPr·PbBr(NHDipp) (**6**) of suitable quality for X-ray crystallography were grown from Et<sub>2</sub>O/hexanes and the refined structure is presented in Fig. 6. Compound **6** represents only the third characterized example of a carbene-lead adduct

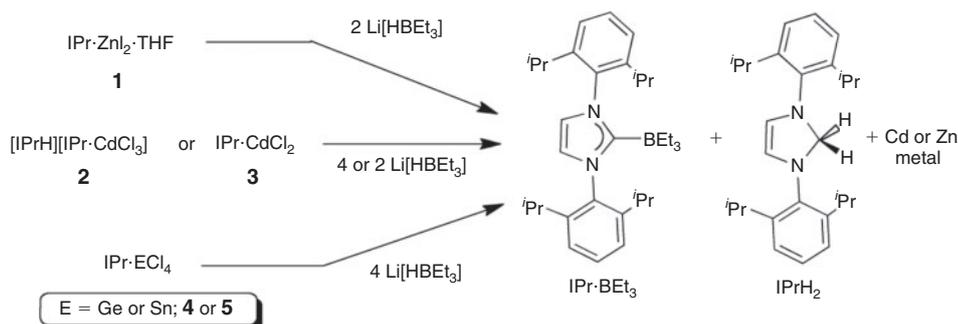


Scheme 4.

with IPr·PbBr<sub>2</sub><sup>[5b]</sup> and Weidenbruch's thermally unstable diarylplumlyene adduct ImMe<sub>2</sub><sup>*i*</sup>Pr<sub>2</sub>·Pb(Trip)<sub>2</sub> (ImMe<sub>2</sub><sup>*i*</sup>Pr<sub>2</sub> = (MeCN<sup>*i*</sup>Pr)<sub>2</sub>C:, Trip = 2,4,6-<sup>*i*</sup>Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sup>[33]</sup> being the other known adducts; compound **6** is, to our knowledge, the first example of a



**Fig. 6.** Thermal ellipsoid plot (30 % probability level) for IPr-PbBr(NHDipp) (**6**). All carbon-bound hydrogen atoms and diethyl ether solvate molecules have been omitted for clarity. Selected bond lengths [Å] and angles [deg.]: Pb–C(1) 2.437(3), Pb–Br 2.7265(4), Pb–N(3) 2.219(3); Br–Pb–C(1) 90.29(6), Br–Pb–N(3) 96.51(7), C(1)–Pb–N(3) 90.58(9).



**Scheme 5.**

stable Pb<sup>II</sup> amide–carbene adduct. Perhaps the most evident structural aspect of **6** is the presence of a highly pyramidalized Pb centre consistent with the presence of a lone pair at Pb with high *s*-character (angle sum at Pb for **6** = 277.38(14)° versus 285.7(5)° in IPr-PbBr<sub>2</sub>). The C<sub>IPr</sub>–Pb distance in **6** is 2.437(2) Å and is the same within error as the related distance in the thermally stable adduct IPr-PbBr<sub>2</sub> (2.443(11) Å);<sup>[5b]</sup> notably, the unstable adduct ImMe<sub>2</sub><sup>i</sup>Pr<sub>2</sub>-Pb(Trip)<sub>2</sub> has a longer C–Pb distance of 2.540(5) Å.<sup>[33]</sup> As with the known adducts IPr-ECl(NHDipp) (E = Si, Ge, and Sn), the Pb–Br bond is nestled in between the flanking Dipp groups of the IPr donor, thus providing possible future steric protection for a Pb–H bond (upon replacement of the bromide group by a hydride substituent).<sup>[34]</sup>

#### Attempted Synthesis of New Group 12 and 14 Hydride Complexes

Following related protocols used by our group to prepare EH<sub>2</sub> and H<sub>2</sub>EEH<sub>2</sub> adducts,<sup>[8–11]</sup> the newly prepared compounds **1–6** were combined with the hydride sources Li[BH<sub>4</sub>] and Li[HBET<sub>3</sub>] in ethereal solvents.

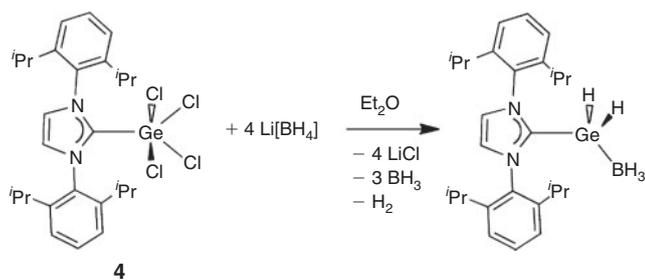
To begin, the zinc adduct IPr-ZnI<sub>2</sub>·THF **1**, and the cadmium complexes [IPrH][IPr-CdCl<sub>3</sub>] (**2**) and IPr-CdCl<sub>2</sub> (**3**) each were

combined with lithium triethylborohydride, Li[HBET<sub>3</sub>] (2–4 equivalents). In each case, product mixtures were obtained which contained the known species IPr-BE<sub>3</sub><sup>[35]</sup> and IPrH<sub>2</sub><sup>[9a]</sup> in varying amounts, as determined by <sup>1</sup>H NMR spectroscopy, and presumably Zn and Cd metal as insoluble products (Scheme 5). Thus it appears that adduct formation between the Lewis acidic BE<sub>3</sub> by-product and IPr was a favourable reaction pathway in each case, with competitive hydride migration to the carbene carbon of either IPr (or transiently generated IPrH<sup>+</sup>) to form the dihydroaminal IPrH<sub>2</sub>. In the reaction of IPr-ZnI<sub>2</sub>·THF (**1**) with Li[HBET<sub>3</sub>], no sign of the formation of the known hydride adduct [IPr-ZnH(μ-H)]<sub>2</sub><sup>[14e]</sup> was observed, confirming that the choice of the hydride reagent is important in dictating the successful formation of carbene-supported hydride complexes. In a similar fashion as the Group 12 systems, both IPr-GeCl<sub>4</sub> (**4**) and IPr-SnCl<sub>4</sub> (**5**) reacted rapidly with four equivalents of Li[HBET<sub>3</sub>] to give mixtures of IPr-BE<sub>3</sub> and IPrH<sub>2</sub> (Scheme 5).

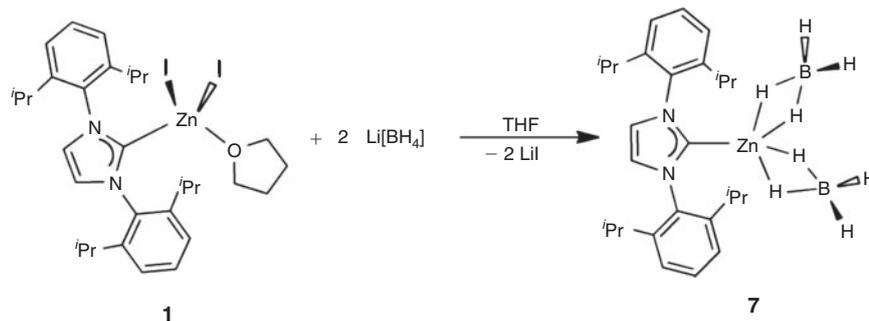
Our group has had considerable success with Li[BH<sub>4</sub>] as a hydride source and, accordingly, the first Ge<sup>II</sup> dihydride complex IPr-GeH<sub>2</sub>-BH<sub>3</sub>,<sup>[8]</sup> and Sn<sup>II</sup> dihydride adduct IPr-SnH<sub>2</sub>-W(CO)<sub>5</sub><sup>[9a]</sup> were each prepared by Cl/H exchange chemistry in the

presence of lithium borohydride. When hydride transfer chemistry was investigated with the higher oxidation state  $E^{IV}$  species  $IPr\cdot ECl_4$  ( $E = Ge$  and  $Sn$ ; **4** and **5**), divergent reaction pathways were noted. For example, when  $IPr\cdot GeCl_4$  (**4**) was combined with excess  $Li[BH_4]$  in  $Et_2O$ , the clean formation of the known  $Ge^{II}$  dihydride  $IPr\cdot GeH_2\cdot BH_3$ <sup>[8]</sup> transpired in a 75 % yield (according to Scheme 6). It is plausible that the formation of a  $Ge^{II}$  species follows by the initial formation of a  $HGeCl_3$  adduct, which undergoes reductive elimination of  $HCl$  to afford  $GeCl_2$  (likely in the form of  $IPr\cdot GeCl_2$ ). A related transformation has been used to generate  $Cl_2Ge$ -dioxane,<sup>[36]</sup> and Roesky and coworkers have investigated parallel chemistry with  $HSiCl_3$  to yield low-oxidation state silicon species.<sup>[29a,37]</sup> Despite repeated attempts, we were unable to locate  $IPr\cdot GeCl_2$  as an intermediate in the reaction between **4** and  $Li[BH_4]$ . The tin(IV) congener  $IPr\cdot SnCl_4$  (**5**) participated in a rapid reaction with four equivalents of  $Li[BH_4]$  to give  $IPr\cdot BH_3$  (quantitative yield) as the only carbene-containing product along with copious amounts of tin metal; this result is not entirely surprising as our attempts to generate the  $Sn^{II}$  hydride  $IPr\cdot SnH_2\cdot BH_3$  exclusively gave  $IPr\cdot BH_3$  and tin metal as involatile products.<sup>[8]</sup>

We were successful in isolating a new borohydride-containing product from the reaction between  $IPr\cdot ZnI_2\cdot THF$  (**1**) and two equivalents of  $Li[BH_4]$  in THF (Scheme 7). Analysis of the crude product by  $^1H$  NMR spectroscopy showed the nearly exclusive ( $\sim 95\%$ ) presence of a new IPr-bound species along with a minor amount of the known  $Zn^{II}$  dihydride adduct  $[IPr\cdot ZnH(\mu-H)]_2$ .<sup>[18c]</sup> The proton-coupled  $^{11}B$  NMR spectrum (in  $C_6D_6$ ) was particularly informative as it afforded one pentet resonance centred at  $-37.7$  ppm ( $^1J_{BH} = 73.3$  Hz) consistent with the retention of  $BH_4^-$  functionality in the product. X-Ray crystallography was performed on colourless crystals grown from THF/hexanes at  $-35^\circ C$  and conclusively identified the material as the bis(borohydride)zinc complex  $IPr\cdot Zn(BH_4)_2$  (**7**) (Fig. 7 and Scheme 7).



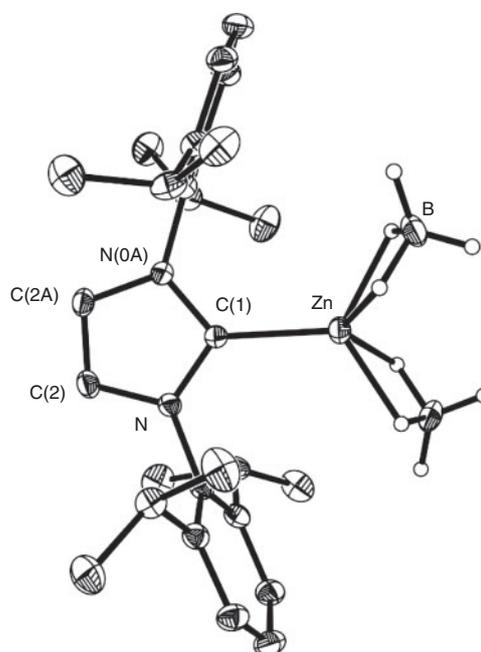
Scheme 6.



Scheme 7.

Compound **7** adopts a symmetrical structure in the solid state with a two-fold rotation axis that is coincident with the  $Zn-C_{IPr}$  bond. The carbene–zinc interaction in **7** ( $2.013(2)$  Å) is shortened with respect to the  $Zn-C_{IPr}$  distance in the precursor  $IPr\cdot ZnI_2\cdot THF$  (**1**) ( $2.0419(4)$  Å). Furthermore, X-ray crystallography confirmed the presence of  $\eta^2$ -coordination between each  $BH_4$  unit and the  $Zn$  centre in **7**. For comparison, the Raston group observed a similar bonding arrangement in  $TMEDA\cdot ZnCl(\eta^2-BH_4)$  ( $TMEDA = Me_2NCH_2CH_2NMe_2$ ),<sup>[38a]</sup> wherein the  $Zn\cdots B$  atomic separation ( $2.29(2)$  Å) was determined to be the same within experimental error as the  $Zn\cdots B$  distance in **7** ( $2.252(2)$  Å). Recently, Robinson and coworkers reported an isostructural beryllium adduct,  $IPr\cdot Be(\eta^2-BH_4)_2$ , which was synthesized by the reaction of  $IPr\cdot BeCl_2$  with two equivalents of  $Li[BH_4]$  in toluene.<sup>[38b]</sup>

The base-free zinc borohydride  $Zn(BH_4)_2$  was initially prepared by Schlesinger and coworkers in 1951<sup>[39]</sup> and was later shown to coordinate to various Lewis bases to yield complexes of improved thermal stability relative to  $Zn(BH_4)_2$



**Fig. 7.** Thermal ellipsoid plot (30% probability level) for  $IPr\cdot Zn(BH_4)_2$  (**7**). All carbon-bound hydrogen atoms have been omitted for clarity, and a two-fold rotation axis exists along the  $C(1)-Zn$  bond. Selected bond lengths [Å] and angles [deg.]:  $Zn-C(1)$   $2.013(2)$ ,  $Zn\cdots B$   $2.252(2)$ ,  $Zn-H$   $1.80(3)$  and  $1.80(3)$ ,  $B-H$   $0.94(3)$  to  $1.14(3)$ ;  $N-C(1)-Zn$   $127.56(10)$ ,  $N-C(1)-N'$   $104.9(2)$ ,  $C(1)-Zn\cdots B$   $126.26(7)$ .

(which decomposes at  $\sim 65^\circ\text{C}$ );<sup>[40]</sup> moreover, these borohydride complexes are useful as mild reducing agents.<sup>[40b]</sup> Thus the synthesis of  $\text{IPr}\cdot\text{Zn}(\text{BH}_4)_2$  (**7**) is a nice addition to this molecular class and we are currently exploring this thermally stable material (mp  $104\text{--}107^\circ\text{C}$  with decomposition) in the domain of  $\text{CO}_2$  activation.<sup>[14f]</sup> Parallel chemistry was explored between  $\text{IPr}\cdot\text{PbBr}(\text{NHDipp})$  (**6**) and  $\text{Li}[\text{BH}_4]$  and despite NMR evidence for the formation of a new  $\text{BH}_4^-$  containing product, we have been unable to obtain crystals of suitable quality for X-ray crystallographic analysis.

## Conclusion

Various new Group 12 and 14 element halide adducts of the hindered carbene donor IPr were prepared and structurally authenticated by X-ray crystallography. Attempts to generate element hydride complexes by halide/hydride metathesis chemistry generally led to carbene–element bond cleavage and the formation of IPr adducts with either  $\text{BEt}_3$  or  $\text{BH}_3$  by-products (when  $\text{Li}[\text{BH}_4]$  and  $\text{Li}[\text{HBEt}_3]$  were used as hydride sources); occasionally the formation of the known dihydroaminal  $\text{IPrH}_2$  transpired. The successful synthesis of the soluble and thermally stable bis(borohydride) zinc complex  $\text{IPr}\cdot\text{Zn}(\text{BH}_4)_2$  was achieved by the reaction of  $\text{IPr}\cdot\text{ZnI}_2\cdot\text{THF}$  with two equivalents of  $\text{Li}[\text{BH}_4]$ ; thus the nature of the hydride source employed in halide metathesis chemistry is very important in dictating product outcome. We are currently exploring the reactivity of  $\text{IPr}\cdot\text{Zn}(\text{BH}_4)_2$  in the context of carbon dioxide reduction chemistry and as a possible soluble precursor to zinc nanomaterials.

## Experimental

### Materials and Instrumentation

All reactions were performed using standard Schlenk line techniques under an atmosphere of nitrogen or in an inert atmosphere glove box (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system<sup>[41]</sup> manufactured by Innovative Technology, Inc., degassed (freeze–pump–thaw method) and stored under an atmosphere of nitrogen before use.  $\text{CdCl}_2$ ,  $\text{ZnI}_2$ ,  $\text{Li}[\text{BH}_4]$ ,  $\text{Li}[\text{HBEt}_3]$  (1.0 M solution in THF),  $\text{GeCl}_4$ ,  $\text{SnCl}_4$  (1.0 M solution in heptane), and thallium(i) trifluoromethane sulfonate ( $\text{Tl}[\text{OTf}]$ ) were purchased from Aldrich and used as received. 1,3-Bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr),<sup>[13]</sup>  $\text{IPr}\cdot\text{PbBr}_2$ ,<sup>[5b]</sup> and  $\text{Li}[\text{NHDipp}]$ <sup>[42]</sup> were prepared according to literature procedures.  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{19}\text{F}\{^1\text{H}\}$ , and  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectra were recorded either on a Varian iNova-400 or on a Varian iNova-500 spectrometer and referenced externally to  $\text{SiMe}_4$  ( $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$ ),  $\text{F}_3\text{B}\cdot\text{OEt}_2$  ( $^{11}\text{B}$ ),  $\text{CFCl}_3$  ( $^{19}\text{F}\{^1\text{H}\}$ ), and  $\text{SnMe}_4$  ( $^{119}\text{Sn}\{^1\text{H}\}$ ). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected.

### Synthetic Procedures

#### Synthesis of $\text{IPr}\cdot\text{ZnI}_2\cdot\text{THF}$ **1**

IPr (0.181 g, 0.466 mmol) and  $\text{ZnI}_2$  (0.149 g, 0.465 mmol) were combined in 10 mL of THF at room temperature. The reaction was allowed to proceed for 12 h, giving a pale yellow solution. Removal of the volatiles from the reaction mixture yielded a pale yellow powder (0.310 g, 86%), which was identified as **1** by  $^1\text{H}$  NMR spectroscopy. Colourless crystals

suitable for X-ray crystallography were obtained by cooling a saturated THF solution of **1** layered with hexanes at  $-35^\circ\text{C}$  for 3 days. Mp  $150\text{--}152^\circ\text{C}$  (dec.).  $\delta_{\text{H}}$  (500 MHz,  $\text{C}_6\text{D}_6$ ) 7.16 (t,  $J$  7.6, 2H, ArH), 7.05 (d,  $J$  7.6, 4H, ArH), 6.40 (s, 2H, N–CH–), 3.59 (m, 4H,  $\text{C}_4\text{H}_8\text{O}$ ), 2.81 (septet,  $J$  6.8, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.52 (d,  $J$  6.8, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.36 (m, 4H,  $\text{C}_4\text{H}_8\text{O}$ ), 0.94 (d,  $J$  6.8, 12H,  $\text{CH}(\text{CH}_3)_2$ ).  $\delta_{\text{H}}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.54 (t,  $J$  8.0, 2H, ArH), 7.55 (d,  $J$  8.0, 4H, ArH), 7.28 (s, 2H, N–CH–), 3.58 (m, 4H,  $\text{C}_4\text{H}_8\text{O}$ ), 2.67 (septet,  $J$  7.2, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.74 (m, 4H,  $\text{C}_4\text{H}_8\text{O}$ ), 1.39 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.15 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ).  $\delta_{\text{C}}$  (126 MHz,  $\text{CD}_2\text{Cl}_2$ ) 173.3 (N–C–N), 146.2 (ArC), 134.2 (ArC), 131.3 (ArC), 125.7 (ArC), 124.8 (N–CH–), 69.3 ( $\text{C}_4\text{H}_8\text{O}$ ), 29.1 ( $\text{CH}(\text{CH}_3)_2$ ), 26.9 ( $\text{CH}(\text{CH}_3)_2$ ), 25.6 ( $\text{C}_4\text{H}_8\text{O}$ ), 23.7 ( $\text{CH}(\text{CH}_3)_2$ ). Anal. Calc. for  $\text{C}_{31}\text{H}_{45}\text{I}_2\text{N}_2\text{OZn}$ : C 47.68, H 5.81, N 3.59. Found: C 47.41, H 5.59, N 3.59%.

#### Synthesis of $[\text{IPrH}][\text{IPr}\cdot\text{CdCl}_3]$ **2**

To a solution of  $\text{CdCl}_2$  (0.14 g, 0.76 mmol) in 4 mL of 1,4-dioxane was added a solution of IPr (0.29 g, 0.76 mmol) in 4 mL of THF. The reaction vial was wrapped in aluminium foil and the reaction mixture was stirred for 18 h to give a pale yellow slurry. The volatiles were removed under vacuum to yield an off-white powder. This material was dissolved in 3 mL THF, and then 5 mL of hexanes was layered on top of the solution and the mixture was stored at  $-35^\circ\text{C}$  overnight. This afforded **2** as a white microcrystalline solid (0.20 g, 27%; the yield was calculated assuming a 1 : 1 mol ratio between the reagents IPr and  $\text{CdCl}_2$  and the final product **2**). Crystals suitable for X-ray crystallography were grown by cooling a THF/hexanes solution of **2** to  $-35^\circ\text{C}$  for 7 days. Mp  $227\text{--}230^\circ\text{C}$ .  $\delta_{\text{H}}$  (500 MHz,  $\text{C}_6\text{D}_6$ ) 9.21 (s, 2H, N–CH–), 7.33 (t,  $J$  7.5, 2H, ArH), 7.25 (d,  $J$  7.5, 4H, ArH), 7.06 (t,  $J$  7.5, 2H, ArH), 6.90 (d,  $J$  7.5, 4H, ArH), 6.57 (s, satellites:  $^4J_{\text{H-Cd}}$  5.6, 2H, N–CH–), 6.32 (br s, 1H, N–CH–N), 3.01 (septet,  $J$  6.5, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 2.50 (septet,  $J$  6.5, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.71 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.10 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.09 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 0.91 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ).  $\delta_{\text{C}}$  (126 MHz,  $\text{C}_6\text{D}_6$ ) 187.9 (N–C–N), 146.2 (ArC), 145.9 (ArC), 135.6 (ArC), 133.7 (N–CH–N), 131.5 (ArC), 130.8 (ArC), 130.4 (ArC), 124.28 (ArC), 124.32 (ArC), 124.2 (N–CH–), 29.1 ( $\text{CH}(\text{CH}_3)_2$ ), 28.8 ( $\text{CH}(\text{CH}_3)_2$ ), 25.8 ( $\text{CH}(\text{CH}_3)_2$ ), 24.4 ( $\text{CH}(\text{CH}_3)_2$ ), 23.8 ( $\text{CH}(\text{CH}_3)_2$ ). Anal. Calc. for  $\text{C}_{54}\text{H}_{73}\text{CdCl}_3\text{N}_4$ : C 65.06, H 7.38, N 5.62. Found: C 65.00, H 7.49, N 5.49%.

#### Reaction of $[\text{IPrH}][\text{IPr}\cdot\text{CdCl}_3]$ **2** with $\text{Tl}[\text{OTf}]$ : Isolation of $\text{IPr}\cdot\text{CdCl}_2\cdot\text{THF}$ **3**

To a clear, colourless solution of  $\text{Tl}[\text{OTf}]$  (39 mg, 0.11 mmol) in 3 mL of THF was added a clear, colourless solution of  $[\text{IPrH}][\text{IPr}\cdot\text{CdCl}_3]$  (**2**) (109 mg, 0.109 mmol) in 3 mL of THF. Immediately upon the addition of **2**, the formation of a white precipitate was noted. The reaction mixture was stirred for 18 h, and then the volatiles removed under vacuum. The resulting off-white solid was extracted with 4 mL of benzene, and filtered to remove insoluble by-products. The volatiles were removed from the resulting filtrate under vacuum to yield a white solid, which was washed with  $2 \times 1$  mL of hexanes and dried under vacuum to yield spectroscopically pure  $\text{IPr}\cdot\text{CdCl}_2$  as a white powder (30 mg, 48%); note: the data presented below is for the THF-free complex  $\text{IPr}\cdot\text{CdCl}_2$ . Crystals suitable for X-ray crystallography were grown by cooling a THF/hexanes solution of **3** to  $-35^\circ\text{C}$  for 5 days. Mp stable to  $260^\circ\text{C}$ .  $\delta_{\text{H}}$  (500 MHz,  $\text{C}_6\text{D}_6$ ) 7.21 (t,  $J$  7.5, 2H, ArH), 7.08 (d,  $J$  7.5, 4H, ArH), 6.41 (s, satellites:  $^4J_{\text{H-Cd}}$  7.2, 2H, N–CH–), 2.70

(septet,  $J$  6.9, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.52 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 0.93 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ).  $\delta_{\text{C}}$  (126 MHz,  $\text{C}_6\text{D}_6$ ) 182.8 (N–C–N), 145.8 (ArC), 134.4 (ArC), 131.1 (ArC), 129.2 (ArC), 124.6 (N–CH–), 29.1 ( $\text{CH}(\text{CH}_3)_2$ ), 25.7 ( $\text{CH}(\text{CH}_3)_2$ ), 23.7 ( $\text{CH}(\text{CH}_3)_2$ ). Anal. Calc. for  $\text{C}_{27}\text{H}_{36}\text{CdCl}_2\text{N}_2$ : C 56.70, H 6.34, N 4.90. Found: C 57.60, H 6.51, N 4.60%.

#### Reaction of $[\text{IPrH}][\text{IPr} \cdot \text{CdCl}_3]$ **2** with $\text{Ti}[\text{OTf}]$ : Isolation of $\text{IPrH}[\text{OTf}]$

To a clear, colourless solution of  $\text{Ti}[\text{OTf}]$  (73 mg, 0.21 mmol) in 3 mL of THF was added a clear, colourless solution of  $[\text{IPrH}][\text{IPr} \cdot \text{CdCl}_3]$  (**2**) (0.205 g, 0.206 mmol) in 3 mL of THF. Immediately upon the addition of **2**, the formation of a white precipitate was noted. The solution was stirred for 48 h, upon which time the mother liquor was filtered. The volatiles were removed from the filtrate under vacuum to yield a white powder, which was washed with  $2 \times 2$  mL of benzene and dried under vacuum to afford a pure sample of  $\text{IPrH}[\text{OTf}]$  (52 mg, 47%). Mp stable to 260°C. NMR spectroscopic values for  $\text{IPrH}[\text{OTf}]$  matched those found in the literature.<sup>[13]</sup>  $\delta_{\text{H}}$  (500 MHz,  $\text{CDCl}_3$ ) 9.10 (s, 1H, N–CH–N), 7.84 (s, 2H, N–CH–), 7.59 (t,  $J$  7.5, 2H, ArH), 7.36 (d,  $J$  7.5, 4H, ArH), 2.42 (septet,  $J$  6.5, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.28 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.22 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ).  $\delta_{\text{C}}$  (126 MHz,  $\text{CDCl}_3$ ) 144.9 (N–CH–), 138.0 (ArC), 132.3 (ArC), 129.7 (ArC), 126.4 (ArC), 29.5 ( $\text{CH}(\text{CH}_3)_2$ ), 24.8 ( $\text{CH}(\text{CH}_3)_2$ ), 24.2 ( $\text{CH}(\text{CH}_3)_2$ ).  $\delta_{\text{F}}$  (470 MHz,  $\text{CDCl}_3$ ) –78.0 (s). Anal. Calc. for  $\text{C}_{28}\text{H}_{37}\text{F}_3\text{N}_2\text{O}_3\text{S}$ : C 62.43, H 6.92, N 5.20. Found: C 62.44, H 6.94, N 5.26%.

#### Synthesis of $\text{IPr} \cdot \text{GeCl}_4$ **4**

$\text{IPr}$  (0.42 g, 1.1 mmol) and  $\text{GeCl}_4$  (0.14 mL, 1.2 mmol) were combined in 12 mL of  $\text{Et}_2\text{O}$  at room temperature. The reaction was allowed to proceed for 3 h to give a white slurry. The white precipitate was isolated by filtration and identified as **4** (0.57 g, 86%). Crystals suitable for X-ray crystallography were grown by cooling a  $\text{CH}_2\text{Cl}_2$ /hexanes solution of **4** to –35°C for 2 days. Mp 185°C (dec.).  $\delta_{\text{H}}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) 7.61 (t,  $J$  7.9, 2H, ArH), 7.41 (d,  $J$  7.9, 4H, ArH), 7.31 (s, 2H, N–CH–), 2.98 (septet,  $J$  6.5, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.40 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.12 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ).  $\delta_{\text{H}}$  (400 MHz,  $\text{C}_6\text{D}_6$ ) 7.22 (t,  $J$  7.8, 2H, ArH), 7.12 (d,  $J$  7.6, 4H, ArH), 6.38 (s, 2H, N–CH–), 3.15 (septet,  $J$  6.8, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.48 (d,  $J$  6.5 Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 0.92 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ).  $\delta_{\text{C}}$  (126 MHz,  $\text{CD}_2\text{Cl}_2$ ) 156.5 (N–C–N), 147.3 (ArC), 132.6 (ArC), 131.5 (ArC), 124.8 (N–CH–), 124.4 (ArC), 29.6 ( $\text{CH}(\text{CH}_3)_2$ ), 26.8 ( $\text{CH}(\text{CH}_3)_2$ ), 22.2 ( $\text{CH}(\text{CH}_3)_2$ ).  $\delta_{\text{C}}$  (126 MHz,  $\text{C}_6\text{D}_6$ ) 147.1 (N–C–N), 132.5 (ArC), 131.7 (ArC), 124.8 (N–CH–), 123.5 (ArC), 29.4 ( $\text{CH}(\text{CH}_3)_2$ ), 26.7 ( $\text{CH}(\text{CH}_3)_2$ ), 22.4 ( $\text{CH}(\text{CH}_3)_2$ ). Anal. Calc. for  $\text{C}_{27}\text{H}_{36}\text{Cl}_4\text{GeN}_2$ : C 53.78, H 6.02, N 4.65. Found: C 53.75, H 6.09, N 4.47%.

#### Synthesis of $\text{IPr} \cdot \text{SnCl}_4$ **5**

To a solution of  $\text{IPr}$  (0.20 g, 0.52 mmol) in 12 mL of toluene was added  $\text{SnCl}_4$  (0.52 mL, 0.52 mmol, 1.0 M solution in heptane) at room temperature. The reaction was allowed to proceed for 12 h to give a white slurry. The white precipitate was isolated by filtration and identified as **5** (0.276 g). A further crop of **5** (colourless crystals of X-ray quality) was obtained by cooling the filtrate layered with hexanes to –35°C for 1 day

(0.013 g; combined yield = 0.289 g, 87%). Mp 190°C (dec.).  $\delta_{\text{H}}$  (500 MHz,  $\text{C}_6\text{D}_6$ ) 7.20 (t,  $J$  7.5, 2H, ArH), 7.09 (d,  $J$  7.5, 4H, ArH), 6.41 (s, satellites:  $^4J_{\text{H}-119/117\text{Sn}}$  12.9, 2H, N–CH–), 2.97 (septet,  $J$  6.8, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.46 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 0.86 (d,  $J$  6.5, 12H,  $\text{CH}(\text{CH}_3)_2$ ).  $\delta_{\text{C}}$  (126 MHz,  $\text{C}_6\text{D}_6$ ) 146.7 (N–C–N), 132.7 (ArC), 131.8 (ArC), 129.3 (ArC), 125.0 (N–CH–), 124.5 (ArC), 29.3 ( $\text{CH}(\text{CH}_3)_2$ ), 26.7 ( $\text{CH}(\text{CH}_3)_2$ ), 22.4 ( $\text{CH}(\text{CH}_3)_2$ ).  $\delta_{119\text{Sn}}$  (185 MHz,  $\text{CD}_2\text{Cl}_2$ ) –422.6 (s). Anal. Calc. for  $\text{C}_{27}\text{H}_{36}\text{Cl}_4\text{SnN}_2$ : C 49.96, H 5.59, N 4.32. Found C 49.65, H 6.06, N 4.69%.

#### Synthesis of $\text{IPr} \cdot \text{PbBr}(\text{NHDipp})$ **6**

A solution of  $\text{Li}[\text{NHDipp}]$  (0.065 g, 0.27 mmol) in 5 mL of cold  $\text{Et}_2\text{O}$  (–35°C) was added dropwise to a cold (–35°C) slurry of  $\text{IPr} \cdot \text{PbBr}_2$  (0.26 g, 0.35 mmol) in 5 mL of  $\text{Et}_2\text{O}$ . The resulting mixture was warmed slowly to room temperature and stirred for 1 h to give a bright orange solution over a precipitate (LiBr). The resulting reaction mixture was filtered through Celite and then removal of volatiles from the filtrate yielded **6** as a yellow solid. Crystals suitable for X-ray crystallography were grown by cooling a  $\text{Et}_2\text{O}$ /hexanes solution of **6** to –35°C for 3 days (0.170 g, 58%). Mp stable to 260°C.  $\nu_{\text{max}}$  (Nujol)/ $\text{cm}^{-1}$  3241 w ( $\nu(\text{N}-\text{H})$ ).  $\delta_{\text{H}}$  (500 MHz,  $\text{C}_6\text{D}_6$ ) 7.22 (br s, 2H, ArH), 7.11 (br, 4H, ArH), 7.05 (t,  $J$  8.0, 1H, ArH), 6.71 (d,  $J$  8.0, 2H, ArH), 6.52 (br, 2H, N–CH–), 4.41 (s, 1H, NH), 3.17 (br, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 2.92 (br, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 2.65 (septet,  $J$  7.0, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.41 (br, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.33 (br, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.14 (d,  $J$  7.0, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 1.09 (br, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.01 (br, 6H,  $\text{CH}(\text{CH}_3)_2$ ).  $\delta_{\text{C}}$  (126 MHz,  $\text{C}_6\text{D}_6$ ) 148.1 (ArC), 146.2 (ArC), 137.6 (ArC), 134.2 (ArC), 131.2 (ArC), 125.3 (ArC), 124.4 (N–CH–), 124.2 (ArC), 123.0 (ArC), 119.0 (ArC), 117.6 (ArC), 29.1 ( $\text{CH}(\text{CH}_3)_2$ ), 28.1 ( $\text{CH}(\text{CH}_3)_2$ ), 26.9 ( $\text{CH}(\text{CH}_3)_2$ ), 25.8 ( $\text{CH}(\text{CH}_3)_2$ ), 23.9 ( $\text{CH}(\text{CH}_3)_2$ ), 23.6 ( $\text{CH}(\text{CH}_3)_2$ ), 22.6 ( $\text{CH}(\text{CH}_3)_2$ ). Anal. Calc. For  $\text{C}_{39}\text{H}_{54}\text{BrN}_3\text{Pb}$ : C 54.98, H 6.39, N 4.39. Found: C 54.85, H 6.41, N 4.89%.

#### Synthesis of $\text{IPr} \cdot \text{Zn}(\text{BH}_4)_2$ **7**

To a suspension of  $\text{LiBH}_4$  (0.005 g, 0.2 mmol) in 2 mL of THF was added a solution of **1** (0.090 g, 0.12 mmol) in 3 mL of THF to yield a pale yellow solution. The reaction mixture was then allowed to stir for 18 h, and then the volatiles were removed under vacuum. The resulting pale yellow solid was washed with  $2 \times 2$  mL of  $\text{Et}_2\text{O}$ , and extracted into 3 mL of benzene before being filtered through Celite. Removal of the solvent from the filtrate under vacuum yielded the desired product as a white solid (0.035 g, 63%). Crystals suitable for X-ray diffraction were obtained after 12 h by layering 2 mL of hexanes on top of a solution of **7** dissolved in 1 mL of THF. Mp 104–107°C (dec.).  $\delta_{\text{H}}$  (500 MHz,  $\text{C}_6\text{D}_6$ ) 7.17 (t,  $J$  8.0, 2H, ArH), 7.04 (d,  $J$  8.0, 4H, ArH), 6.40 (s, 2H, N–CH–), 2.64 (septet,  $J$  6.0, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 1.39 (d,  $J$  6.0, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 0.94 (d,  $J$  6.8, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 0.61 (br, 8H,  $\text{BH}_4^-$ ; assignment confirmed by broadband  $^{11}\text{B}$  decoupling).  $\delta_{\text{C}}$  (126 MHz,  $\text{C}_6\text{D}_6$ ) 145.6 (ArC), 133.6 (ArC), 131.6 (ArC), 124.8 (ArC), 124.6 (N–CH–), 29.0 ( $\text{CH}(\text{CH}_3)_2$ ), 25.8 ( $\text{CH}(\text{CH}_3)_2$ ), 23.1 ( $\text{CH}(\text{CH}_3)_2$ ). We were unable to locate the N–C–N resonance.  $\delta_{\text{B}}$  (160 MHz,  $\text{C}_6\text{D}_6$ ) –37.3 (pentet,  $J$  73.3,  $\text{BH}_4^-$ ). Despite repeated attempts, elemental analyses consistently gave low values for C and N content: Anal. Calc. for  $\text{C}_{27}\text{H}_{44}\text{B}_2\text{N}_2\text{Zn}$ : C 67.05, H 9.17, N 5.79. Found: C 65.50, H 9.15, N 4.46%. See the Supplementary Material for copies of the NMR spectra for **7** (Figs S2 and S3).

*Reaction of IPr·ZnI<sub>2</sub>·THF 1 with Li[HBtEt<sub>3</sub>]*

To a cold (−35°C) solution of **1** (100 mg, 0.128 mmol) in 8 mL of THF was added Li[HBtEt<sub>3</sub>] (0.282 mL, 1.0 M solution in THF). The reaction mixture was allowed to warm to room temperature and stirred for 12 h resulting in the formation of a black slurry. The resulting slurry was then filtered through Celite and the volatiles were removed under vacuum to yield a pale yellow solid (58 mg), which was identified as a mixture of IPr·BEt<sub>3</sub><sup>[35]</sup> (~90% by <sup>1</sup>H NMR spectroscopy), (HCNDipp)<sub>2</sub>CH<sub>2</sub> (IPrH<sub>2</sub>)<sup>[9a]</sup> (~2% by <sup>1</sup>H NMR spectroscopy), and ~8% of other unidentified products.

*Reaction of [IPrH][IPr·CdCl<sub>3</sub>] 2 with Li[HBtEt<sub>3</sub>]*

Compound **2** was combined with Li[HBtEt<sub>3</sub>] following a similar procedure as above, and gave a mixture of IPr·BEt<sub>3</sub><sup>[35]</sup> (~68% by <sup>1</sup>H NMR spectroscopy) and IPrCH<sub>2</sub><sup>[9a]</sup> (~32% by <sup>1</sup>H NMR spectroscopy).

*Reaction of IPr·CdCl<sub>2</sub> with Li[HBtEt<sub>3</sub>]*

IPr·CdCl<sub>2</sub> was combined with Li[HBtEt<sub>3</sub>] following a similar procedure as stated above with the exception that benzene was used as the reaction solvent. A mixture of IPr·BEt<sub>3</sub><sup>[35]</sup> (~50% by <sup>1</sup>H NMR spectroscopy) and IPrH<sub>2</sub><sup>[9a]</sup> (~50% by <sup>1</sup>H NMR spectroscopy) was generated.

*Reaction of IPr·ECl<sub>4</sub> (E = Ge and Sn; 4 and 5) with Four Equivalents of Li[HBtEt<sub>3</sub>]*

To a solution of IPr·ECl<sub>4</sub> (0.15 mmol) in 12 mL of Et<sub>2</sub>O was added Li[HBtEt<sub>3</sub>] (~0.68 mmol) at room temperature. The reaction mixture was stirred for 12 h. The mother liquor was separated from a yellow precipitate by filtration, and removal of the volatiles from the filtrate under vacuum gave a white solid in each case. For E = Ge, the product contained a mixture of IPr·BEt<sub>3</sub> (~90%)<sup>[35]</sup> and IPrH<sub>2</sub> (~10%)<sup>[9b]</sup> as determined by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>11</sup>B NMR spectroscopy; whereas for E = Sn, the product contained a mixture of IPr·BEt<sub>3</sub> (~81%)<sup>[35]</sup> and IPrH<sub>2</sub> (~19%)<sup>[9b]</sup> as determined by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>11</sup>B NMR spectroscopy.

*Reaction of IPr·GeCl<sub>4</sub> 4 with Li[BH<sub>4</sub>]: Alternate Preparation of IPr·GeH<sub>2</sub>·BH<sub>3</sub>*

To a mixture of **4** (0.197 g, 0.33 mmol) and Li[BH<sub>4</sub>] (0.032 g, 1.5 mmol) was added 12 mL of Et<sub>2</sub>O at room temperature. The reaction mixture was allowed to proceed for 12 h to give a yellow slurry. The volatiles were removed under vacuum and the product was extracted with 10 mL of benzene. Filtration of the mixture followed by removal of the solvent from the filtrate yielded a white solid (0.120 g, 75%), which was identified as IPr·GeH<sub>2</sub>·BH<sub>3</sub> by <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy.<sup>[8]</sup>

*Reaction of IPr·SnCl<sub>4</sub> 5 with Four Equivalents of Li[BH<sub>4</sub>]: Generation of IPr·BH<sub>3</sub>*

IPr·SnCl<sub>4</sub> **5** (0.10 g, 0.15 mmol) and Li[BH<sub>4</sub>] (14 mg, 0.64 mmol) were combined in 12 mL of diethyl ether. The reaction mixture was stirred for 12 h and the mother liquor was separated from the black precipitate by filtration. The solvent was removed from the filtrate under vacuum to give the known species IPr·BH<sub>3</sub><sup>[43]</sup> as a white powder (62 mg, quantitative yield)

which was characterized by <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy.

**Crystallographic Details***General Details*

Crystals suitable for X-ray diffraction studies were removed from a vial in a glove box freezer and immediately coated with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then mounted on a glass fibre, and quickly placed in a low temperature stream of nitrogen on the X-ray diffractometer.<sup>[44]</sup> All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using MoK<sub>α</sub> or CuK<sub>α</sub> radiation, with the crystals cooled to −100°C. The data were corrected for absorption through Gaussian integration from the indexing of the crystal faces or multi-scan procedures (*SADABS*<sup>[45]</sup> for compounds **1** and **5**; *TWINABS*<sup>[46]</sup> for compound **2**). Crystal structures were solved using either direct methods (*SHELXS-97*<sup>[47]</sup> for compounds **1**, **2**, and **4–7**; *SIR 97*<sup>[48]</sup> for compound **3**) and refined using *SHELXL-97*.<sup>[47]</sup> The assignment of carbon-bound hydrogen atoms were based on the sp<sup>2</sup> or sp<sup>3</sup> hybridisation geometries of their attached carbon atoms, and were given thermal parameters 20% greater than those of their parent atoms.

*Crystal Data for IPr·ZnI<sub>2</sub>·THF (1)*

C<sub>31</sub>H<sub>44</sub>I<sub>2</sub>N<sub>2</sub>OZn, *M* 779.85, colourless plate, 0.48 × 0.31 × 0.15 mm<sup>3</sup>, monoclinic, space group *C2/c*, *a* 40.7207(14) Å, *b* 9.6340(3) Å, *c* 17.0987(6) Å, β 99.7678(3)°, *V* 6610.6(4) Å<sup>3</sup>, *Z* 8, *D<sub>c</sub>* 1.567 g cm<sup>−3</sup>, 2θ<sub>max</sub> 52.76°, μ(MoK<sub>α</sub>) 2.635 mm<sup>−1</sup>, *T* 173(1) K, 25 661 reflections collected, 6749 unique reflections [*R*(int) 0.0118], Final GoF 1.047, *R*<sub>1</sub> (on *F*<sup>2</sup>) 0.0213; *wR*<sub>2</sub> (on *F*<sup>2</sup>) 0.0544 [*I* > 2σ(*I*)], max/min electron density 1.072/−0.786 e Å<sup>−3</sup>, CCDC No. 934973.

*Crystal Data for [IPrH][IPr·CdCl<sub>3</sub>] (2·2.5 Toluene)*

C<sub>71.5</sub>H<sub>93</sub>CdCl<sub>3</sub>N<sub>4</sub>, *M* 1227.25, colourless plate, 0.49 × 0.18 × 0.08 mm<sup>3</sup>, triclinic, space group *P1̄*, *a* 14.985(2) Å, *b* 16.849(2) Å, *c* 18.063(2) Å, α 61.6908(15)°, β 73.7219(16)°, γ 58.9672(15)°, *V* 3436.7(8) Å<sup>3</sup>, *Z* 2, *D<sub>c</sub>* 1.186 g cm<sup>−3</sup>, 2θ<sub>max</sub> 55.20°, μ(MoK<sub>α</sub>) 0.476 mm<sup>−1</sup>, *T* 173(1) K, 67 722 reflections collected, 27 625 unique reflections [*R*(int) 0.0702], Final GoF 1.061, *R*<sub>1</sub> (on *F*<sup>2</sup>) 0.0602; *wR*<sub>2</sub> (on *F*<sup>2</sup>) 0.1702 [*I* > 2σ(*I*)], max/min electron density 1.890/−1.275 e Å<sup>−3</sup>, CCDC No. 934974. Special refinement conditions: Both components of the twin were indexed with the program *CELL\_NOW*.<sup>[49]</sup> The second twin component can be related to the first component by 180° rotation about the [0 1 0] axis in real space and about the [1/2 1 1/2] axis in reciprocal space. Integrated intensities for the reflections from the two components were written into a *SHELX-97* HKLF 5 reflection file with the data integration program *SAINTE* (version 7.68A)<sup>[50]</sup> using all reflection data (exactly overlapped, partially overlapped, and non-overlapped). The refined value of the twin fraction (*SHELXL-97* BASF parameter) was 0.5057(7).

*Crystal Data for IPr·CdCl<sub>2</sub>·THF (3·THF)*

C<sub>35</sub>H<sub>52</sub>CdCl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>, *M* 716.09, colourless block, 0.38 × 0.32 × 0.24 mm<sup>3</sup>, orthorhombic, space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*, *a* 13.9468(8) Å, *b* 15.8702(9) Å, *c* 16.5113(9) Å, *V* 3654.6(4) Å<sup>3</sup>, *Z* 4, *D<sub>c</sub>* 1.301 g cm<sup>−3</sup>, 2θ<sub>max</sub> 54.88°, μ(MoK<sub>α</sub>) 0.774 mm<sup>−1</sup>, *T* 173(1) K, 32 290 reflections collected, 8318 unique reflections [*R*(int) 0.0288], Final GoF 1.027, *R*<sub>1</sub> (on *F*<sup>2</sup>) 0.0249; *wR*<sub>2</sub> (on *F*<sup>2</sup>) 0.0671

$[I > 2\sigma(I)]$ , max/min electron density  $0.762/-0.332 \text{ e } \text{Å}^{-3}$ , Flack parameter  $-0.021(16)$ , CCDC No. 934975.

#### Crystal Data for $\text{IPr} \cdot \text{GeCl}_4$ (4)

$\text{C}_{27}\text{H}_{36}\text{Cl}_4\text{N}_2\text{Ge}$ ,  $M$  602.97, colourless plate,  $0.50 \times 0.43 \times 0.25 \text{ mm}^3$ , monoclinic, space group  $P2_1/n$ ,  $a$  10.9535(6) Å,  $b$  13.9137(8) Å,  $c$  19.7796(10) Å,  $\beta$  104.6640(10)°,  $V$  2961.3 (3) Å<sup>3</sup>,  $Z$  4,  $D_c$  1.373 g cm<sup>-3</sup>,  $2\theta_{\text{max}}$  54.84°,  $\mu(\text{MoK}\alpha)$  1.435 mm<sup>-1</sup>,  $T$  173(1) K, 25 317 reflections collected, 5880 unique reflections [ $R(\text{int})$  0.0203], Final GoF 1.044,  $R_1$  (on  $F^2$ ) 0.0267;  $wR_2$  (on  $F^2$ ) 0.0700 [ $I > 2\sigma(I)$ ], max/min electron density  $0.595/-0.448 \text{ e } \text{Å}^{-3}$ , CCDC No. 934976.

#### Crystal Data for $\text{IPr} \cdot \text{SnCl}_4$ (5)

$\text{C}_{27}\text{H}_{36}\text{Cl}_4\text{N}_2\text{Sn}$ ,  $M$  649.07, colourless plate,  $0.40 \times 0.15 \times 0.11 \text{ mm}^3$ , monoclinic, space group  $P2_1/c$ ,  $a$  20.016(2) Å,  $b$  10.1625(12) Å,  $c$  16.1110(19) Å,  $\beta$  109.0380(10)°,  $V$  3097.9 (6) Å<sup>3</sup>,  $Z$  4,  $D_c$  1.392 g cm<sup>-3</sup>,  $2\theta_{\text{max}}$  55.12°,  $\mu(\text{MoK}\alpha)$  1.187 mm<sup>-1</sup>,  $T$  173(1) K, 26 165 reflections collected, 7114 unique reflections [ $R(\text{int})$  0.0320], Final GoF 1.063,  $R_1$  (on  $F^2$ ) 0.0320;  $wR_2$  (on  $F^2$ ) 0.0733 [ $I > 2\sigma(I)$ ], max/min electron density  $0.929/-0.310 \text{ e } \text{Å}^{-3}$ , CCDC No. 934977.

#### Crystal Data for $\text{IPr} \cdot \text{PbBr}(\text{NHDipp})$ (6 · Et<sub>2</sub>O)

$\text{C}_{43}\text{H}_{64}\text{BrN}_3\text{OPb}$ ,  $M$  926.07, pale yellow block,  $0.34 \times 0.31 \times 0.21 \text{ mm}^3$ , monoclinic, space group  $P2_1/c$ ,  $a$  12.1775(8) Å,  $b$  18.1343(12) Å,  $c$  20.6224(14) Å,  $\beta$  105.4880(10)°,  $V$  4388.7 (5) Å<sup>3</sup>,  $Z$  4,  $D_c$  1.402 g cm<sup>-3</sup>,  $2\theta_{\text{max}}$  55.24°,  $\mu(\text{MoK}\alpha)$  4.787 mm<sup>-1</sup>,  $T$  173(1) K, 38 522 reflections collected, 10 146 unique reflections [ $R(\text{int})$  0.0331], Final GoF 1.015,  $R_1$  (on  $F^2$ ) 0.0264;  $wR_2$  (on  $F^2$ ) 0.0639 [ $I > 2\sigma(I)$ ], max/min electron density  $1.984/-0.648 \text{ e } \text{Å}^{-3}$ , CCDC No. 934978.

#### Crystal Data for $\text{IPr} \cdot \text{Zn}(\text{BH}_4)_2$ (7)

$\text{C}_{27}\text{H}_{44}\text{B}_2\text{N}_2\text{Zn}$ ,  $M$  483.63, colourless plate,  $0.21 \times 0.12 \times 0.07 \text{ mm}^3$ , monoclinic, space group  $C2/c$ ,  $a$  16.6074(5) Å,  $b$  9.4081(3) Å,  $c$  17.7919(5) Å,  $\beta$  90.3920(10)°,  $V$  2779.81(14) Å<sup>3</sup>,  $Z$  4,  $D_c$  1.156 g cm<sup>-3</sup>,  $2\theta_{\text{max}}$  140.34°,  $\mu(\text{CuK}\alpha)$  1.320 mm<sup>-1</sup>,  $T$  173(1) K, 9055 reflections collected, 2600 unique reflections [ $R(\text{int})$  0.0196], Final GoF 1.043,  $R_1$  (on  $F^2$ ) 0.0338;  $wR_2$  (on  $F^2$ ) 0.0994 [ $I > 2\sigma(I)$ ], max/min electron density  $1.412/-0.320 \text{ e } \text{Å}^{-3}$ , CCDC No. 935984.

### Supplementary Material

Crystallographic data for  $\text{IPr} \cdot \text{ZnI}_2$  and NMR data for  $\text{IPr} \cdot \text{Zn}(\text{BH}_4)_2$  are available on the Journal's website.

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