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ARTICLE

# Synthesis and characterization of extremely bulky amido-germanium(II) halide complexes

Terrance J. Hadlington, Jiaye Li, and Cameron Jones

**Abstract:** The extremely bulky aryl/silyl secondary amines, $HN(Ar)(SiMe_3)$, Ar = $C_6H_2$-*i*-$Pr_2(CPh_3)$-2,6,4 ($L^{Dip}H$), $C_6H_2\{C(H)Ph_2\}_2$-*i*-Pr-2,6,4 ($L^{\dagger}H$), or $C_6H_2\{C(H)Ph_2\}_2$-*t*-Bu-2,6,4 ($L^{t\text{-}Bu}H$), have been synthesized via salt metathesis reactions between the appropriate lithium anilide complex and $ClSiMe_3$. The related diaryl secondary amines, $HN(Ar^*)(R)$, $Ar^*$ = $C_6H_2\{C(H)Ph_2\}_2Me$-2,6,4 and R = $C_6H_3Me_2$-3,5 ($L^{Me}H$), $C_6H_3(CF_3)_2$-3,5 ($L^{CF3}H$), or $C_6H_2$-*i*-$Pr_3$-2,4,6 ($L^{Trip}H$), were prepared via palladium catalyzed cross-coupling reactions. Three of the amines were crystallographically characterized. Treatment of $GeCl_2$·dioxane with 1 equiv. of each of the deprotonated amines led to the isolation of the amido-germanium(II) chloride complexes, [LGeCl] (L = $L^{\dagger}$, $L^{t\text{-}Bu}$, $L^{CF3}$, or $L^{Trip}$). Similarly, reaction of the known amido-digermyne, [$L^*$Ge–Ge$L^*$] ($L^*$ = –N($Ar^*$)($SiMe_3$)), with $I_2$ resulted in the oxidative cleavage of the Ge–Ge bond of the digermyne, and the formation of the first two-coordinate amido-germanium(II) iodide complex, [$L^*$GeI]. Crystallographic characterization of [$L^{t\text{-}Bu}$GeCl] and [$L^*$GeI] revealed both to have similar monomeric structures. The compounds described in this study should prove useful as synthons for synthetic chemists working in the field of low oxidation state main group chemistry.

*Key words:* germylene, steric bulk, amide, germanium, crystal structure.

**Résumé :** On a synthétisé les arylsilylamines secondaires très encombrées, $HN(Ar)(SiMe_3)$, Ar = $C_6H_2$-*i*-$Pr_2(CPh_3)$-2,6,4 ($L^{Dip}H$), $C_6H_2\{C(H)Ph_2\}_2$-*i*-Pr-2,6,4 ($L^{\dagger}H$), ou $C_6H_2\{C(H)Ph_2\}_2$-*t*-Bu-2,6,4 ($L^{t\text{-}Bu}H$), par des réactions de métathèse entre le complexe anilide lithium approprié et le $ClSiMe_3$. On a préparé les diarylamines secondaires apparentées, $HN(Ar^*)(R)$, $Ar^*$ = $C_6H_2\{C(H)Ph_2\}_2Me$-2,6,4 et R = $C_6H_3Me_2$-3,5 ($L^{Me}H$), $C_6H_3(CF_3)$2-3,5 ($L^{CF3}H$), ou $C_6H_2$-*i*-$Pr_3$-2,4,6 ($L^{Trip}H$), par des réactions de couplage croisé catalysées par le palladium. Trois de ces amines ont été caractérisées par cristallographie. Le traitement du GeCl2·dioxane avec 1 equiv. de chacune des amines déprotonées a permis d'isoler les complexes chlorure de germanium(II) amido, [LGeCl] (L = $L^{\dagger}$, L-*t*-Bu, $L^{CF3}$ ou $L^{Trip}$). Similairement, la réaction de l'amidodigermyne connu, [$L^*$Ge–Ge$L^*$] ($L^*$ = –N($Ar^*$)($SiMe_3$)), avec $I_2$ a donné lieu au clivage oxydatif de la liaison Ge–Ge du digermyne et à la formation du premier complexe à deux coordinats iodure de germanium(II) amido, [$L^*$GeI]. La caractérisation du [L-*t*-BuGeCl] et du [$L^*$GeI] par cristallographie a révélé qu'ils possèdent des structures monomériques similaires. Les composés décrits dans la présente étude devraient être des synthons utiles pour les spécialistes de la chimie de synthèse dont le travail porte sur les éléments du groupe principal dans un faible état d'oxydation. [Traduit par la Rédaction]

*Mots-clés :* germylène, encombrement stérique, amide, germanium, structure cristalline.

## Introduction

The chemistry of compounds containing the main group elements in very low oxidation states and (or) with very low coordination numbers has rapidly expanded over the past 20 years.[1–4] The growing interest in this area has largely been driven by advances it has offered to our fundamental understanding of bonding, structure, and compound stability. More recently, however, the recognition that low oxidation state main group compounds can possess electronic structures similar to those of d-block metal complexes has led to the former finding a variety of "transition metal-like" synthetic applications.[5–8] Pertinent examples here are the, sometimes reversible, activations of small molecules, e.g., $H_2$, $CO_2$, $C_2H_4$, $NH_3$, etc., that are central to many catalytic processes. Most developments in this aspect of the field have occurred with low oxidation state group 14 element complexes, the kinetic stabilization of which has been permitted by the growing number of sterically encumbered ligands that are available to the synthetic inorganic chemist.

Our contributions to the design and synthesis of kinetically stabilizing ligands have largely centered on bulky anionic, bidentate N-donor ligands. Of most note are the very hindered guanidinate and amidinate ligand systems, $[(DipN)_2CR]^-$ (Dip = $C_6H_3$-*i*-$Pr_2$-2,6 and R = bulky amino, alkyl, aryl), which we have applied to the stabilization of a variety of metallacycles containing metal centers in the +1 (or +2) oxidation state, not only from the s- and p-blocks,[9] but also from the d- and f-blocks.[10,11] Over the past two years, we have extended this study to the preparation of a new class of monodentate amide ligands of unprecedented steric bulk, e.g., –N(Ar)(R) (Ar = $C_6H_2\{C(H)Ph_2\}_2R'$-2,6,4; R′ = Me ($Ar^*$) or *i*-Pr ($Ar^{\dagger}$); and R = $SiMe_3$, $SiPh_3$, $SiPr^i_3$, Ph, or mesityl (Mes)).[12–14] These have been used to stabilize a variety of one- and two-coordinate p-block (and d-block) metal(I or II) complexes, which, in many cases, display fascinating reactivity.[12–21] Most success has been had with low-valent germanium systems such as the amido-digermynes, [$L^*$Ge–Ge$L^*$][17] and [L′Ge=GeL′][21] ($L^*$ = –N($Ar^*$)($SiMe_3$) and L′ = –N($Ar^{\dagger}$)(Si-*i*-$Pr_3$)), which are closely related to Power's[22] celebrated bulky terphenyl substituted digermynes, e.g.,

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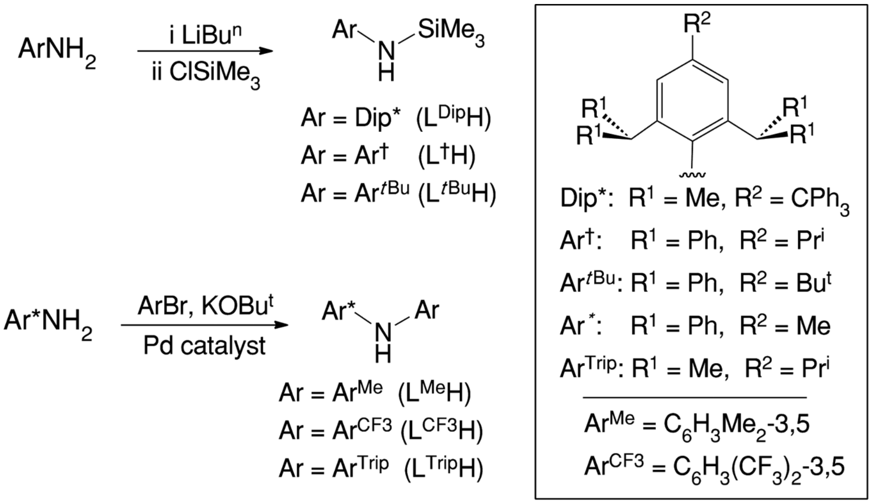
**Scheme 1.** Synthesis of bulky secondary amines.



[Ar′Ge=GeAr′] (Ar′ = $-C_6H_3(C_6H_3$-*i*-$Pr_2$-2,6$)_2$-2,6). Not only can the Ge–Ge bond order in these systems be readily controlled by subtle variations in amido ligand bulk, but they can also activate both $H_2$ and $CO_2$ at temperatures well below 0 °C, and at atmospheric pressure.[16,17,21] To extend the range of amido-digermynes, and to explore the effects that ligand (L) sterics and electronics have on their properties and reactivity, new germanium(II) halide precursors, [LGeX] (X = halide), to these complexes need to be available. Herein, we describe the development of several new bulky secondary amine proligands, and the use of these in the preparation of a number of monomeric amido-germanium(II) halide complexes.

## Results and discussion

At the outset of this study, it was decided to target two specific variations of the general class of bulky amido ligands, –N(Ar)(R), which we have previously developed.[12–14] The first group of these, $-N(Ar)(SiMe_3)$, Ar = $C_6H_2$-*i*-$Pr_2(CPh_3)$-2,6,4 (Dip*), Ar†, or $C_6H_2\{C(H)Ph_2\}_2$-*t*-Bu-2,6,4 ($Ar^{t\text{-}Bu}$), is related to the well-used $-N(Ar^*)(SiMe_3)$ (L*) ligand,[12] but has both less bulky (Dip*) and more bulky (Ar† or $Ar^{t\text{-}Bu}$) aryl substituents. The second group of ligands, –N(Ar*)(R), R = $C_6H_3Me_2$-3,5 ($Ar^{Me}$), $C_6H_3(CF_3)_2$-3,5 ($Ar^{CF3}$), or $C_6H_2$-*i*-$Pr_3$-2,4,6 ($Ar^{Trip}$), is related to the previously employed diaryl amide ligands, –N(Ar*)(Ph) and –N(Ar*)(Mes),[13] but have varying steric bulk and electronic properties. With respect to the latter property, the $Ar^{CF3}$ substituted ligand might be expected to be more electron withdrawing than the other diaryl amides.

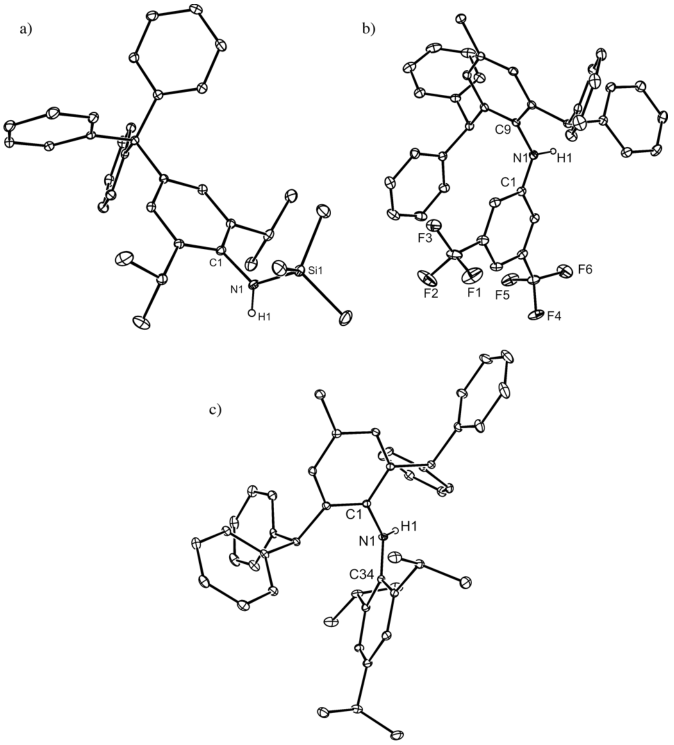
Two synthetic routes were employed to synthesize the secondary amine proligands in moderate to high yields (Scheme 1). The silyl substituted amines, $HN(Ar)(SiMe_3)$, Ar = Dip* ($L^{Dip}H$), Ar† (L†H), or $Ar^{t\text{-}Bu}$ ($L^{t\text{-}Bu}H$), were readily prepared by quenching the in situ generated lithiated anilines, "LiN(Ar)H", with chlorotrimethylsilane. In contrast, the diaryl amines, HN(Ar*)(R), R = $Ar^{Me}$ ($L^{Me}H$), $Ar^{CF3}$ ($L^{CF3}H$), or Trip ($L^{Trip}H$), were synthesized by palladium catalyzed cross-coupling reactions, based on a literature procedure,[23] between ArBr and the aniline $Ar^*NH_2$. A gauge of the acidity of the amino protons of these ligands can be drawn from the chemical shifts of their $^1H$ NMR signals. Those for both the silyl substituted amines (δ 1.65–2.05 ppm) and the diaryl amines (δ 4.46–4.59 ppm) fall in narrow, but distinct, ranges that are comparable to chemical shifts reported for related systems, e.g., $HN(Ar^*)(SiMe_3)$ (δ 1.75 ppm) and HN(Ar*)(Mes) (δ 4.32 ppm), respectively. It is of note that the fluorine substitution in $L^{CF3}H$ appears to have little effect on the acidity of its amine proton, relative to those in $L^{Me}H$ and $L^{Trip}H$. It is also worthy to mention that singlet resonances were observed in the $^{29}Si\{^1H\}$ NMR spectra of the silyl amines (range: δ 3.30–18.01 ppm, cf. δ 3.20 ppm for L*H) and the $^{19}F\{^1H\}$ NMR spectrum of $L^{CF3}H$ (δ −62.7 ppm).

Three of the secondary amines ($L^{Dip}H$, $L^{CF3}H$, and $L^{Trip}H$) were crystallographically characterized, and their molecular structures can be found in Fig. 1. The increasing steric bulk around the N center of this series of amines is clear, with the bulk of $L^{Trip}H$ being especially significant. Despite this, the C/Si–N–C angles of the compounds fall in a fairly narrow range (121.22(10)–124.44(18)°) and their N–C/Si bond lengths are unexceptional. One feature of the solid state structure of $L^{Trip}H$ that is worth mentioning is that one of its ortho-isopropyl groups appears to be sandwiched between two phenyl groups of its benzhydryl substituents. However, the simplicity of the $^1H$ NMR spectrum of the compound suggests that this does not greatly hinder rotation of the Ar* and Trip groups, relative to each other, in solution.

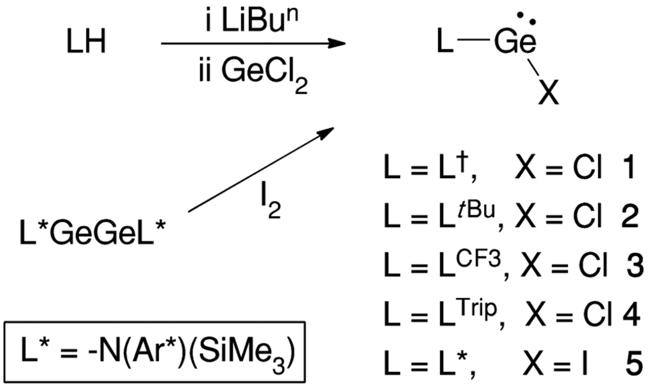
Attempts were made to prepare amido-germanium(II) chloride complexes, [LGeCl], by deprotonating all of the secondary amines with Li-*n*-Bu, followed by treatment of tetrahydrofuran (THF) solutions of $GeCl_2$·(dioxane) with the in situ generated lithium amides (Scheme 2). These reactions afforded moderate to good yields of the expected compounds from all of the lithium amides, except $LiL^{Dip}$ and $LiL^{Me}$, for which intractable product mixtures were obtained. It is perhaps not surprising that [$L^{Dip}$GeCl] could not be readily accessed, as the closely related system [$(Dip)(Me_3Si)NGeCl$] can only be prepared in very low yield.[20] It is, however, worth noting that from one attempted crystallization of [$L^{Dip}$GeCl] from a diethyl ether extract of the reaction mixture, a few crystals of the cocrystallized, lithium amide complexes, [$L^{Dip}Li(THF)(OEt_2)$][$L^{Dip}Li(THF)_3$], were obtained. Details of the molecular structure of the [$L^{Dip}Li(THF)(OEt_2)$] component of this cocrystal can be found in the Supplementary data.

While compounds **1**–**4** will likely prove useful as precursors to a variety of lower oxidation state systems via reduction methodologies, it would be useful to be able to access the iodo-germylene analogues of these species. One reason for this is that it is well known that reductions of p-block metal iodide complexes are typically more facile and higher yielding than those of metal chlorides.[1–8] While it is likely that compounds of the type [LGeI] should be easily synthesized from reactions of lithium amides with $GeI_2$, the very high cost of the latter reagent makes this route prohibitive. As a demonstration of the feasibility of an alternative route to amido-germanium(II) iodide complexes, we carried out the reaction of the known digermyne [L*Ge–GeL*][17] with 1 equiv. of $I_2$.[24] This, indeed, afforded a moderate yield of the monomeric amido-germanium(II) iodide compound, [L*GeI] (**5**), via oxidative cleavage of the Ge–Ge bond of the digermyne. The spectroscopic data for

**Fig. 1.** Thermal ellipsoid plot (25% probability surface) of the molecular structures of (*a*) L$^{Dip}$H, (*b*) L$^{CF3}$H, and (*c*) L$^{Trip}$H. Hydrogen atoms (except amino protons) are omitted. C/Si–N–C angles (°): 121.22(10) for L$^{Dip}$H, 124.44(18) for L$^{CF3}$H, and 124.05(11) for L$^{Trip}$H.



**Scheme 2.** Synthesis of compounds **1–5**.



this compound are very similar to those for [L*GeCl], and are consistent with its proposed structure. This is also the case for the data for **1–4**, though it is noteworthy that the spectra for **4** display a number of very broad resonances, which suggests that, unlike for the free amine L$^{Trip}$H, the Ar* and Trip substituents of the compound cannot freely rotate in solution at room temperature. Variable temperature solution state NMR studies did not lead to any significant sharpening of these signals.

Although it only proved possible to obtain X-ray crystal structures of **2** and **5** (see Fig. 2), it is very likely that compounds **1**, **3**, and **4** have related monomeric structures in the solid state.[25] Moreover, the structures of **2** and **5** are very similar to that of [L*GeCl],[12] while compound **5** represents the first crystallographically characterized two-coordinate amido-germanium(II) iodide species. It is clear from Fig. 2 that the reluctance of **2** and **5** to dimerize is partly due to the Ge centers of the complexes being sandwiched by two phenyl substituents of their Ar moieties. The closest C···E interactions in these complexes involve the ipso- and one ortho-aromatic carbon atom of each flanking phenyl group (~3.17–3.40 Å for **2** and 3.08–3.10 Å for **5**), which are well outside the sum of the covalent radii for Ge and C (1.90 Å).[26] An examination of the N–Ge–halide angles of **2** (99.19(5)°) and **5** (102.02(9)°) shows them to be similar to each other, and to that for [L*GeCl] (98.85(9)°).[12] Moreover, the Si–N–Ge halide fragment of each compound is essentially planar, which could suggest some overlap of the N p-orbital lone pair with the empty p-orbital at Ge, as has been postulated for [L*GeCl]. Indeed, the Ge–N distances in **2** and **5** are at the short end of the known range of distances for Ge$^{II}$–N (mean: 1.979 Å) interactions.[27]

## Conclusions

In summary, a range of extremely bulky secondary amines have been synthesized and fully characterized. The majority of these have been utilized in the preparation of new amido-germanium(II) chloride complexes, one of which has been crystallographically characterized and shown to be monomeric in the solid state. A related monomeric amido-germanium(II) iodide compound has been prepared in good yield via the oxidative cleavage of the Ge–Ge bond of an amido-digermyne with I$_2$. The amide ligands and the amido-germanium(II) halide complexes described in this study should prove useful synthons for synthetic inorganic chemists, especially those with an interest in the chemistry of low oxidation state/low coordination number metal complexes.

## Experimental section

### General methods

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. THF, hexane, and toluene were distilled over potassium, whilst diethyl ether was distilled over a Na/K alloy (1:1). Dichloromethane was distilled over CaH$_2$. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded on Bruker Avance III 400 or Varian Inova 500 spectrometers and were referenced to the resonances of the solvent used. $^{29}$Si{$^1$H} and $^{19}$F{$^1$H} NMR spectra were recorded on a Bruker Avance III 400 spectrometer and were referenced to external SiMe$_4$ and CFCl$_3$, respectively. Mass spectra were obtained from the Engineering and Physical Sciences Research Council (EPSRC) National Mass Spectrometric Service Centre at Swansea University. FT-IR spectra were recorded using a PerkinElmer RX1 spectrometer as Nujol mulls between NaCl plates, or on solid samples protected from the atmosphere with a film of Nujol using an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Microanalyses were carried out by the Science Centre, London Metropolitan University. Reproducible microanalyses of the majority of the germylene halide complexes could not be acquired as they could either not be obtained as crystalline solids or their recrystallization consistently led to contamination with small amounts (~5%) of the free secondary amine proligands, which have similar solubilities to the germylene complexes. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. The compounds Ar*NH$_2$, [(IPr)Pd(Im)] (IPr = C{N(Dip)C(H)}$_2$ and Im = 1-methylimidazole),[23] Dip*NH$_2$,[28] and [L*GeGeL*][17] were prepared by literature procedures. All other reagents were used as received.

### Ar$^†$NH$_2$

Diphenylmethanol (10.0 g, 74 mmol), 4-isopropylaniline (27.3 g, 148 mmol), ZnCl$_2$ (5.0 g), and 8.3 mL of 34% aqueous HCl were added to a flask under dinitrogen, vented to a bubbler, and the mixture was heated at 160 °C for 3 h before being cooled to room temperature. The mixture was then extracted with dichloromethane (100 mL) and the extract washed with a saturated aqueous solution of K$_2$CO$_3$. The dichloromethane layer was separated and then evaporated to dryness. The solid residue was washed with

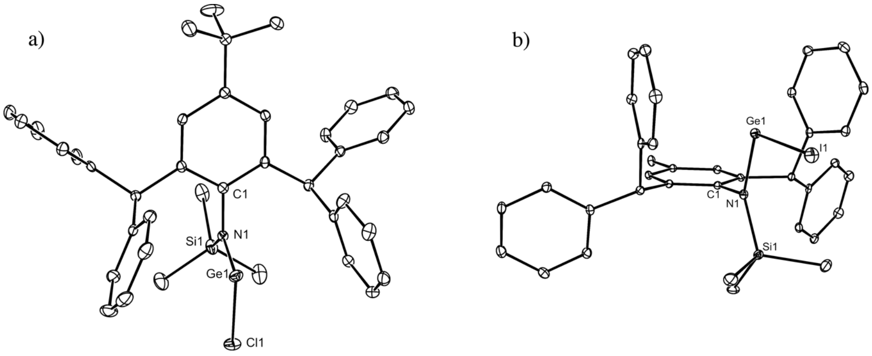


**Fig. 2.** Thermal ellipsoid plot (25% probability surface) of the molecular structures of (*a*) [$\mathrm{L}^{t\text{-Bu}}$GeCl] (**2**) and (*b*) [L*GeI] (**5**). Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°) for **2**: Ge(1)–N(1) 1.8481(15), Ge(1)–Cl(1) 2.2374(7), Si(1)–N(1) 1.7642(16), N(1)–C(1) 1.448(2), N(1)–Ge(1)–Cl(1) 99.19(5), C(1)–N(1)–Si(1) 119.15(12), C(1)–N(1)–Ge(1) 108.87(11), Si(1)–N(1)–Ge(1) 131.98(9). Selected bond lengths (Å) and angles (°) for **5**: I(1)–Ge(1) 2.6641(4), Ge(1)–N(1) 1.865(3), Si(1)–N(1) 1.753(3), N(1)–C(1) 1.453(4), N(1)–Ge(1)–I(1) 102.02(9), C(1)–N(1)–Si(1) 118.8(2), C(1)–N(1)–Ge(1) 106.2(2), Si(1)–N(1)–Ge(1) 134.95(17).

ethyl acetate (~25 mL) and then dried under vacuum to give $\mathrm{Ar^{\dagger}NH_2}$ as a colorless solid (23.5 g, 68%); mp 165–168 °C. IR (ATR, cm$^{-1}$) *ν*: 3427 (N-H str., m), 3365 (N-H str., m). $^1$H NMR (400 MHz, $\mathrm{CDCl_3}$, 298 K) δ: 0.93 (d, *J* = 6.9 Hz, 6H, $\mathrm{CH(C}H_3)_2$), 2.53 (br m, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.26 (s, 2H, $\mathrm{N}H_2$), 5.44 (s, 2H, $\mathrm{C}H\mathrm{Ph_2}$), 6.42 (s, 2H, *m*-Ar-*H*), 7.04–7.32 (m, 20H, Ar-*H*). $^{13}$C{$^1$H} NMR (101 MHz, $\mathrm{CDCl_3}$, 298 K) δ: 24.1 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 33.3 ($C\mathrm{H(CH_3)_2}$), 52.7 ($C\mathrm{HPh_2}$), 126.5, 126.6, 128.5, 129.1, 129.6, 137.9, 140.0, 143.0 (Ar-*C*). ESI-MS *m*/*z* (%): 468.2 ($\mathrm{Ar^{\dagger}NH_3^+}$, 100). Accurate (acc.) mass ESI-MS calcd. for $\mathrm{C_{35}H_{34}N}$ ($\mathrm{Ar^{\dagger}NH_3^{+}}$): 468.2691; found: 468.2684.

### $\mathrm{Ar}^{t\text{-Bu}}\mathrm{NH_2}$

A similar procedure was used as for the preparation of $\mathrm{Ar^{\dagger}NH_2}$, except 4-*tert*-butylaniline was employed (yield 31%); mp 195–200 °C. IR (Nujol, cm$^{-1}$) *ν*: 3421 (N-H str.), 3358 (N-H str., m). $^1$H NMR (400 MHz, $\mathrm{CDCl_3}$, 298 K) δ: 0.97 (s, 9H, $\mathrm{C(C}H_3)_3$), 3.33 (s, 2H, $\mathrm{N}H_2$), 5.47 (s, 2H, $\mathrm{C}H\mathrm{Ph_2}$), 6.58 (s, 2H, *m*-Ar-*H*), 7.08–7.29 (m, 20H, Ar-*H*). $^{13}$C{$^1$H} NMR (101 MHz, $\mathrm{CDCl_3}$, 298 K) δ: 31.4 ($\mathrm{C(}C\mathrm{H_3)_3}$), 34.0 ($C\mathrm{(CH_3)_3}$), 52.8 ($C\mathrm{HPh_2}$), 125.6, 126.6, 128.5, 128.6, 129.6, 139.6, 140.1, 143.0 (Ar-*C*). ESI-MS *m*/*z* (%): 482.2 ($\mathrm{Ar}^{t\text{-Bu}}\mathrm{NH_3^+}$, 100). Acc. mass ESI-MS calcd. for $\mathrm{C_{36}H_{36}N}$ ($\mathrm{Ar}^{t\text{-Bu}}\mathrm{NH_3^{+}}$): 482.2848; found: 482.2843.

### $\mathrm{L^{Dip}H}$

Li-*n*-Bu (1.5 mL of a 1.6 mol/L solution in hexane) was added to a solution of $\mathrm{Dip^*NH_2}$ (1.0 g, 2.38 mmol) in THF at −80 °C. The resultant solution was warmed to room temperature and stirred for 1 h before being cooled again to −80 °C. Neat $\mathrm{ClSiMe_3}$ (0.30 mL, 0.257 g, 2.38 mmol) was added to this solution and the reaction mixture allowed to warm to room temperature, after which time it was stirred for an additional 3 h. Volatiles were then removed in vacuo to afford a viscous oil. This was extracted with toluene (10 mL), the extract filtered, and hexane (5 mL) added to the filtrate. The resultant solution was placed at −20 °C overnight affording colorless crystals of $\mathrm{L^{Dip}H}$ (0.57 g, 48%); mp 120–124 °C. IR (Nujol, cm$^{-1}$) *ν*: 3376 (N-H str., m). $^1$H NMR (400 MHz, $\mathrm{C_6D_6}$, 298 K) δ: 0.10 (s, 9H, $\mathrm{Si(C}H_3)_3$), 1.08 (d, *J* = 6.9 Hz, 12H, $\mathrm{CH(C}H_3)_2$), 2.05 (s, 1H, N*H*), 3.39 (sept, *J* = 6.9 Hz, 2H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 6.96–7.45 (m, 17H, Ar-*H*). $^{13}$C{$^1$H} NMR (151 MHz, $\mathrm{C_6D_6}$, 298 K) δ: 0.8 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 23.8 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 28.5 ($C\mathrm{H(CH_3)_2}$), 65.6 ($C\mathrm{Ph_3}$), 126.1, 126.9, 127.7, 131.7, 137.7, 141.7, 143.0, 148.0 (Ar-*C*). $^{29}$Si{$^1$H} NMR (80 MHz, $\mathrm{C_6D_6}$, 298 K) δ: 3.33 (s). ESI-MS *m*/*z* (%): 491.3 (M$^+$, 2), 420.2 ($\mathrm{Dip^*NH_2^+}$, 100).

### $\mathrm{L^{\dagger}H}$

Li-*n*-Bu (6.7 mL of a 1.6 mol/L solution in hexane) was added to a solution of $\mathrm{Ar^{\dagger}NH_2}$ (5.0 g, 10.7 mmol) in THF (40 mL) at −80 °C. The resultant solution was warmed to room temperature and stirred for 1 h before being cooled again to −80 °C. Neat $\mathrm{SiMe_3Cl}$ (1.42 mL, 1.22 g, 11.1 mmol) was added to this solution and the reaction mixture allowed to warm to room temperature, after which time it was stirred for 4 h. Volatiles were then removed in vacuo to afford a gummy solid. The residue was extracted with dichloromethane (60 mL), the extract filtered, and then evaporated to dryness. The solid residue was washed with hexane (~15 mL) and then dried under vacuum to give $\mathrm{L^{\dagger}H}$ as a colorless solid (3.29 g, 57%); mp 118–120 °C. IR (Nujol, cm$^{-1}$) *ν*: 3357 (N-H str., m). $^1$H NMR (400 MHz, $\mathrm{CDCl_3}$, 298 K) δ: 0.14 (s, 9H, $\mathrm{SiC(C}H_3)_3$), 0.98 (d, *J* = 6.9 Hz, 6H, $\mathrm{CH(C}H_3)_2$), 1.65 (s, 1H, N*H*), 2.61 (sept, *J* = 6.9 Hz, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 5.94 (s, 2H, $\mathrm{C}H\mathrm{Ph_2}$), 6.56 (s, 2H, *m*-Ar-*H*), 6.98–7.26 (m, 20H, Ar-*H*). $^{13}$C{$^1$H} NMR (101 MHz, $\mathrm{C_6D_6}$, 298 K) δ: 1.4 ($\mathrm{Si(}C\mathrm{H_3)_3}$), 24.1 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 33.3 ($C\mathrm{H(CH_3)_2}$), 52.7 ($C\mathrm{HPh_2}$), 126.1, 126.5, 126.6, 128.2, 128.5, 129.1, 129.6, 137.9, 140.0, 141.0, 143.0, 144.4 (Ar-*C*). $^{29}$Si{$^1$H} NMR (80 MHz, $\mathrm{C_6D_6}$, 298 K) δ: 18.0 (s). ESI-MS *m*/*z* (%): 541.3 (MH$^+$, 2), 468.2 ($\mathrm{Ar^{\dagger}NH_3^+}$, 100).

### $\mathrm{L}^{t\text{-Bu}}\mathrm{H}$

Li-*n*-Bu (3.5 mL of a 1.6 mol/L solution in hexane) was added to a solution of $\mathrm{Ar}^{t\text{-Bu}}\mathrm{NH_2}$ (2.50 g, 5.19 mmol) in THF (40 mL) at −80 °C. The resultant solution was warmed to room temperature and stirred for 1 h before being cooled again to −80 °C. Neat $\mathrm{SiMe_3Cl}$ (0.75 mL, 0.642 g, 5.87 mmol) was added to this solution and the reaction mixture allowed to warm to room temperature, after which time it was stirred for 4 h. Volatiles were then removed in vacuo to afford a solid residue. This was extracted with dichloromethane (50 mL), the extract filtered, and evaporated to dryness. The residue was washed with hexane (~10 mL) and the remaining solid dried under vacuum to give $\mathrm{L}^{t\text{-Bu}}\mathrm{H}$ as a colorless solid (1.97 g, 71%); mp 165–170 °C. IR (Nujol, cm$^{-1}$) *ν*: 3360 (N-H str., m). $^1$H NMR (400 MHz, $\mathrm{C_6D_6}$, 298 K) δ: 0.12 (s, 9H, $\mathrm{SiC(C}H_3)_3$), 1.06 (s, 9H, $\mathrm{C(C}H_3)_3$), 1.83 (s, 1H, N*H*), 6.19 (s, 2H, $\mathrm{C}H\mathrm{Ph_2}$), 7.02–7.23 (m, 22H, Ar-*H*). $^{13}$C{$^1$H} NMR (101 MHz, $\mathrm{C_6D_6}$, 298 K) δ: 1.3 ($\mathrm{Si(CH_3)_3}$), 31.3 ($\mathrm{C(}C\mathrm{H_3)_3}$), 34.4 ($C\mathrm{(CH_3)_3}$), 53.2 ($C\mathrm{HPh_2}$), 126.3, 126.5, 128.6, 130.0, 140.4, 141.1, 144.9, 145.7 (Ar-*C*). $^{29}$Si{$^1$H} NMR (80 MHz, $\mathrm{CDCl_3}$, 298 K) δ: 3.53. ESI-MS *m*/*z* (%): 554.5 (MH$^+$, 17), 482.2 ($\mathrm{Ar}^{t\text{-Bu}}\mathrm{NH_3^+}$, 100).

### $\mathrm{L^{Me}H}$

A suspension of $\mathrm{Ar^*NH_2}$ (5.0 g, 11.4 mmol), KO-*t*-Bu (1.78 g, 15.9 mmol), [(IPr)Pd(Im)] catalyst (184 mg, 2.5 mol%), and 3,5-dimethylbromobenzene (1.11 mL, 8.20 mmol) in toluene (60 mL) was heated at reflux for 2 h. The reaction mixture was allowed to cool to room temperature, whereupon further portions of [(IPr)Pd(Im)] catalyst (184 mg, 2.5 mol%) and 3,5-dimethyl bromobenzene (0.74 mL, 5.47 mmol) were added, and the reaction mixture heated again under reflux. The mixture was then cooled to room temperature and all volatiles were removed in vacuo. The residue was extracted with dichloromethane (3 × 25 mL), the combined

**Table 1.** Summary of crystallographic data for $L^{Dip}H$, $L^{CF3}H$, $L^{Trip}H$, **2**, and **5**.

| | $L^{Dip}H$ | $L^{CF3}H$ | $L^{Trip}H$ | **2** | **5** |
|---|---|---|---|---|---|
| Empirical formula | $C_{34}H_{41}NSi$ | $C_{41}H_{31}F_6N$ | $C_{48}H_{51}N$ | $C_{39}H_{42}ClGeNSi$ | $C_{36}H_{36}GeINSi$ |
| Formula weight | 491.77 | 651.67 | 641.90 | 660.87 | 710.24 |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Monoclinic | Orthorhombic |
| Space group | $P2_1/c$ | $P$-1 | $P2_1/n$ | $P2_1/n$ | $Pmn2_1$ |
| $a$ (Å) | 9.6943(2) | 13.5647(6) | 12.608(3) | 10.6827(3) | 17.4012(6) |
| $b$ (Å) | 14.2774(3) | 15.8217(7) | 16.096(3) | 16.8010(5) | 9.2802(2) |
| $c$ (Å) | 20.9242(6) | 16.2151(8) | 18.938(4) | 20.0684(6) | 9.9933(3) |
| $\alpha$ (°) | 90 | 88.585(2) | 90 | 90 | 90 |
| $\beta$ (°) | 93.024(2) | 69.334(2) | 98.95(3) | 103.594(3) | 90 |
| $\gamma$ (°) | 90 | 89.568(2) | 90 | 90 | 90 |
| Volume (Å$^3$) | 2892.07(12) | 3255.1(3) | 3796.4(13) | 3500.97(18) | 1613.78(8) |
| $Z$ | 4 | 4 | 4 | 4 | 2 |
| $\rho$ (calcd.) (g cm$^{-3}$) | 1.129 | 1.330 | 1.123 | 1.254 | 1.462 |
| $\mu$ (mm$^{-1}$) | 0.103 | 0.101 | 0.064 | 1.013 | 1.968 |
| $F$ (000) | 1064 | 1352 | 1384 | 1384 | 716 |
| Reflections collected | 18863 | 28039 | 48942 | 22660 | 11153 |
| Unique reflections | 5664 | 11222 | 6664 | 6886 | 3612 |
| $R_{int}$ | 0.0300 | 0.0259 | 0.1114 | 0.0271 | 0.0302 |
| $R_1$ indices ($I > 2\sigma(I)$) | 0.0423 | 0.0491 | 0.0556 | 0.0325 | 0.0249 |
| $wR_2$ indices (all data) | 0.1048 | 0.1279 | 0.1493 | 0.0817 | 0.0512 |
| CCDC No. | 957840 | 957839 | 957845 | 957844 | 957843 |

extracts filtered, and volatiles removed in vacuo to afford an off-white solid. This residue was washed with hexane (10 mL) to give $L^{Me}H$ as an off-white powder (4.33 g, 70%); mp 113–116 °C. IR (ATR, cm$^{-1}$) $\nu$: 3288 (N-H str., m). $^1H$ NMR ($C_6D_6$, 400 MHz, 298 K) δ: 1.54 (s, 6H, Ar$^{Me}$-*m*-C*H*$_3$), 1.87 (s, 3H, Ar*-*p*-C*H*$_3$), 4.46 (s, 1H, N*H*), 5.93 (s, 2H, Ar$^{Me}$-*o*-C*H*), 6.07 (s, 2H, C*H*Ph$_2$), 6.41 (s, 1H, Ar$^{Me}$-*p*-C*H*), 6.99–7.09 (m, 22H, Ar-*H*). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.5 MHz, 298 K) δ: 21.5 (Ar$^{Me}$-*m*-*C*H$_3$), 30.1 (Ar*-*p*-*C*H$_3$), 52.3 (*C*HPh$_2$), 111.2, 120.6, 126.6, 128.6, 129.8, 130.4, 136.1, 136.6, 139.0, 144.3, 144.6, 147.6 (Ar-*C*). EI-MS *m*/*z* (%): 544.1 (MH$^+$, 95). Acc. mass ESI-MS calcd. for $C_{41}H_{37}N$ (M$^+$): 543.2926; found: 543.2895.

### $L^{CF3}H$

This compound was prepared similarly to $L^{Me}H$, except Ar*NH$_2$ (5.0 g, 11.4 mmol), KO-*t*-Bu (1.78 mg, 15.9 mmol), [(IPr)Pd(Im)] catalyst (184 mg, 2.5 mol%), and 3,5-bis(trifluoromethyl)bromobenzene (1.41 mL, 8.20 mmol) were used in the initial stage of the reaction. [(IPr)Pd(Im)] (184 mg, 2.5 mol%) and 3,5-bis(trifluoromethyl) bromobenzene (0.94 mL, 5.47 mmol) were used in the latter stage of the reaction. $L^{CF3}H$ was obtained by extraction of the crude reaction mixture into hexane, followed by slow evaporation to afford colorless crystals (2.38 g, 32%); mp 102–108 °C. IR (ATR, cm$^{-1}$) $\nu$: 3387 (N-H str., m). $^1H$ NMR ($C_6D_6$, 400 MHz, 298 K) δ: 1.78 (s, 3H, *p*-C*H*$_3$), 4.53 (s, 1H, N*H*), 5.54 (s, 2H, C*H*Ph$_2$), 6.41–7.16 (m, 25H, Ar-*H*). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.5 MHz, 298 K) δ: 21.4 (*p*-*C*H$_3$), 52.5 (*C*HPh$_2$), 112.0 (*C*F$_3$), 126.8, 127.9, 128.7, 129.6, 130.6, 132.4, 132.8, 133.3, 138.2, 143.2, 144.8, 148.4. $^{19}F\{^1H\}$ NMR ($C_6D_6$, 282 MHz, 298 K) δ: −62.74 (s). EI-MS *m*/*z* (%): 652.1 (MH$^+$, 27). Acc. mass ESI-MS calcd. for $C_{41}H_{30}F_6N$ (M$^+$-H): 650.2282; found: 650.2278.

### $L^{Trip}H$

This compound was prepared similarly to $L^{Me}H$, except Ar*NH$_2$ (5.0 g, 11.4 mmol), KO-*t*-Bu (1.78 mg, 15.9 mmol), [(IPr)Pd(Im)] catalyst (184 mg, 2.5 mol%), and 2,4,6-triisopropylbromobenzene (2.08 mL, 8.20 mmol) were used in the initial stage of the reaction. [(IPr)Pd(Im)] (184 mg, 2.5 mol%) and 2,4,6-triisopropylbromobenzene (1.39 mL, 5.47 mmol) were used in the latter stage of the reaction. $L^{Trip}H$ was obtained by extraction of the crude reaction mixture into dichloromethane, filtration, and removal of all volatiles from the filtrate in vacuo. The residue was recrystallized from diethyl ether to afford $L^{Trip}H$ as colorless crystals (1.78 g, 24%); mp 178–182 °C. $^1H$ NMR ($C_6D_6$, 400 MHz, 298 K) δ: 0.96 (d, *J* = 6.9 Hz, 12H, *o*-CH(C*H*$_3$)$_2$), 1.29 (d, *J* = 6.9 Hz, 6H, *p*-CH(C*H*$_3$)$_2$), 1.87 (s, 3H, *p*-C*H*$_3$), 2.85 (sept, *J* = 6.9 Hz, 1H, *p*-C*H*(CH$_3$)$_2$), 2.87 (sept, *J* = 6.9 Hz, 2H, *o*-C*H*(CH$_3$)$_2$), 4.66 (s, 1H, N*H*), 5.93 (s, 2H, C*H*Ph$_2$), 6.94 (s, 2H, Ar*-*m*-C*H*), 6.98–7.10 (m, 22H, Ar-*H*). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75.5 MHz, 298 K) δ: 21.7 (*p*-CH(*C*H$_3$)$_2$), 24.3 (*o*-CH(*C*H$_3$)$_2$), 25.2 (*o*-*C*H(CH$_3$)$_2$), 29.0 (*p*-*C*H(CH$_3$)$_2$), 35.2 (Ar*-*p*-*C*H$_3$), 53.0 (s, 2H, *C*HPh$_2$), 122.3, 127.1, 129.2, 130.5, 131.4, 132.0, 137.7, 139.0, 140.9, 141.7, 144.1, 145.1 (Ar-*C*). IR (ATR, cm$^{-1}$) $\nu$: 3411 (N-H str., w). EI-MS *m*/*z* (%): 642.4 (MH$^+$, 4), 440.2 (Ar*NH$^+$, 28). Acc. mass calcd. for $C_{48}H_{52}N$ (MH$^+$): 642.4099; found: 642.4095.

### [$L^{\dagger}$GeCl] (1)

Li-*n*-Bu (2.4 mL of a 1.6 mol/L solution in hexane) was added to a solution of $L^{\dagger}H$ (2.0 g, 3.9 mmol) in THF (25 mL) at −80 °C. The resultant red solution was warmed to room temperature and stirred for 1 h. This solution was added to a solution of GeCl$_2$·dioxane (0.95 g, 4.1 mmol) in THF (10 mL) at −80 °C. The mixture was then warmed to room temperature and stirred overnight. Volatiles were then removed in vacuo, the residue extracted with toluene (50 mL), the extract filtered, and volatiles removed from the filtrate in vacuo. The residue was washed with hexane (~10 mL) and the remaining solid dried under vacuum yielding **1** as a colorless solid (1.92 g, 81%); mp 208–212 °C (decomp.). IR (ATR, cm$^{-1}$) $\nu$: 1600 (m), 1378 (s), 1252 (s), 1204 (m), 1076 (m), 891 (m), 699 (s). $^1H$ NMR (400 MHz, $C_6D_6$, 298 K) δ: 0.72 (s, 9H, Si(C*H*$_3$)$_3$), 0.94 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 2.47 (sept, *J* = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 5.92 (s, 2H, C*H*Ph$_2$), 6.79–7.26 (m, 22H, Ar-*H*). $^{13}C\{^1H\}$ NMR (101 MHz, $C_6D_6$, 298 K) δ: 4.4 (Si(*C*H$_3$)$_3$), 24.0 (CH(*C*H$_3$)$_2$), 33.8 (*C*H(CH$_3$)$_2$), 53.8 (*C*HPh$_2$), 126.8, 126.9, 127.9, 128.8, 129.9, 130.0, 131.1, 142.2, 143.3, 143.4, 144.7, 145.2 (Ar-*C*). $^{29}Si\{^1H\}$ NMR (80 MHz, $C_6D_6$, 298 K) δ: 6.04 (s). EI-MS *m*/*z* (%): 647.2 (M$^+$, 3, correct isotopic distribution), 539.3 ($L^{\dagger+}$, 40), 467.2 (Ar$^{\dagger}$NH$_3^+$, 100).

### [$L^{t\text{-}Bu}$GeCl] (2)

Li-*n*-Bu (1.3 mL of a 1.6 mol/L solution in hexane) was added to a solution of $L^{t\text{-}Bu}H$ (1.0 g, 1.81 mmol) in THF (25 mL) at −80 °C. The resultant solution was warmed to room temperature and stirred for 1 h. This was added to a solution of GeCl$_2$·dioxane (0.46 g, 1.99 mmol) in THF (10 mL) at −80 °C. The reaction mixture was then warmed to room temperature, after which it was stirred overnight. Volatiles were subsequently removed in vacuo and the residue extracted with toluene (50 mL). The extract was filtered, the filtrate evaporated to dryness, and the residue washed with hexane (~10 mL). This left **2** as an off-white solid (0.60 g, 50%).

X-ray quality crystals of the compound were grown from a toluene/hexane solution; mp 230–234 °C (decomp.). IR (ATR, cm$^{-1}$) $\nu$: 1600 (s), 1076 (s), 1030 (s), 891 (s), 765 (w). $^{1}$H NMR (400 MHz, $C_6D_6$, 298 K) δ: 0.72 (s, 9H, SiC(C$H_3$)$_3$), 1.06 (s, 9H, C(C$H_3$)$_3$), 5.93 (s, 2H, C*H*Ph$_2$), 6.79–7.27 (m, 22H, Ar-*H*). $^{13}$C{$^{1}$H} NMR (101 MHz, $C_6D_6$, 298 K) δ: 4.4 (Si($C$H$_3$)$_3$), 31.2 (C($C$H$_3$)$_3$), 34.6 ($C$(CH$_3$)$_3$), 53.9 ($C$HPh$_2$), 126.0, 126.8, 128.7, 128.2, 129.8, 130.0, 131.1, 141.9, 143.4, 143.5, 147.4, 144.3 (Ar-*C*). $^{29}$Si{$^{1}$H} NMR (80 MHz, $C_6D_6$, 298 K) δ: 6.0. EI-MS *m*/*z* (%): 661.2 (M$^+$, 13, correct isotopic distribution), 552.3 (L$^{t\text{-Bu}+}$, 100). Anal. calcd. for $C_{39}H_{42}ClGeNSi$ (%): C, 70.87; H, 6.41; N, 2.12; found: C, 70.94; H, 6.38; 2.17.

### [L$^{\mathrm{CF3}}$GeCl] (3)

Li-*n*-Bu (0.53 mL, 1.6 mol/L in hexane) was added to a solution of L$^{\mathrm{CF3}}$H (0.50 g, 0.77 mmol) in THF (30 mL) at −80 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. The resultant solution was then added to a solution of $GeCl_2$·dioxane (0.20 g, 0.85 mmol) in THF (5 mL) at −80 °C. The resultant solution was warmed to room temperature over 16 h, whereupon volatiles were removed in vacuo. The residue was extracted with warm toluene (20 mL), the extract filtered, and volatiles removed in vacuo to give a yellow-brown oil. The residue was washed with hexane (5 mL) and dried in vacuo to give **3** as a pale brown powder (321 mg, 55%); mp 142–145 °C. IR (ATR, cm$^{-1}$) $\nu$: 3062 (w), 3026 (w), 1610 (m), 1032 (m), 995 (m), 956 (s), 864 (m), 748 (m). $^{1}$H NMR ($C_6D_6$, 400 MHz, 298 K) δ: 1.78 (s, 3H, *p*-C$H_3$), 5.48 (s, 2H, C*H*Ph$_2$), 6.41–7.68 (m, 25H, Ar-*H*). $^{13}$C{$^{1}$H} NMR ($C_6D_6$, 75.5 MHz, 298 K) δ: 25.2 (*p*-$C$H$_3$), 52.7 ($C$HPh$_2$), 69.0 (*m*-$C$F$_3$), 114.2, 117.7, 129.8, 130.4, 132.3, 132.7, 137.9, 138.0, 142.1, 143.8, 144.4, 150.6 (Ar-*C*). $^{19}$F{$^{1}$H} NMR ($C_6D_6$, 282 MHz, 298 K) δ: −62.8. EI-MS *m*/*z* (%): 759.0 (M$^+$, <1, correct isotopic distribution), 651.1 (L$^{\mathrm{CF3}+}$, 100).

### [L$^{\mathrm{Trip}}$GeCl] (4)

Li-*n*-Bu (1.07 mL, 1.6 mol/L in hexane) was added to a solution of L$^{\mathrm{Trip}}$H (1.00 g, 1.56 mmol) in THF (30 mL) at −80 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. The resultant solution was then added to a solution of $GeCl_2$·dioxane (0.397 g, 1.72 mmol) in THF (5 mL) at −80 °C. The resultant solution was warmed to room temperature over 16 h, whereupon volatiles were removed in vacuo. The residue was extracted with warm toluene (20 mL), the extract filtered, and volatiles removed in vacuo to give a yellow-brown oil. The residue was washed with hexane (5 mL) and dried in vacuo to give **4** as a bright yellow powder (970 mg, 82%); mp 96–108 °C (melt), mp 242–248 °C (decomp.). IR (ATR, cm$^{-1}$) $\nu$: 1598 (w), 1164 (w), 1032 (w), 881 (w), 744 (m). $^{1}$H NMR ($C_6D_6$, 400 MHz, 298 K) δ: 0.51–1.35 (v br, 12H, *o*-CH(C$H_3$)$_2$), 1.23 (d, *J* = 6.9 Hz, 6H, *p*-CH(C$H_3$)$_2$), 1.83 (s, 3H, *p*-C$H_3$), 2.76 (sept, *J* = 6.9 Hz, 1H, *p*-C*H*(CH$_3$)$_2$), 3.82 (v br, 2H, *o*-C*H*(CH$_3$)$_2$), 5.89 (br, 2H, C*H*Ph$_2$), 6.60–7.50 (br m, 24H, Ar-*H*). $^{13}$C{$^{1}$H} NMR ($C_6D_6$, 75.5 MHz, 298 K) δ: the broadness of the majority of the signals in this spectrum made them difficult to confidently assign. EI-MS *m*/*z* (%): 749.3 (M$^+$, 5, correct isotopic distribution), 641.4 (L$^{\mathrm{Trip}+}$, 100).

### [L*GeI] (5)

To a solution of [L*GeGeL*] (0.10 g, 0.09 mmol) in toluene (15 mL) at −80 °C was added solid iodine (0.02 g, 0.086 mmol). The resultant solution was warmed to room temperature and stirred overnight. Volatiles were then removed in vacuo and the residue was dissolved in toluene (5 mL). Hexane (15 mL) was subsequently layered onto the solution, from which grew colorless crystals of **5** (0.04 g, 34%); mp 230–234 °C (decomp.). $^{1}$H NMR (400 MHz, $C_6D_6$, 298 K) δ: 0.82 (s, 9H, Si(C$H_3$)$_3$), 1.87 (s, 3H, ArC$H_3$), 5.89 (s, 2H, C*H*Ph$_2$), 6.81–7.33 (m, 22H, Ar-*H*). $^{13}$C{$^{1}$H} NMR (126 MHz, $C_6D_6$) δ: 5.3 (Si($C$H$_3$)$_3$), 21.2 (Ar$C$H$_3$), 53.6 ($C$HPh$_2$), 126.9, 127.1, 128.8, 129.7, 129.8, 130.0, 130.24, 130.7, 134.9, 142.6, 142.9, 143.0 (Ar-*C*). $^{29}$Si{$^{1}$H} NMR (80 MHz, $CD_2Cl_2$) δ: 0.07. IR (ATR, cm$^{-1}$) $\nu$: 1092 (w), 1020 (w) 866 (w), 700 (s). EI-MS *m*/*z* (%): 710.0 (M$^+$, 1, correct isotopic distribution), 584.1 (L*Ge$^+$, 100), 511.2 (L*$^+$, 41).

### X-ray crystallography

Crystals of L$^{\mathrm{Dip}}$H, L$^{\mathrm{CF3}}$H, L$^{\mathrm{Trip}}$H, **2**, **5**, [L$^{\mathrm{Dip}}$Li(THF)(OEt$_2$)][L$^{\mathrm{Dip}}$Li(THF)$_3$], [L*Ge-GeL*], and [L$^{\dagger}$SiBr$_3$] suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using either Oxford Gemini Ultra or Bruker Apex X8 diffractometers using a graphite monochromator with MoKα radiation (λ = 0.71073 Å) or the MX1 beamline of the Australian Synchrotron (λ = 0.71080 Å, L$^{\mathrm{Trip}}$H) at 123 K. The software package Blu-Ice[29] was used for synchrotron data acquisition, while the program XDS[30] was employed for synchrotron data reduction. The structures were solved by direct methods and refined on $F^2$ by full-matrix least-squares (SHELX97)[31] using all unique data. All nonhydrogen atoms are anisotropic with hydrogen atoms included in calculated positions (riding model). Two crystallographically independent molecules were refined in the asymmetric unit of the crystal structure of L$^{\mathrm{CF3}}$H. There are no significant geometric differences between them. The absolute structure parameter for the crystal structure of **5** was refined at −0.003(10). Crystal data, details of data collections, and refinement are given in Table 1 and Table S1 of the Supplementary data.

## Supplementary data

Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2013-0394. CCDC 957838-957845 contain the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/csd/ request (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1E2, UK; fax: +44 1223 33603; e-mail: deposit@ccdc.cam.ac.uk).

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(24) During the course of this study, a polymorphic X-ray crystal structure of the previously structurally characterized compound [L*GeGeL*] (see ref. 17) was obtained. Full details of this crystal structure can be found in the Supplementary Material.

(25) During the course of this study, a related compound, [L†SiBr$_3$], incorporating the L† ligand was synthesized and structurally authenticated. Synthetic and crystallographic details for the compound can be found in the Supplementary Material.

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