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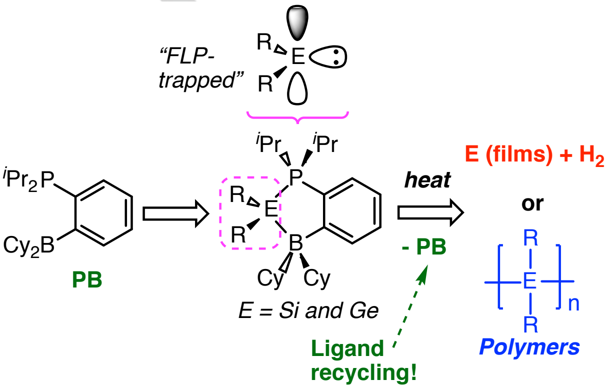
Frustrated Lewis Pair Chelation as a Vehicle for Low Temperature Semiconductor Element and Polymer Deposition

Alvaro A. Omaña,[a] Rachel K. Green,[a] Ryo Kobayashi,[b] Yingjie He,[a] Evan R. Antoniuk,[a] Michael J. Ferguson,[a] Yuqiao Zhou,[a] Jonathan G. C. Veinot,[a] Takeaki Iwamoto,[b] Alex Brown,[a] Eric Rivard*,[a]

Abstract: The stabilization of silicon(II) and germanium(II) dihydrides by an intramolecular Frustrated Lewis Pair (FLP) ligand, **PB**, $^{i}Pr_2P(C_6H_4)BCy_2$ (Cy = cyclohexyl) is reported. The resulting hydride complexes [PB{SiH_2}] and [PB{GeH_2}] are indefinitely stable at room temperature, yet can deposit films of silicon and germanium, respectively, upon mild thermolysis in solution. Hallmarks of this work include: (1) the ability to recycle the FLP phosphine-borane ligand (**PB**) after element deposition, and (2) the single-source precursor [PB{SiH_2}] deposits Si films at a record low temperature from solution (110 °C). The dialkylsilicon(II) adduct [PB{$SiMe_2$}] was also prepared, and shown to release poly(dimethylsilane) $[SiMe_2]_n$ upon heating. Overall, this study introduces a "closed loop" deposition strategy for semiconductors that steers materials science away from the use of harsh reagents or high temperatures.

Main group chemistry represents one of the pillars of molecular synthesis, with the ongoing discovery of new inorganic multiple bonds, non-metal mediated catalytic transformations, and the recent fixation of nitrogen by the light element boron receiving widespread attention.[1] Despite such breakthroughs, it is rare that modern synthetic chemistry makes a deep impact in the realm of materials science, a field that often relies upon decades-to-centuries old methods and harsh reaction conditions for synthesis. In this Communication, we provide a general, solution-based route to semiconducting Si or Ge films and a σ-conjugated polysilane by harnessing labile Frustrated Lewis Pair (FLP) chelation[2] to access the storable precursors [FLP{ER_2}] (E = Si or Ge; R = H or Me).

Frustrated Lewis Pairs (FLPs) contain unquenched Lewis basic and acidic sites, leading to the cooperative activation of typically inert substrates, such as H_2, CO or CO_2.[2] Furthermore, FLPs are being explored as next generation main group catalysts.[3] As outlined in Scheme 1, we sought to use the intramolecular FLP $^{i}Pr_2P(C_6H_4)BCy_2$ (**PB**; Cy = cyclohexyl)[4] to stabilize silicon(II) and germanium(II) dihydrides.[5] Herein, the singlet EH_2 units (E = Si or Ge) engage in synergistic donor-acceptor interactions with **PB**. Knowing that the Ge(II) dihydride donor-acceptor complex $Ph_3PCMe_2{\bullet}GeH_2{\bullet}BH_3$ can afford luminescent Ge nanoparticles from solution, albeit at a high temperature of 190 °C under microwave irradiation,[6] we hoped that the new [PB{EH_2}] chelates could release bulk Si or Ge and H_2 (via free EH_2) at much lower temperatures, while enabling the eventual recycling of the **PB** ligand. This Communication documents our success with this approach, leading to the low temperature (≤ 110 °C) deposition of semiconducting Si and Ge films onto substrates from solution. We also prepare the dialkylsilicon(II) adduct[7] [PB{$SiMe_2$}] and use this storable species to generate poly(dimethylsilane) $[SiMe_2]_n$, an inorganic polymer precursor to silicon carbide.[8]



Scheme 1. General concept of FLP-assisted semiconductor (E) and polymer $[ER_2]_n$ deposition (E = Si, Ge).

The requisite FLP for this study $^{i}Pr_2P(C_6H_4)BCy_2$ (**PB**) was obtained via a modification of a procedure by Bourissou and coworkers.[4,9] Addition of $Cl_2Ge{\bullet}$dioxane to **PB** in toluene afforded the FLP adduct [PB{$GeCl_2$}] (**1**) in a 94 % yield,[9] which was then converted to the target Ge(II) dihydride [PB{GeH_2}] (**2**) (59 % yield) upon treatment of **1** with two equiv. of Li[$HBEt_3$] in Et_2O (Scheme 2); **2** can be also synthesized in one-pot starting from **PB**.[9,10]

As expected, [PB{GeH_2}] (**2**) affords a $^{11}B\{^{1}H\}$ NMR resonance at 2.8 ppm in C_6D_6, consistent with a four-coordinate boron environment. For comparison, the three-coordinate boron center in free **PB** resonates at 75.6 ppm in C_6D_6. The Ge*H_2* unit in **2** yields a ^{1}H NMR signal at 3.81 ppm and a ν(Ge-H) IR band at 1990 cm^{-1}.[11] The solid state structures of **1** and **2** have been determined by single-crystal X-ray crystallography and are depicted as Figures S5[9] and **1** (left), respectively. The Ge–P distance in [PB{GeH_2}] (**2**) [2.3447(3) Å] is similar in length as the coordinative Ge–P length in Marschner's disilylgermylene $Me_3P{\bullet}[Ge\{Si(SiMe_3)_3\}_2]$ [2.3484(6) Å].[12] The Ge–B distance in **2** [2.1490(15) Å] is slightly longer than in the corresponding Ge–B bond in Kinjo's germylene adduct $Me_3P{\bullet}[GeB(Mes)N(Ad)CH{=}CHC(SiMe_3)_2]$ [2.121(2) Å] (Ad = adamantyl; Mes = 2,4,6-$Me_3C_6H_2$).[13]

Two routes to the Si(II)-FLP complex [PB{$SiCl_2$}] (**3**) were developed, each involving the *in situ* generation of $SiCl_2$[14] (Scheme 2). The highest isolated yield of pure **3** (colorless

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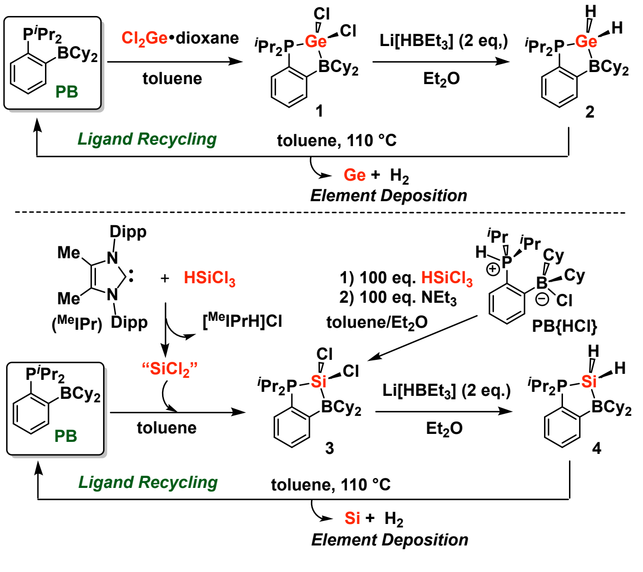
Supporting information for this article can be found under: DOI xxxxxx crystals) was 35 % starting from $^{i}Pr_2P(H)(C_6H_4)BCy_2(Cl)$ **[PB{HCl}]** and 100 equiv. of both Et_3N and $HSiCl_3$. The solid state structure of **3** was confirmed by X-ray crystallography (Figure S6).[9] Conversion of **3** into the Si(II) dihydride $[PB\{SiH_2\}]$ (**4**) was accomplished in a 86 % yield via the addition of two equiv. of $Li[HBEt_3]$ in Et_2O (Scheme 2).



Scheme 2. Routes to $[PB\{GeH_2\}]$ (**2**) and $[PB\{SiH_2\}]$ (**4**) and thermolysis to yield recyclable **PB** and Ge/Si.

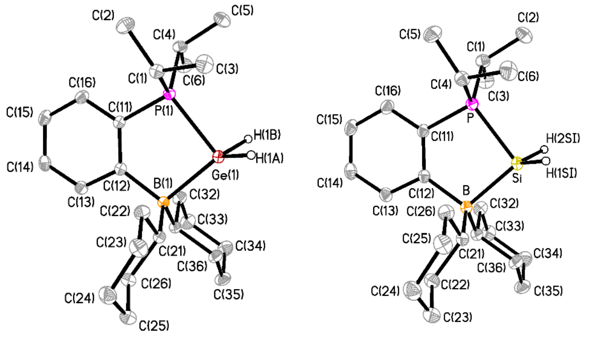


Figure 1. Molecular structures of $[PB\{GeH_2\}]$ (**2**) (left) and $[PB\{SiH_2\}]$ (**4**) (right) with thermal ellipsoids at a 30 % probability level. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: **2**: Ge1–P1 2.3447(3), Ge1–B1 2.1490(15), Ge1–H1A 1.49(2), Ge1–H1B 1.58(2); P1–Ge1–B1 92.32(4), H1A–Ge1–H1B 102.99(11). **4**: Si–P 2.2787(5), Si–B 2.0769(15), Si–H1 1.414(19), Si–H2 1.415(19); P–Si–B 94.09(4), H1–Si–H2 102.9(11).

The NMR spectra of $[PB\{SiH_2\}]$ (**4**) are consistent with the assigned structure, including a diagnostic triplet ^{29}Si NMR resonance at -84.0 ppm [$^1J_{SiH}$ = 158 Hz] (Figure S64).[9] The SiH_2 unit appears as a ν(Si-H) IR band at 2107 cm^{-1}.[15] The X-ray structure of **4** is depicted in Figure 1 (right), which shows a similar heterocyclic structure as in $[PB\{GeH_2\}]$ (**2**). The coordinative Si–P bond in **4** [2.2787(5) Å] is slightly shorter than in Baceiredo's silicon(II) hydride $[(Me_2Si(N^tBu)_2)P](C_8H_{10})N(Dipp)]SiH$ [2.318(15) Å].[1b] While the Si–B distance in **4** [2.0769(15) Å] is longer than in Cui's Si(II)-hydride adduct IMe_4•$Si(H)\{(N(Boryl)CH_2)_2\}$ (Boryl = $[B(NDippCH_2)_2]$; IMe_4 = $(MeCNMe)_2C$:) [2.014(5) Å].[16]

A major goal of this study was to use the newly prepared FLP-EH_2 complexes (**2** and **4**) as single-source precursors for the deposition of the bulk semiconductors Ge and Si. To start, $[PB\{GeH_2\}]$ (**2**) was subjected to thermal gravimetric analysis (TGA), which showed an onset of decomposition at 115 °C, with a residual mass after heating to 550 °C of 15 % (Figure S29);[9] this value corresponds very well with the expected wt. % Ge of 16 % in **2**. For $[PB\{SiH_2\}]$ (**4**), the onset of decomposition was significantly lower (67 °C), with 14 wt. % remaining after heating to 550 °C (Figure S30).[9] The expected weight % of Si after the decomposition of **4** is *ca.* 7 %, suggesting incomplete degradation of **4** in the solid state and/or partial oxidation of the reactive Si(0) surface.

Encouraged by the low decomposition temperatures for the $[PB\{EH_2\}]$ adducts **2** and **4**, and by our computations that show decomposition of these hydrides into **PB**, E (solid) and H_2 to be exoergic (ΔG) in toluene by -25.5 kcal/mol (Ge) and -13.7 kcal/mol (Si) (Figure S76),[9,17] we explored the release of Ge and Si from solution. Heating solutions of **2** and **4** in toluene-D_8 to 110 °C (8 hrs) deposited Ge and Si, respectively, with the sole species detected in solution being dissolved H_2 and the starting ligand, **PB**.[9] When element deposition was conducted on a preparative scale, we were able to recover/re-use up to *ca.* 80 % of **PB**, thus forming a complete "closed loop" cycle for element deposition (Scheme 2). Notably, the solution-phase deposition of Si from **4** at 110 °C represents, to our knowledge, the lowest temperature deposition of this ubiquitous semiconductor from a storable single-source molecular precursor.[18]

To characterize the morphology and elemental composition of the deposited Si and Ge films, SEM imaging and EDX maps were obtained (Figures 2 and S7-S25).[9] When element deposition was repeated onto Si or Ge wafers from solution, SEM revealed the presence of Si and Ge films with thicknesses of 110(15) nm and 14(4) μm, respectively (Figures 2a/b, S8 and S17-20).[9] Si or Ge deposition in the absence of substrates gave fused nanoparticle clusters (Figures S7, S9-S11, and S13-S15).[9] Furthermore, EDX showed negligible P atom content in all cases,[9] thus sample contamination with **PB** or starting $PB[\{EH_2\}]$ complex (E = Si or Ge) was minimal. The oxidation state of the deposited Si and Ge was probed by XPS, which showed one Si(0) environment for the Si films (Figure 2c), while both Ge(0) and Ge(II) environments could be found for the Ge films (Figure S23).[9] Oxidation of deposited Ge is likely due to brief exposure to air during sample transfer to the XPS stage.[19] Raman spectroscopy confirmed the presence of amorphous Si and Ge, with broad Si-Si (485 cm^{-1}) and Ge-Ge (280 cm^{-1}) peaks present (Figures S26 and S27).[9]

Our strategy also enables the formation of FLP-diorganosilylene complexes, as demonstrated by the synthesis of $[PB\{SiMe_2\}]$ (**5**) (Figure 3a) in a 70 % yield from the reaction between **3** and two equiv. of MeLi. The X-ray structure of **5** is presented in Figure 3b. Heating **5** in toluene at 110 °C for 15 hrs yields predominantly free **PB** (by $^{31}P\{^1H\}$ NMR) and an orange mixture. Dissolution of the products in THF and precipitation into cold (-30 °C) pentane afforded poly(dimethylsilane) $[SiMe_2]_n$ as a white solid, which was identified using FT-IR (Figure S31),[9] ^1H-^{29}Si HMBC (Figure S71),[9] and gel permeation chromatography (Figure S32).[9] ^1H-^{29}Si HMBC analysis is consistent with a predominantly linear polymer structure,[9,20] while GPC data shows unimodal distribution with a number average molecular weight (M_n) of 2.7 kDa (45 repeat units), and a polydispersity index (PDI) of 2.2.[9] Zybill and coworkers have previously observed the extrusion of oligomeric $[SiMe_2]_x$ (mol. weight = 550±10 Da, by cryoscopy) upon heating their silicon-iron adduct $[(Me_2N)_3PO•Me_2Si•Fe(CO)_4]$ to 120 °C, releasing toxic $OP(NMe_2)_3$ and metal carbonyls in the process.[21] Our formation of $[SiMe_2]_n$, a demonstrated precursor to silicon carbide,[8] is a promising new direction for FLP chemistry. The synthetic protocol introduced here should provide future access to a wide range of poly(diorganotetrelanes) $[GeR_2]_n$ and $[SiR_2]_n$ of tuneable composition (R = alkyl or aryl groups).

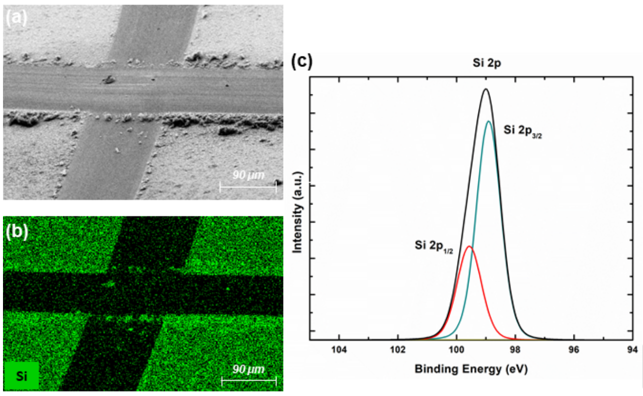


Figure 2. (a) Secondary-electron SEM image of deposited Si film where the intersection was carved with a needle on a Ge wafer; (b) EDX map (Si) of the imaged section in Figure 2a; (c) High-resolution XPS spectrum of Si (black) with fits to $2p_{1/2}$ (red) and $2p_{3/2}$ peaks (cyan) shown. Related data for deposited Ge can be found in the Supporting Information.[9]

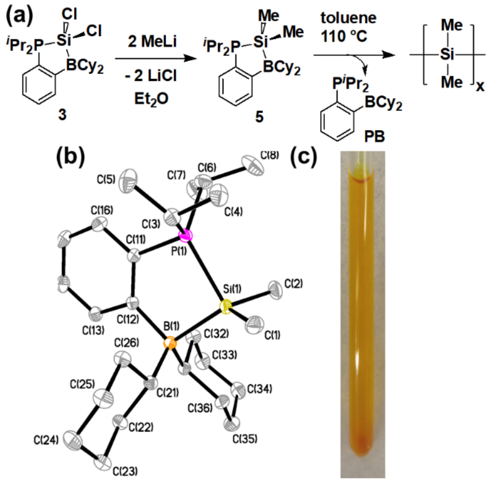


Figure 3. (a) Synthesis of $[PB\{SiMe_2\}]$ (**5**) and the subsequent extrusion of $[SiMe_2]_n$; (b) Molecular structure of $[PB\{SiMe_2\}]$ (**5**) with thermal ellipsoids at a 30 % probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–P1 2.3055(6), Si1–B1 2.0746(17), Si1–C1 1.890(2), Si1–C2 1.8902(19); P1–Si1–B1 93.63(5), C1–Si1–C2 104.21(10); (c) Photograph of deposited crude $[SiMe_2]_n$ in C_6D_6 after heating **5** in toluene at 110 °C for 15 hrs.

This Communication introduces the FLP-stabilized adducts $[PB\{GeH_2\}]$ (**2**) and $[PB\{SiH_2\}]$ (**4**), and the diorganosilylene complex $[PB\{SiMe_2\}]$ (**5**). The E(II) dihydride complexes represent bottleable single-source precursors for the deposition of bulk Ge and Si upon mild heating in solution. Another hallmark of this work is the ability to isolate/recycle the FLP ligand (**PB**) after element deposition. To our knowledge, the deposition of Si at 110 °C from the single-source molecular Si(II) dihydride precursor **4** in solution represents the lowest temperature for such a process. We also show that $[SiMe_2]_n$ can be deposited from the diorganosilylene adduct $[PB\{SiMe_2\}]$ (**5**). Future work will involve expanding FLP-assisted deposition to include other optoelectronically active elements and polymers.

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Keywords: Frustrated Lewis Pairs • Hydrides • Element Deposition • Inorganic Bonding • Group 14 Elements

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[9] For full synthetic, crystallographic (CCDC 2011820-2011828) and computational details, see the ESI. The X-ray structures of $^{i}Pr_2P(C_6H_4)BCy_2$ (**PB**), $[^{i}Pr_2P(C_6H_4)Li(OEt_2)]_2$, $^{i}Pr_2P(C_6H_4)BMes_2$ (**PB^{Mes}**), $[PB\{GeCl_2\}]$ (**1**) and $[PB\{SiCl_2\}]$ (**2**) are provided in the ESI.

[10] We also explored the coordination chemistry of $^{i}Pr_2P(C_6H_4)BMes_2$ (**PB^{Mes}**) (Mes = 2,4,6-$Me_3C_6H_2$), but observed no reaction with Cl_2Ge•dioxane, presumably due to the greater steric bulk at boron in this ligand (*vs.* in **PB**).

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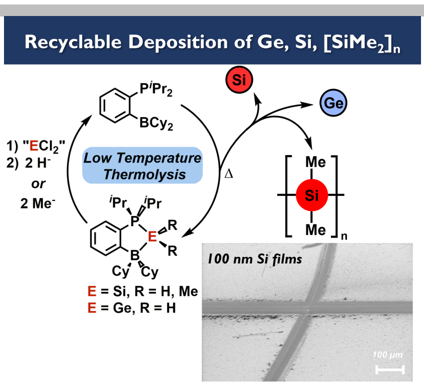
Entry for the Table of Contents

Putting Frustration to Work: We use a phosphinoborane Frustrated Lewis Pair (FLP) ligand to stabilize ER_2 species (E = Si, Ge; R = H or Me) for the subsequent deposition of semiconducting elements and polymers from solution, with ligand recycling possible.



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