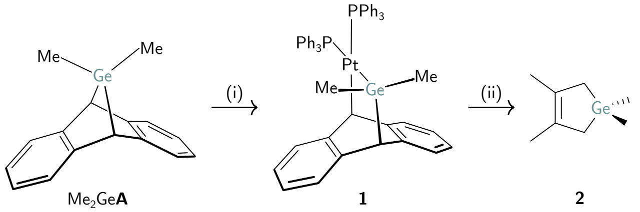
Identification of Reactive Intermediates Relevant to Dimethylgermylene Group Transfer Reactions of an Anthracene-Based Precursor

Michael B. Geeson, Wesley J. Transue, and Christopher C. Cummins*
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

Received August 13, 2019; E-mail: ccummins@mit.edu

Abstract: Dimethylgermylene ([Me_2Ge]) group transfer from the anthracene-based precursor dibenzo-7-dimethylgermanorbornadiene ($Me_2Ge\mathbf{A}$, $\mathbf{A}$ = $C_{14}H_{10}$, anthracene) was investigated. Transfer of [Me_2Ge] from $Me_2Ge\mathbf{A}$ to 2,3-dimethylbutadiene to give a dihydrogermole (**2**) was mediated by a platinum metallagermacycle (**1**), formed by oxidative addition of the platinum(0) species $(Ph_3P)_2Pt(C_2H_4)$ into the strained Ge–C bond of $Me_2Ge\mathbf{A}$ with concomitant loss of ethylene. Metallagermacycle **1** was characterized by multinuclear NMR spectroscopy, single crystal X-ray diffraction and elemental analysis. The strained Ge–C bond of $Me_2Ge\mathbf{A}$ was also found to undergo an addition reaction with pyridine, resulting in the [2.2.3]-bicyclic compound **3**. Kinetics experiments on both the platinum- and pyridine-promoted systems implicate low-valent dimethylgermylene-containing species as reaction intermediates.



Scheme 1. Synthesis of **1** from $Me_2Ge\mathbf{A}$ and subsequent group transfer of dimethylgermylene to 2,3-dimethylbutadiene. Conditions: (i) $(Ph_3P)_2Pt(C_2H_4)$, THF, 6 h, 23 °C. (ii): 2,3-dimethylbutadiene (20 equiv), benzene-d_6.

Group transfer is an important tool in chemistry, enabling the synthesis of functional groups such as cyclopropanes,[1] aziridines,[2] and epoxides.[3] An important strategy for group transfer is loss of a stable neutral species, such as dinitrogen or iodobenzene, from a precursor molecule with concomitant formation of the desired product. Our group has a long-standing interest in group transfer using anthracene-based precursors, enabling the transfer of phosphinidenes,[4] methylene,[5] sulfur monoxide,[6] P_2[7] and single atoms such as C-atom,[8] and N-mono-anion[9] and O-atom.[10]

We recently prepared dibenzo-7-dimethylgermanorbornadiene, ($Me_2Ge\mathbf{A}$, Scheme 1), in a convenient high-yielding reaction from magnesium anthracene ($Mg\mathbf{A}\cdot THF_3$)[11] and dichloro(dimethyl)germane, and explored its value as a reagent for dimethylgermylene transfer.[12] A number of molecular precursors for dimethylgermylene have previously been prepared, and the transfer of dimethylgermylene to unsaturated substrates described.[13] In some cases, transfer has been facilitated by weak nucleophiles[14] or transition-metal compounds[15,16] which has led to the speculation of the identity of various reactive intermediates, but these intermediates are rarely experimentally detected.[16,17] In the present work, we describe experimental observation of intermediates that have been speculated to play a role in dimethylgermylene transfer chemistry.

Despite the formulation of $Me_2Ge\mathbf{A}$ as a source of dimethylgermylene, with loss of anthracene as a driving force, heating $Me_2Ge\mathbf{A}$ (70–85 °C) in the presence of a variety of unsaturated substrates such as 1,3-cyclohexadiene, 2,3-dimethylbutadiene or trans,trans-1,4-diphenylbutadiene did not give rise to the anticipated germanium-containing products (S1.2). Instead, formation of $(Me_2Ge)_2\mathbf{A}$[12,18] was observed by ^1H NMR spectroscopy, resulting from formal transfer of dimethylgermylene to $Me_2Ge\mathbf{A}$, accompanied by the formation of one equivalent of anthracene, according to eqn. 1:

$$2Me_2Ge\mathbf{A} \rightarrow (Me_2Ge)_2\mathbf{A} + \mathbf{A} \qquad (1)$$

$(Me_2Ge)_2\mathbf{A}$ has been described previously, and one synthetic route of note involves intercepting the transient tetramethyldigermene ($Me_2Ge{=}GeMe_2$) with anthracene in a [2+4] cycloaddition.[19] In the pursuit of observing dimethylgermylene transfer to substrates other than $Me_2Ge\mathbf{A}$, we turned to the elements of the d-block in search of a molecular transition-metal complex that might facilitate dimethylgermylene transfer.

Treatment of $Me_2Ge\mathbf{A}$ with one equivalent of $(Ph_3P)_2Pt(C_2H_4)$[20] led to oxidative addition of platinum(0) into the Ge–C bond of $Me_2Ge\mathbf{A}$ to give metallagermacycle **1**, isolated in 38% yield (Scheme 1). The low yield was in part attributed to subsequent reactivity of the product (vide infra). Compound **1** was initially identified by a characteristic ^1H NMR multiplet (Fig. 1B) assigned to the bridgehead proton (located on C1 in Fig. 1A), arising from coupling to two chemically inequivalent ^{31}P nuclei ($^3J_{P-H}$ = 8.3, 23.0 Hz) and displaying satellites due to the ^{195}Pt nuclei ($^2J_{Pt-H}$ = 99.7 Hz). Single crystals of **1** were grown from a saturated diethyl ether solution at –35 °C, allowing for the molecular structure to be determined by X-ray crystallography. The solid-state structure of **1** features a square-planar platinum center (sum of angles around Pt = 363.69(10)°), and a flattening of the anthracene fragment compared to $Me_2Ge\mathbf{A}$; in $Me_2Ge\mathbf{A}$ the angle defined by the planes in the two benzo- rings is 123° whereas this increases to 149° in **1**.

Platinum-insertion product **1** displays reduced thermal stability with respect to $Me_2Ge\mathbf{A}$; while $Me_2Ge\mathbf{A}$ is stable as a solution in benzene-d_6 at 60 °C for at least 24 h, **1** readily loses anthracene at 50 °C. The isolation and struc-

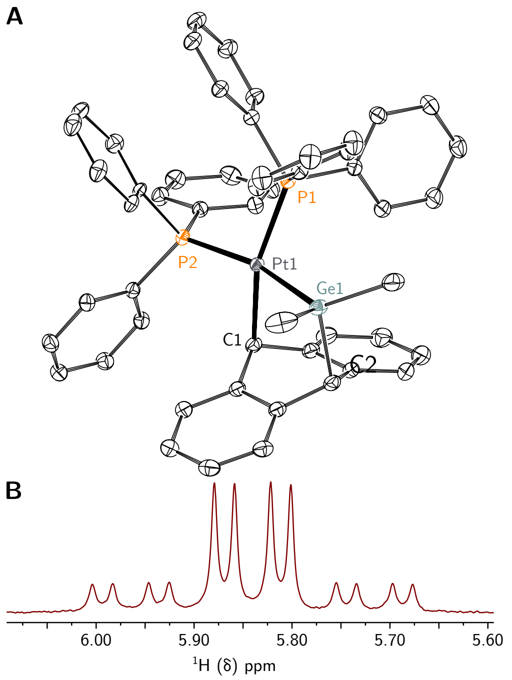
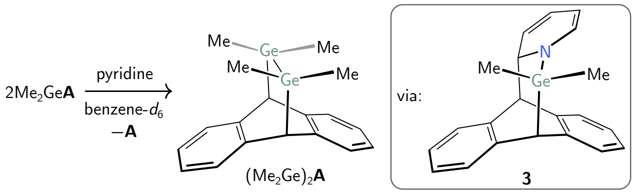


Figure 1. **A**: Molecular structure of **1** with ellipsoids shown at the 50% probability level. The hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pt1–Ge1: 2.4596(6); Pt1–C1: 2.177(1); Pt1–P1: 2.2789(4); Pt1–P2: 2.3161(6); Ge1–C2: 2.038(1); C1–Pt1–Ge1: 85.56(1); Pt1–Ge1–C2: 102.77(3). **B**: Selected region of the ^{1}H NMR spectrum of **1**, corresponding to the resonance of the proton located on C1. The multiplet arises from coupling to P1, P2 and Pt1. $^3J_{\mathrm{P-H}} = 8.3$, 23.0 Hz. $^2J_{\mathrm{Pt-H}} = 99.7$ Hz

tural characterization of **1** provides unequivocal evidence that group-10 metallagermacycles are viable species, and are plausible intermediates in, for example, palladium-mediated dimethylgermylene transfer to unsaturated substrates.[17]

With **1** in hand, we set out to test its value for dimethylgermylene transfer. Heating a benzene-d_6 solution of **1** to 50 °C in the presence of excess 2,3-dimethylbutadiene (20 equiv) led to the formation of the known[21] dihydrogermole **2** (Scheme 1) in ca. 50% yield, as determined by ^{1}H NMR spectroscopy. Having observed thermal loss of anthracene in the absence of a trap, we wondered if the reaction pathway might proceed through a platinum-germylene intermediate. Platinum-germylene compounds have been described previously, and typically require sterically encumbering substituents on either germanium or the platinum-bound phosphine ligands to permit isolation.[22] The thermal loss of anthracene from **1** was monitored by ^{1}H NMR spectroscopy to determine whether the intermediacy of a platinum germylene was kinetically plausible. At 72 °C in benzene-d_6, the unimolecular decay of **1** displayed a first order rate constant of $2.6(2) \times 10^{-4}$ s^{-1} independent of 2,3-dimethylbutadiene concentration (measured over the range of 0–30 equiv of diene to Me$_2$Ge**A**, S1.6). This rate law is consistent with a mechanism in which loss of anthracene is the rate-determining step, and the so-formed platinum-germylene intermediate undergoes a fast reaction with 2,3-dimethylgermylene to eventually furnish dihydrogermole **2**.

Interested in achieving catalytic dimethylgermylene transfer to 2,3-dimethylbutadiene, Me$_2$Ge**A** was heated with excess 2,3-dimethylbutadiene (20 equiv) and 20 mol% of either (Ph$_3$P)$_2$Pt(C$_2$H$_4$) or **1** in benzene-d_6. In both cases, (Me$_2$Ge)$_2$**A** was observed as the major dimethylgermylene-containing product, along with low (15–25%) yields of **2**. As development of free PPh$_3$ was observed during this reaction, a control experiment was performed revealing that PPh$_3$ alone catalyzes formation of (Me$_2$Ge)$_2$**A** from Me$_2$Ge**A** even in the presence of a large excess of 2,3-dimethylbutadiene (S1.9).



Scheme 2. Pyridine catalyzed formation of (Me$_2$Ge)$_2$**A** from Me$_2$Ge**A**, via a pyridine-insertion intermediate.

The weak nucleophilicity of PPh$_3$ prompted us to investigate the ability of other weak bases to effect this transformation. When Me$_2$Ge**A** was treated with pyridine (15 equiv) in benzene-d_6, an intermediate was observed by ^{1}H NMR spectroscopy, corresponding to the insertion of pyridine into the germanium-carbon bond of Me$_2$Ge**A** to give compound **3** (Fig. 2). Evidence for the connectivity of **3** was provided by 1D and 2D NMR experiments (Fig. S11, S1.7), showing five chemically inequivalent proton resonances that were assigned to protons formerly composing the pyridine molecule. Such 1,2-insertion reactions of pyridine into other M–C bonds are known (M = p-block metal), and such reactions typically lead to stable, isolable products.[23] In the case of pyridine reacting with Me$_2$Ge**A**, we were unable to isolate **3**, which was fully consumed at the end of the reaction, pointing to its existence only as a relatively short-lived intermediate. With the aim of isolating intermediate **3**, substituted pyridines were tested under otherwise identical reaction conditions. The use of a more electron-rich or -deficient (4-(dimethylamino)pyridine or pentafluoropyridine, respectively), however, did not lead to the formation of the corresponding analogs of **3** as determined by ^{1}H NMR spectroscopy. In the case of 4-(dimethylamino)pyridine the reaction led to rapid formation of (Me$_2$Ge)$_2$**A**, while for pentafluropyridine the reaction mixture remained unchanged after 24 h at 23 °C.

Interested in the fate of the unanticipated [2.2.3] bicyclic compound **3**, its concentration over time and the overall kinetics of the reaction were monitored by ^{1}H NMR spectroscopy. The reaction of Me$_2$Ge**A** with varying equivalents of pyridine to produce (Me$_2$Ge)$_2$**A** in benzene-d_6 at 72 °C was found to be first order in both pyridine and Me$_2$Ge**A**. The concentration of Me$_2$Ge**A** and **3** could be suitably modeled over the course of the reaction according to the following elementary steps (eqns. 2 and 3) and rate laws (eqns. 4 and 5):

$$\mathrm{Me_2Ge}\mathbf{A} + \mathrm{pyridine} \xrightarrow{k_1} \mathbf{3} \tag{2}$$

$$\mathbf{3} \xrightarrow{k_2} \mathrm{products} \tag{3}$$

$$\frac{d}{dt}[\mathrm{Me_2Ge}\mathbf{A}] = k_1[\mathrm{Me_2Ge}\mathbf{A}][\mathrm{pyridine}] \tag{4}$$

$$\frac{d}{dt}[\mathbf{3}] = k_1[\mathrm{Me_2Ge}\mathbf{A}][\mathrm{pyridine}] - k_2[\mathbf{3}] \tag{5}$$

with rate constants $\mathrm{k_1} = 1.066(36)\times10^{-4}$ M^{-1} s^{-1} and $\mathrm{k_2} = 1.31(43)\times10^{-3}$ s^{-1}, determined by fit with the experimental data. Unimolecular decomposition of **3** via a retro-[4+2] cycloaddition would presumably lead to anthracene and a pyridine adduct of dimethylgermylene;[24] such Lewis base-supported germylene species have been implicated by UV-Vis spectroscopy.[13]

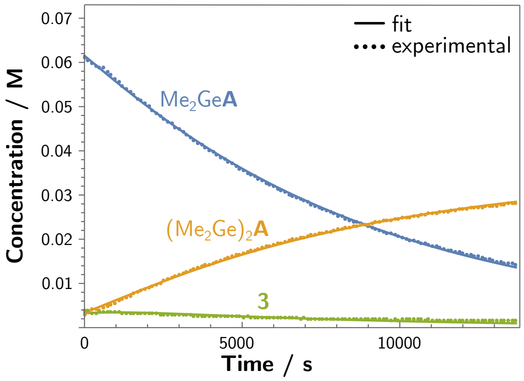


Figure 2. Plot of the experimental kinetic data for the reaction of Me$_2$Ge**A** to give (Me$_2$Ge)$_2$**A** in the presence of pyridine (10 equiv).

The observation of pyridine-accelerated loss of dimethylgermylene from Me$_2$Ge**A** prompted us to investigate whether pyridine might permit the transfer of dimethylgermylene from Me$_2$Ge**A** to the 2,3-dimethylbutadiene. Despite the use of an excess (10 equiv) of 2,3-dimethylbutadiene, only formation of (Me$_2$Ge)$_2$**A** and anthracene was observed. Clearly, Me$_2$Ge**A** is a better (kinetic) trap for dimethylgermylene than 2,3-dimethylbutadiene. This result is in line with previous discussions in the literature, where the naphthalene-analog of Me$_2$Ge**A** was described as a "powerful germylene-scavenger"[18] by virtue of the large ring-strain-energy resulting from the acute C–Ge–C angle (for example, 77.72° in Me$_2$Ge**A**), enforced by the [2.2.1]-bicyclic framework.

The ring-strain-energy present in Me$_2$Ge**A** provides a clear thermodynamic driving force for addition reactions across the Ge–C bond to generate [2.2.2]- or [2.2.3]-bicyclic-containing products. These bicyclic structures were experimentally observed for the reaction of Me$_2$Ge**A** using (Ph$_3$P)$_2$Pt(C$_2$H$_4$) and pyridine, respectively. Extrusion and aromatization of anthracene provides an additional thermodynamic driving force for the release of low-valent germylene-containing intermediates, implicated by kinetics experiments (Fig. 2). With this work, we expand the compounds available downstream from Me$_2$Ge**A** and provide evidence for the existence of intermediates relevant to germylene-transfer chemistry.

Acknowledgement We thank the National Science Foundation (NSF-CHE-1664799) for financial support of this research.

Supporting Information Available: Experimental details, characterization data, and X-ray crystallographic information are provided in the Supporting Information document. Crystallographic data are available from the Cambridge Structural Database under the refcode 1920811. This material is available free of charge via the Internet at `http://pubs.acs.org/`.

References

(1) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. Stereoselective Cyclopropanation Reactions. *Chem. Rev.* **2003**, *103*, 977–1050.

(2) Müller, P.; Fruit, C. Enantioselective Catalytic Aziridinations and Asymmetric Nitrene Insertions into CH Bonds. *Chem. Rev.* **2003**, *103*, 2905–2920.

(3) Grigoropoulou, G.; Clark, J. H.; Elings, J. A. Recent developments on the epoxidation of alkenes using hydrogen peroxide as an oxidant. *Green Chem.* **2003**, *5*, 1–7.

(4) (a) Velian, A.; Cummins, C. C. Facile Synthesis of Dibenzo-$7\lambda^3$-phosphanorbornadiene Derivatives Using Magnesium Anthracene. *J. Am. Chem. Soc.* **2012**, *134*, 13978–13981; (b) Transue, W. J.; Velian, A.; Nava, M.; García-Iriepa, C.; Temprado, M.; Cummins, C. C. Mechanism and Scope of Phosphinidene Transfer from Dibenzo-7-phosphanorbornadiene Compounds. *J. Am. Chem. Soc.* **2017**, *139*, 10822–10831; (c) Szkop, K. M.; Geeson, M. B.; Stephan, D. W.; Cummins, C. Synthesis of acyl(chloro)phosphines enabled by phosphinidene transfer. *Chem. Sci.* **2019**, *10*, 3627–3631.

(5) Joost, M.; Transue, W. J.; Cummins, C. C. Diazomethane umpolung atop anthracene: an electrophilic methylene transfer reagent. *Chem. Sci.* **2018**, *9*, 1540–1543.

(6) Joost, M.; Nava, M.; Transue, W. J.; Martin-Drumel, M.-A.; McCarthy, M. C.; Patterson, D.; Cummins, C. C. Sulfur monoxide thermal release from an anthracene-based precursor, spectroscopic identification, and transfer reactivity. *PNAS* **2018**, *115*, 5866–5871.

(7) Velian, A.; Nava, M.; Temprado, M.; Zhou, Y.; Field, R. W.; Cummins, C. C. A Retro Diels–Alder Route to Diphosphorus Chemistry: Molecular Precursor Synthesis, Kinetics of P$_2$ Transfer to 1,3-Dienes, and Detection of P$_2$ by Molecular Beam Mass Spectrometry. *J. Am. Chem. Soc.* **2014**, *136*, 13586–13589.

(8) Joost, M.; Nava, M.; Transue, W. J.; Cummins, C. C. An exploding N-isocyanide reagent formally composed of anthracene, dinitrogen and a carbon atom. *Chem. Commun.* **2017**, *53*, 11500–11503.

(9) Mindiola, D. J.; Cummins, C. C. Deprotonated 2,3:5,6-Dibenzo-7-aza bicyclo[2.2.1]hepta-2,5-diene as a Nitrido Nitrogen Source by Anthracene Elimination: Synthesis of an Iodide(nitride)chromium(VI) Complex. *Angew. Chem. Int. Ed.* **1998**, *37*, 945–947.

(10) Palluccio, T. D.; Rybak-Akimova, E. V.; Majumdar, S.; Cai, X.; Chui, M.; Temprado, M.; Silvia, J. S.; Cozzolino, A. F.; Tofan, D.; Velian, A.; Cummins, C. C.; Captain, B.; Hoff, C. D. Thermodynamic and Kinetic Study of Cleavage of the N–O Bond of N-Oxides by a Vanadium(III) Complex: Enhanced Oxygen Atom Transfer Reaction Rates for Adducts of Nitrous Oxide and Mesityl Nitrile Oxide. *J. Am. Chem. Soc.* **2013**, *135*, 11357–11372.

(11) Freeman, P. K.; Hutchinson, L. L. Magnesium anthracene dianion. *J. Org. Chem.* **1983**, *48*, 879–881.

(12) Velian, A.; Transue, W. J.; Cummins, C. C. Synthesis, Characterization, and Thermolysis of Dibenzo-7-dimethylgermanorbornadiene. *Organometallics* **2015**, *34*, 4644–4646.

(13) Neumann, W. P. Germylenes and stannylenes. *Chem. Rev.* **1991**, *91*, 311–334.

(14) Egorov, M. P.; Galminas, A. M.; Ezhova, M. B.; Kolesnikov, S. P.; Nefedov, O. M. Nucleophile-catalyzed cleavage of germanium(silicon)-carbon bonds in the strained heterocycles 7-germa(sila)norbornadienes. **1993**, *6*, 15–21.

(15) (a) Tsumuraya, T.; Ando, W. Carbon-unsubstituted germoles: palladium-catalyzed reactions of germylenes with acetylene. *Organometallics* **1990**, *9*, 869–871; (b) Brauer, H.; Neumann, W. P. Palladium-Catalyzed Cycloaddition of Alkynes (RC≡CR') with Dimethylgermylene. *Synlett* **1991**, *1991*, 431–432; (c) Mochida, K.; Hirakue, K.; Suzuki, K. Palladium-Catalyzed Addition of Tetragermetanes to Alkynes. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1023–1028.

(16) Billeb, G.; Brauer, H.; Neumann, W. P.; Weisbeck, M. Chemistry of heavy carbene analogs R$_2$M (M = silicon, germanium, tin). 16. Reactions of free dimethylgermylene with alkynes and their palladium catalysis. *Organometallics* **1992**, *11*, 2069–2074.

(17) Egorov, M. P.; Galminas, A. M.; Ezhova, M. B.; Kolesnikov, S. P.; Nefedov, O. M. Palladium-Catalyzed Generation of Dimethylgermylene from 7-Germanorbornadiene. *Main Group Met. Chem.* **1990**, *13*, 269–277.

(18) Bleckmann, P.; Minkwitz, R.; Neumann, W. P.; Schriewer, M.; Thibud, M.; Watta, B. Dimethyl germylene insertion into a strained C–Ge bond and matrix isolation of tetramethyl digermene Me$_2$Ge=GeMe$_2$. *Tetrahedron Lett.* **1984**, *25*, 2467–2470.

(19) Sakurai, H.; Nakadaira, Y.; Tobita, H. Generation and trapping of tetramethyldigermene. *Chem. Lett.* **1982**, *11*, 1855–1858.

(20) Nagel, U. Einfache Synthese von (η^2-Ethen)bis(triphenylphosphan)platin(0). *Chem. Ber.* **1982**, *115*, 1998–1999.

(21) Leigh, W. J.; Harrington, C. R.; Vargas-Baca, I. Organogermanium Reactive Intermediates. The Direct Detection and Characterization of Transient Germylenes and Digermenes in Solution. *J. Am. Chem. Soc.* **2004**, *126*, 16105–16116.

(22) (a) Litz, K. E.; Henderson, K.; Gourley, R. W.; Holl, M. M. B. Reversible Insertion Reactions of a Platinum Germylene Complex. *Organometallics* **1995**, *14*, 5008–5010; (b) Litz, K. E.; Bender, J. E.; Sweeder, R. D.; Banaszak Holl, M. M.; Kampf, J. W. Photochemistry of Transition Metal Germylenes and Metallacycles. *Organometallics* **2000**, *19*, 1186–1189; (c)

Hupp, F.; Ma, M.; Kroll, F.; Jimenez-Halla, J. O. C.; Dewhurst, R. D.; Radacki, K.; Stasch, A.; Jones, C.; Braunschweig, H. Platinum Complexes Containing Pyramidalized Germanium and Tin Dihalide Ligands Bound through , M=E Multiple Bonds. *Chem. - Eur. J.* **2014**, *20*, 16888–16898; (d) Waterman, R.; Handford, R. C.; Tilley, T. D. Element–Hydrogen Bond Activations at Cationic Platinum Centers To Produce Silylene, Germylene, Stannylene, and Stibido Complexes. *Organometallics* **2019**, *38*, 2053–2061.

(23) (a) Giam, C. S.; Stout, J. L. Isolation and characterization of crystalline -complexes from organolithium compounds and pyridine derivatives. *J. Chem. Soc. D* **1969**, *0*, 142–142; (b) Giam, C. S.; Stout, J. L. A new synthesis of 2,5-disubstituted pyridines. *J. Chem. Soc. D* **1970**, 478; (c) Li, X.; Duan, L.; Song, H.; Ni, C.; Cui, C. Facile Generation of Aluminum 1,2-Dihydropyridyl and Hydroxyl Derivatives from an Aluminum Cyclopropene Analogue. *Organometallics* **2006**, *25*, 5665–5667; (d) Protchenko, A. V.; Saleh, L. M. A.; Vidovic, D.; Dange, D.; Jones, C.; Mountford, P.; Aldridge, S. Contrasting reactivity of anionic boron- and gallium-containing NHC analogues: EC vs. EM bond formation (E = B, Ga). *Chem. Commun.* **2010**, *46*, 8546; (e) Hill, M. S.; MacDougall, D. J.; Mahon, M. F. Magnesium hydride-promoted dearomatisation of pyridine. *Dalton Trans.* **2010**, *39*, 11129; (f) Lichtenberg, C.; Spaniol, T. P.; Perrin, L.; Maron, L.; Okuda, J. Reversible 1,4-Insertion of Pyridine Into a Highly Polar Metal-Carbon Bond: Effect of the Second Metal. *Chem. Commun.* **2012**, *18*, 6448–6452.

(24) Tashkandi, N. Y.; Cook, E. E.; Bourque, J. L.; Baines, K. M. Addition of Isocyanides to Tetramesityldigermene: A Comparison of the Reactivity between Surface and Molecular Digermenes. *Chem. - Eur. J.* **2016**, *22*, 14006–14012.

Graphical TOC Entry