Main-Group Chemistry

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Diverse Activation Modes in the Hydroboration of Aldehydes and Ketones with Germanium, Tin, and Lead Lewis Pairs

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Abstract: *Intramolecular germylene, stannylene, and plumbylene Lewis pairs were reacted with hexanal and yielded the cyclic addition products only with the germanium and tin reagents. In further reactivity studies, the hydroboration of aldehydes and ketones catalyzed by intramolecular germylene, stannylene, and plumbylene Lewis pairs was studied. In the case of the cyclic germylene Lewis pair, the product of the oxidative addition of pinacolborane at the germylene moiety was observed. According to stoichiometric as well as catalytic experiments, the intramolecular germylene Lewis pair acts as a catalyst in the hydroboration of aldehydes and ketones. The homologous stannylene Lewis pair forms a reactive tin hydride during the catalysis, which can also act as a catalyst in this transformation.*

Over the last decade, the activation of small molecules with main-group-element compounds has received major attention.[1] The concept of frustrated Lewis pairs was developed, and catalytic transformations with these reactive molecules have been studied.[2] Main-group-element hydrides, which were investigated with respect to catalytic hydroborations of aldehydes, ketones, and alkynes as well as dehydrocoupling reactions, are also in the focus of interest.[1n,3] Furthermore, elemental steps known for the mechanisms of reactions of transition-metal complexes with small molecules, such as oxidative addition or reductive elimination, were explored in p-block chemistry.[1d,i,4]

As part of our investigations concerning the reactivity of intramolecular Lewis pairs between low-valent Group 14 fragments and phosphine moieties in strained cyclic arrangements, we became interested in the activation of small molecules by these main-group-element adducts.[5] Therefore, additions of alkynes, olefins, and azides with Group 14 Lewis pairs were studied.[6] We found that the E←P (E = Ge, Sn) bond displays distinct reactivity, which adds to small molecules under ring expansion.

An enantioselective hydroboration based on a metal-free oxazaborolidine was published in 1987 by Corey and co-workers,[7a] and Woodward et al. described enantioselective reductions of ketones with a chiral Ga complex in 2000.[7b] The groups of Hill, Jones, Kinjo, and Stasch recently developed main-group hydroboration catalysts based on magnesium, tin, and phosphorus hydrides.[3b–d,g] Herein, we present the results of hydroboration studies with intramolecular tetrylene-based Lewis pairs (Figure 1).

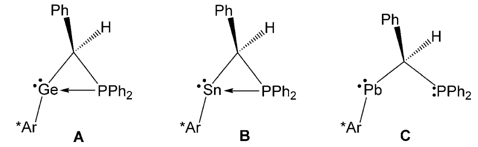
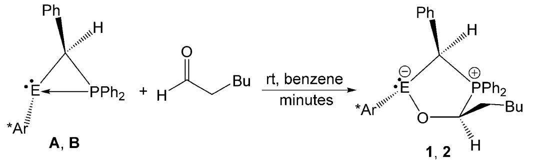


Figure 1. Intramolecular tetrylene Lewis pairs. Ar* = 2,6-(2,4,6-$i\text{Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$.

The three-membered-ring molecules **A** and **B** react with hexanal within minutes at room temperature to quantitatively and regioselectively give (on the basis of NMR spectroscopy) the addition products **1** and **2** (Scheme 1). In the case of the lead Lewis pair **C**, we were not able to structurally identify the product of the reaction with hexanal. However, a resonance at $\delta = -7.4$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this reaction product, compared to resonances around 22 ppm for the five-membered-ring molecules **1** and **2**, could be a hint towards a geometry different from that for **1** and **2**. The chemical shift of $\delta = -7.4$ ppm rather suggests a structure with an uninvolved phosphine moiety. In a plausible reaction mechanism for the formation of **1** and **2**, the polar C=O unit of the aldehyde could react as a nucleophile and attack the electrophilic ylene moiety of **A** or **B**.



Scheme 1. Addition of hexanal. **1**: E = Ge, **2**: E = Sn.

The hexanal addition products **1** and **2** were characterized by means of elemental analysis, NMR spectroscopy, and single-crystal structure analysis. Owing to the stereochemical requirements of the phenyl and terphenyl groups, **A** and **B** were isolated as pairs of enantiomers with the substituents in *trans* position. After regioselective addition of hexanal, a further center of chirality is formed, and molecules **1** and

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2 were isolated as mixtures of diastereomers (**1**: 1:4.9; **2**: 1:1.2). 2D ^{1}H–^{1}H NOESY/EXSY experiments of compound **1** revealed the configuration indicated in Scheme 1 as the major diastereomer, and no exchange between the two diastereomers could be observed on the NMR timescale. As the molecular structures of **1** and **2** are closely related, only the molecular structure of the germanium derivative in the solid state is shown in Figure 2, and selected interatomic distances and angles of both the germanium and tin derivatives are listed.

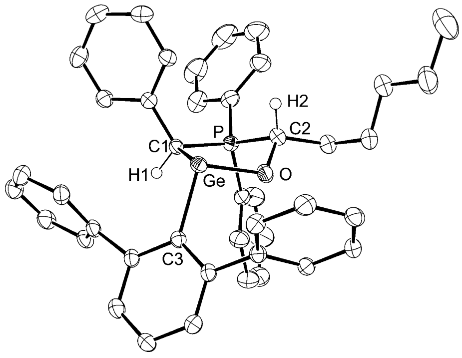
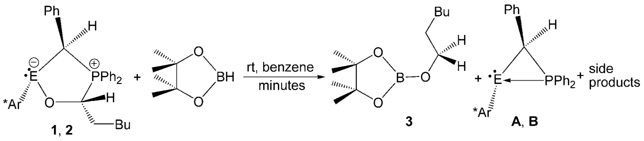


Figure 2. Molecular structure of addition product **1** (ellipsoids set at 50% probability) in the solid state. Isopropyl groups and all hydrogen atoms except H1 and H2 are omitted for clarity. Selected bond lengths [Å] and angles [°] (values for tin derivative **2** given in square brackets): E–C1 2.161(2) [2.382(5)], E–C3 2.051(2) [2.273(5)], E–O 1.929(2) [2.104(4)], C1–P 1.780(2) [1.776(5)], P–C2 1.857(2) [1.860(6)], C2–O 1.399(3) [1.392(7)]; O-E-C3 98.78(8) [97.2(2)], O-E-C1 88.80(7) [83.0(2)], C3-E-C1 102.83(8) [99.5(2)], C2-O-E 112.8(1) [114.2(3)], C1-P-C2 103.9(1) [105.2(3)], O-C2-P 101.5(1) [102.5(4)], P-C1-E 102.9(1) [103.0(3)].

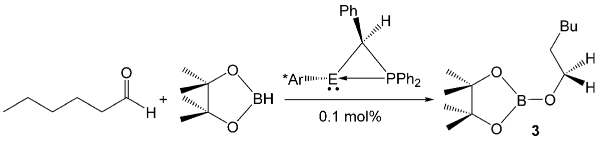
Interesting features of the solid-state structures are the pyramidalization at the Ge or Sn atom (sum of angles for **1**: 290.4°; **2**: 279.7°), which is a good indicator for the presence of a lone pair at the low-valent Group 14 atom, and the elongation of the C2−O bond (**1**: 1.399(3) Å, **2**: 1.392(7) Å), which is in the range of a C−O single bond (1.41 Å) rather than a C=O double bond (1.20 Å).[8] Comparison of the IR spectra of hexanal and the hexanal addition product **1** (see the Supporting Information) confirmed the presence of a C−O single bond rather than a C=O double bond, as no ν(C=O) stretch was observable around 1700 cm^{-1}.

As we were interested in confirming the putative activation of the aldehyde C=O bond by adduct formation with the Lewis pair, we studied the reactions of **1** and **2** with pinacolborane. Both adducts reacted with the boron hydride at room temperature to give the hexanal hydroboration product **3** (Scheme 2), Lewis adducts **A** or **B**, and further side products (see below; NMR spectra are given in the Supporting Information).

The result of the stoichiometric hydroboration experiment led us to investigate whether the hydroboration of hexanal could be conducted in catalytic fashion with the intramolecular Lewis pairs **A** and **B** acting as the catalysts (Scheme 3). These catalysts (0.1 mol%) were added to a mixture of hexanal and pinacolborane, and the formation of product **3** was analyzed by NMR spectroscopy: the yield of **3** amounted to 96.3% (E = Ge) or 79.4% (E = Sn) after 30 min. In a control experiment without either catalyst, the hydroboration yield amounted to 67.4% after 4 h 35 min. As we had also synthesized the lead derivative of **A** and **B**, which does not show a cyclic but an open geometry (**C**; Figure 1), we tested this plumbylene and found even higher activity in hydroboration catalysis (> 99.9% conversion after 7 min). However, after the catalytic reaction had finished, elemental lead could be observed, which hints towards decomposition of the plumbylene during catalysis. The hydroboration of other carbonyl compounds, such as ferrocenyl aldehyde, benzaldehyde, and acetophenone, with pinacolborane or catecholborane could also be catalyzed by the germanium and tin Lewis pairs **A** and **B**.



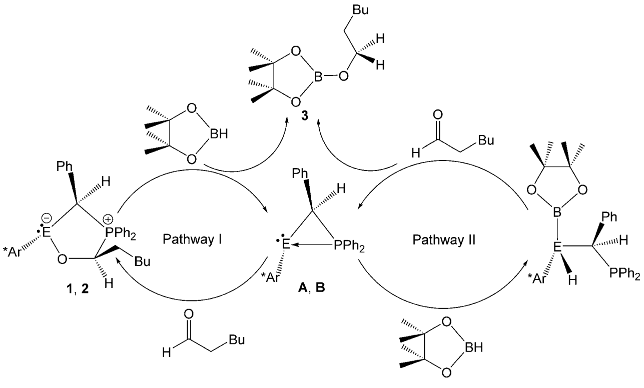
Scheme 2. Stoichiometric reactions of the aldehyde addition products with pinacolborane.



Scheme 3. Catalytic hydroboration of hexanal catalyzed by the intramolecular Lewis pairs **A** (E = Ge), **B** (E = Sn), and **C** (E = Pb).

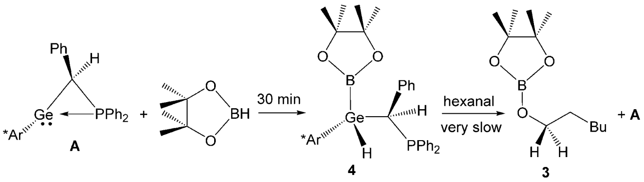
Two reaction pathways seemed plausible for the catalysis. As in the stoichiometric approach (Scheme 2), the catalytic cycle could start with adduct formation between Lewis pair and aldehyde followed by hydroboration of the C−O unit within the five-membered ring and regeneration of the catalyst (Pathway I, Scheme 4).

Another possible pathway (Pathway II, Scheme 4) begins with a reaction between catalyst and borane. To confirm the feasibility of this first reaction step between catalyst and borane, we reacted the Lewis pairs **A**, **B**, and **C** with pinacolborane. In the case of the Ge^{II} Lewis pair **A**, we



Scheme 4. Two possible pathways for the catalytic hydroboration (E = Ge, Sn).

isolated the B–H addition product (Scheme 5) and characterized the new boryl germanium hydride **4** by single-crystal X-ray diffraction (Figure 3), elemental analysis, and NMR (^{11}B NMR resonance at $\delta = 38.3$ ppm) and IR spectroscopy.



Scheme 5. Reaction of pinacolborane with the intramolecular germylene adduct **A** and formation of boryl germanium hydride **4**.

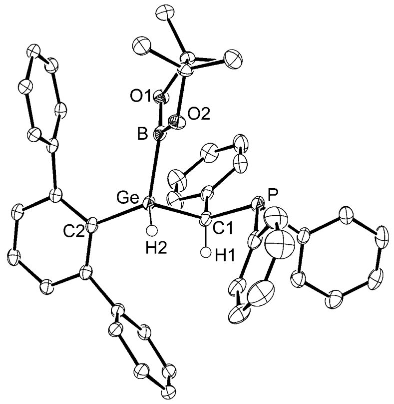
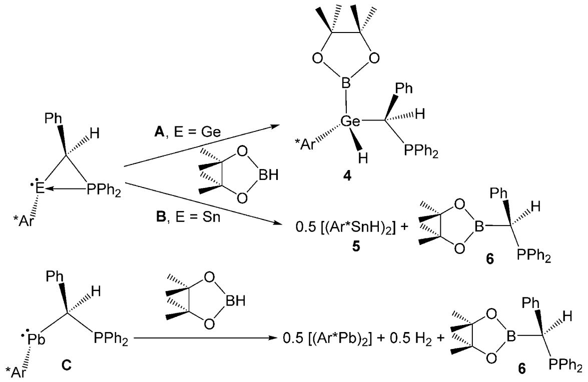


Figure 3. Molecular structure of germanium hydride **4** (ellipsoids set at 50% probability) in the solid state. Isopropyl groups and all hydrogen atoms except H1 and H2 are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge–C1 2.014(2), Ge–B 2.059(2), Ge–C2 1.980(2), P–C1 1.864(2); C2-Ge-C1 113.5(1), C2-Ge-B 122.8(1), B-Ge-C1 102.3(1), Ge-C1-P 107.2(1).

From a comparison of the spectroscopic data of **4** and the characterized side products of the stoichiometric reaction of **1** with pinacolborane (Scheme 2), we concluded that **4** is the spectroscopically observed side product. As we wanted to investigate the possible role of germanium hydride **4** in the catalytic hydroboration, we reacted **4** with hexanal in a stoichiometric reaction. Formation of the hydroboration product **3** is very slow under these conditions, and its yield was very small (9% yield after 16 h on the basis of NMR spectroscopy). Therefore, catalytic pathway II was discarded for the hydroboration with germylene Lewis pair **A**. Furthermore, on the basis of these findings, we concluded that **4**, which might also be formed as a side product during the catalysis with **A**, is not responsible for the fast and essentially quantitative hydroboration. Based on this experimental insight, we propose pathway I as the main pathway of the catalysis with **A** to form **3**.

The oxidative addition of catecholborane to dimethylgermylene has previously been studied by Nöth and co-workers: the addition product exhibited a ^{11}B NMR resonance at $\delta = 37.3$ ppm.[9] Oxidative addition at germylenes is a known reaction and has been studied with many different substrates.[4e,10] The B–Ge–H structural motive is known in the literature from BH$_3$ adducts with germylene hydrides and products of the oxidative addition of a B–H bond of Me$_3$NBH$_3$ at a germylene.[11,11] In these structures, the B–Ge distances [2.15(7)–2.064(6) Å] are comparable to the found value of **4**.

To confirm the relevance of the aldehyde addition product **2** for the hydroboration reaction with the tin catalyst, the reaction between stannylene Lewis pair **B** and pinacolborane was also investigated: the use of stannylene **B** leads to a different reaction than germylene **A**. The cyclic molecule **B** reacted slowly with an excess of pinacolborane (tenfold excess pinBH, 95% conversion after 14 days) to give the known terphenyl substituted tin(II) hydride **5** and the previously unknown P/B Lewis pair **6** (Scheme 6).[12,13] This reaction can be rationalized as the hydroborolysis of a Sn–C bond. Hydroborolysis reactions of Sn–N and Sn–O bonds are known and were reported by the groups of Jones and Power as a method for the preparation of tin(II) hydrides.[3c,12] Oxidative addition of the B–H unit, as in the germanium case, was not observed. Comparison of the spectroscopic data (see the Supporting Information) revealed that **5** and **6** are the side products in the stoichiometric reaction of the five-membered hexanal adduct **2** with pinacolborane (Scheme 2). As amidotin hydrides are known to catalyze hydroborations of aldehydes and ketones, we determined the reactivity of compound **5**, which was separately synthesized following a procedure developed by Power, with respect to hydroboration.[3c,13] Tin hydride **5** and its derivatives reacted quantitatively with hexanal and pinacolborane to give the hydroboration product. As a consequence, we have to conclude that tin hydride **5**, which might also be formed during catalysis in the tin case, can act as a catalyst in the hydroboration. Therefore, with the tin reagent, both Lewis pair **B** as well as its hydroborolysis decomposition product tin hydride **5** can be expected to act as hydroboration catalysts. The other side product, compound **6**, was completely characterized (see the Supporting Information for its crystal structure). A further side product (see compound **7** in the Supporting Information) was identified from the reaction between **B** and pinacolborane.



Scheme 6. Group 14 Lewis pairs react with pinacolborane: oxidative addition and hydroborolysis.

Overall, the formation of the side products in the stoichiometric reactions of **1** and **2** (Scheme 2) with pinacolborane can be rationalized as subsequent reactions of the formed Lewis pairs **A** and **B** with pinacolborane (Schemes 5 and 6; see also the Supporting Information). Therefore, the Lewis pairs **A** and **B** undergo decomposition pathways during catalysis with the hydroborane, in the tin case leading to a putatively even more reactive catalyst. In the stoichiometric reaction between plumbylene **C** and pinacolborane, we were able to observe the formation of P/B Lewis pair **6** and hydrogen evolution. Therefore, we speculate that a previously unknown hydride Ar*PbH might be formed, which then yields the formal diplumbyne Ar*PbPbAr* under elimination of hydrogen (Scheme 6). This diplumbyne has been characterized by Power et al. and was identified in the ^{1}H NMR spectrum of the reaction mixture (see the Supporting Information).[14] The Ar*PbH intermediate might play a role in the catalysis.

Obviously the homologous tetrylene–phosphine Lewis pairs **A**, **B**, and **C** show different reactivity towards pinacolborane, namely oxidative addition of the B–H bond with the germylene and hydroborolysis with the tin and lead reagents (Scheme 6).

In summary, we have described the addition of aldehydes and a ketone to cyclic tetrylene Lewis pairs. Especially in the case of germylene **A**, the intramolecular Lewis pair was shown to act as a main-group-element catalyst for the hydroboration of aldehydes and ketones. In the case of stannylene Lewis pair **B**, the catalysis is accompanied by tin(II) hydride formation, and both the stannylene Lewis pair as well as the formed aryl tin(II) hydride can act as catalysts of the hydroboration reaction.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: germylenes · hydroboration · Lewis pairs · main-group catalysis · stannylenes

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Main-Group Chemistry

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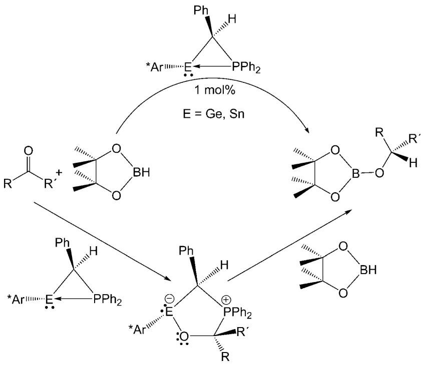
Diverse Activation Modes in the Hydroboration of Aldehydes and Ketones with Germanium, Tin, and Lead Lewis Pairs



Divergent reactivity: Intramolecular germylene, stannylene, and plumbylene Lewis pairs were reacted with hexanal but only the germanium and tin reagents yielded the cyclic addition products. In further reactivity studies, the hydroboration of aldehydes and ketones catalyzed by these intramolecular Lewis pairs was investigated.