Cooperative N–H bond activation by amido-Ge(II) cations†

Xueer Zhou,a Petra Vasko,a,b Jamie Hicks,a M. Ángeles Fuentes,a Andreas Heilmann,a Eugene L. Kolychev,a,b and Simon Aldridgeb,∗a

N-heterocyclic carbene (NHC) and tertiary phosphine-stabilized germylium-ylidene cations, [R(L)Ge+]†, featuring tethered amido substituents at R have been synthesized via halide abstraction. Characterization in the solid state by X-ray crystallography shows these systems to be monomeric, featuring a two-coordinate C,N- or P,N-ligated germanium atom. The presence of the strongly Lewis acidic cationic germanium centre and proximal amide function allows for facile cleavage of N–H bonds in 1,2-fashion: the products resulting from reactions with carbazole feature a tethered secondary amine donor bound to a three-coordinate carbazolyl-GeII centre. In each case, addition of the components of the N–H bond occurs to the same face of the germanium amide function, consistent with a coordination/proton migration mechanism. Such as sequence is compatible with the idea that substrate coordination via the π orbital at germanium reduces the extent of N-to-Ge π donation from the amide, thereby enhancing the basicity of the proximal N-group.

Introduction

The metal-mediated activation of N–H bonds (particularly those in ammonia) is a challenging fundamental chemical step with potential significance to a number of important transformations of industrial relevance.1 The scarcity of transition metal systems capable of effecting N–H cleavage via oxidative addition, in a manner familiar for a plethora of other E–H bonds, reflects the competing tendency of ammonia to form classical Werner complexes at unsaturated metal centres.2

Within p-block chemistry, a number of systems have been reported in the last 15 years which will cleave ammonia to give a derivative containing the E(H)[NH3] function,3,4 including several carbene and related heavier group 14 species in the +2 oxidation state.3 The presence of a low-lying formally vacant π orbital in such systems allows for simple coordination of amines (akin to d-block metal complexes); facile N-to-E proton transfer, however, has been proposed to offer a route to generate an amido hydride species without the need for amine dissociation.3e,h,s, Moreover, in addition to single site N–H oxidative addition, heavier group 14 analogues of carbenes have also been shown to offer a number of alternative (cooperative) pathways for N–H cleavage involving H-atom transfer to a ligand site (Scheme 1). The relative propensity for different modes of activation has been shown to reflect the identity of the group 14 element/supporting ligand set (and the associated E/I redox potential). In the case of germylene systems, for example, both single site (1,1 addition) and ligand-assisted 1,4 activation modes have been reported, depending not only the basicity of ligand backbone sites, but

Scheme 1 Different modes of N–H activation previously reported for germylene and related systems [Ar = 2,6-C6H3Mes2; Mes = 2,4,6-Me3C6H2; Dipp = 2,6-(i-Pr)2C6H3].

† Electronic supplementary information (ESI) available: Additional synthetic and characterizing data, representative NMR spectra of new compounds, xyz file for DFT optimized structure; CIFs available from the CCDC, references 1952095–1952095, 1952095 and 2005217–2005219. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0dt01960g.
also the ability of the donor set to promote formation of the GeIV oxidation state.\(^\text{3b-f}\)

While charge-neutral tetracenes of the type EX\(_2\) have been investigated in some depth,\(^\text{1}\) isoelectronic cations of the type \([\text{R}[\text{L}]\text{E}]^+\) have been less extensively studied,\(^\text{7-12}\) despite the fact that the net positive charge should promote initial coordination of ammonia/amines, enhance the acidity of the NH bond and thereby promote N-to-E proton migration. We have recently examined the chemistry of N-nacnac supported tetrylium-ylidene cations towards N–H containing substrates, with the isolation of products derived from oxidative addition or simple amide adduct formation being found to be dependent on the group 14 element (Scheme 2).\(^\text{13}\)

Given the lack of productivity in N–H activation exhibited by germium-ylidene systems stabilized by these \(\beta\)-diketiminate (amido/imin) systems we were interested in (i) exploring the possibilities for the synthesis of two-coordinate amidogermanium-ylidene species stabilized by alternative (strong) donor sets (e.g. carbenes\(^\text{14}\) and phosphines) which might promote the formation of Ge\(^\text{IV}\) products; and (ii) exploring the mode(s) of reactivity of such systems towards N–H bonds. These studies are reported in this manuscript.

Results and discussion

Germium-ylidene synthesis

We initially targeted halo-germylene precursors featuring amido/NHC ligand \([L^1]^-\) or amido/phosphine ligand \([L^2]^-\) (Scheme 3). NHC-ligated bromo-germylene precursor 1 can be synthesized via one of two routes: (i) the reaction between protio-ligand \([L^1][\text{H}]_2\text{Br}\) and one equivalent of the germanium (ii) bis amide \(\text{Ge}[\text{N}([\text{SiMe}_3]_2))_2\)\(^\text{14,15}\) or (ii) in situ double deprotonation of \([L^2][\text{H}]_2\text{Br}\) (e.g. with \(^{\text{Bu}}\text{Li}\)) followed by metathesis with GeCl\(_2\)-dioxane. In our hands, route (i) is preferable, leading to yields of ca. 90%. By contrast, chloro-germylene complex 2 is most readily synthesized by deprotonation of \((L^2)^-\) H, followed by reaction of the lithiated ligand with GeCl\(_2\)-dioxane. The overall yield for the two steps combined is typically in the region of 50%. Both 1 and 2 have been characterized by standard spectroscopic and analytical methods, and by X-ray crystallography (Fig. 1). The structures of both compounds in the solid state are in line with related complexes, featuring angles at the germanium centre which are close to 90\(^\circ\) (e.g. 90.0(1)–98.9(1)\(^\circ\) for 1) consistent with the expected (low) degree of ns/np mixing for \(n = 4\).\(^\text{16}\)

From these precursors, two-coordinate NHC- or phosphine-stabilized Ge\(^\text{II}\) cations (germylium-ylidenes) can be synthesised by halide abstraction, most conveniently using Li[Al(OC\(_2\text{CF}_3)\text{Me})_3]\(_4\) as a weakly coordinating anion (WCA) source (Scheme 4).\(^\text{17}\) Treatment of 1 or 2 with Li[Al(OC\(_2\text{CF}_3)\text{Me})_3]\(_4\) in bromobenzene at room temperature leads to the formation of the respective cationic species 3 and 4 in reasonable yields (30–40\%).\(^\text{18}\) In both cases, the \(^1\text{H}\) and \(^13\text{C}\) NMR spectra reveal distinct changes from the respective bromogermylene precursor: for 3 the \(^{\text{Bu}}\text{N}\) signal is shifted from \(\delta^\text{H} = 1.42\) to 0.98 ppm, and the carbene \(^13\text{C}\) resonance is shifted upfield from \(\delta^\text{C} = 169.5\) to 165.6 ppm. In the case of phosphine-ligated system 4, the \(^3\text{P}\) resonance is shifted from \(\delta^\text{P} = -24.4\) (for 2) to \(-2.2\) ppm.

Both 3 and 4 could be obtained as single crystals suitable for X-ray diffraction, to allow for unambiguous confirmation of the monomeric two-coordinate structures in the solid state (Fig. 2). Cation formation is reflected in marked shortening of the Ge–N bonds compared to precursors 1 and 2, presumably due to enhanced possibilities for N-to-Ge \(\pi\) bonding in the two-coordinate systems (e.g. \(d(\text{Ge–N}) = 1.889(1), 1.811(3)\) Å for 2 and 4, respectively). Consistently, in both cases, the geometry
The e respectively) reflecting the constraints of the six-membered
lengths for – appear not to be statistically significant: the Ge

around the amido nitrogen is significantly more planar than in the halo-germylene precursor (e.g. 359.7° for 3 vs. 350.0° for 1). The distances from germanium to the neutral NHC or phosphine donor, on the other hand, are much less affected by halide abstraction (e.g. d(Ge–P) = 2.446(1), 2.449(1) Å for 2 and 4, respectively). In each cation, the angle subtended at germanium is relatively narrow (91.9(2) and 88.5(1)° for 3 and 4, respectively) reflecting the constraints of the six-membered chelate ring. The effect of the differing strengths of the neutral donor (i.e. NHC vs. phosphine) on the Ge–N moieties appear not to be statistically significant: the Ge–N bond lengths for 3 and 4 are 1.829(4) and 1.811(3) Å, respectively.

These studies also reveal that the product obtained is strongly dependent on the conditions employed. In the case of 3, clean product formation requires the use of a haloarene solvent (fluoro- or bromobenzene), while the use of benzene leads to the formation of different products arising from incomplete halide abstraction.14 If the reaction is carried out in benzene using 0.5 equiv. of Li[Al(O(CF3)3)4] the bromide-bridged digermylen system \([[(L^1)Ge]_2(μ-Br)]\)Al[OC(CF3)3]4 \(5\) is obtained, via trapping of the \([L^1Ge]^+\) cation by unreacted 1 (Scheme 5 and Fig. 3).

**Reactivity studies – activation of N–H bonds**

Mechanistically, the pathways for activation of E•H bonds by tetrelene and related systems are known to be dependent on the nature of E. For H2, mechanisms have been advanced for carbene and silylene systems which involve simultaneous interaction of the substrate with the C/Si centred lone pair and the orthogonal, formally vacant, p orbital.2 The orientation of the H2 molecule in the transition state then reflects the relative importance of the donor and acceptor capabilities of the tetrelene. Such mechanistic proposals emphasize the importance of the n-to-p energy gap (which is often equivalent to the HOMO–LUMO gap) in facilitating the activation of H2.20

On the other hand, protic substrates, such as ammonia, have been shown to be activated by an alternative coordination/proton migration pathway.2 The sequence involves initial coordination of the NH3 molecule, with the tetrelene acting as an electrophile. Subsequent N-to-E proton migration (facilitated, for example, by a second molecule of NH3) then completes the formal N–H oxidative addition process.2 In this case it is the energy of the vacant p orbital of the tetrelene, and its consequent ability to coordinate and activate the NH3 substrate that is thought to be important in bond cleavage.
In the cases of cationic systems 3 and 4, the presence of strongly \( \pi \)-donor amido \( \alpha \)-substituents would be expected to lead to significant elevation of the Ge-centred \( \pi \) orbital, and this, taken together with the relative narrow angle at germanium in each case (and the associated high degree of 4s character in the lone pair) would be expected to lead to a wide \( \pi \)-to-\( \pi \) energy separation.\(^{2,22}\) Consistently, DFT calculations (PBE1PBE, Def2-TZVP level of theory), exemplified for 3 (Fig. 4) reveal that this separation is >400 kJ mol\(^{-1}\). The LUMO features significant Ge \( \pi \) character, with some delocalization onto the carbene carbon, and the expected anti-bonding phase relationship with the N \( \pi \) orbital (Fig. 4). The germanium-centred lone pair is relatively low in energy, being associated with the HOMO-3.

Unsurprisingly then, we find that neither 3 and 4 shows any hint of reactivity towards \( \text{H}_2 \), or the hydridic E--H bonds present in \( \text{PhSiH}_3 \), \( \text{Et}_3\text{SiH} \) or \( \text{Me}_3\text{N} \cdot \text{BH}_3 \), for which more-or-less concerted oxidative activation would be expected. On the other hand, the low-lying nature of the orbital manifold (and the implied high Lewis acidity) for both systems would appear to be better suited to the activation of polar bonds, such as N--H linkages. Accordingly, the cleavage of N--H bonds can be demonstrated explicitly through the reactions of 3 and 4 with carbazole (Scheme 6). The corresponding reactions with ammonia are much more difficult to control in terms of stoichiometry,\(^{2,3}\) and invariably result in the presence of protonated ligand among the products formed. Carbazole, by contrast, can easily be added stoichiometrically and its planar structure proves to be critical in isolating the reaction product by crystallization.

In contrast to two-coordinate diaryl germylene and cationic \( \beta \)-diketiminate silylum-ylidene complexes (Schemes 1 and 2), for which single-site N--H activation processes result in net oxidative addition at the group 14 element, the mode of activation in the cases of 3 and 4 involves 1,2-addition across the amido Ge--N bond (Scheme 6). As such, products 6 and 7 are generated, in which the Ge\(^{\text{II}}\) oxidation state is retained, the amido donor is protonated (to generate a secondary amine) and coordination of the anionic carbazolyl conjugate base increases the germanium coordination number from two to three.

**Fig. 4** Key germanium-centred frontier orbitals for the cationic component of 3.

**Scheme 6** Activation of N--H bonds in 1,2-fashion by NHC and phosphine stabilized germylum-ylidenes (anions omitted for clarity).
at the highly Lewis acidic germanium centre followed by proton migration to the proximal amido ligand. Precedent for the formation of an initial donor/acceptor adduct of this sort comes from a recently reported β-diketiminate supported germymylidene cation, which can be isolated due to the presence of a less acidic N–H bond and a less basic amido ligand. Subsequent proton transfer to a basic ligand site has previously been reported for Nacnac-derived germanium and aluminium/gallium systems, and finds more general precedent in the pyridine-derived ligand systems pioneered by Milstein and co-workers.

Conclusions

NHC- and phosphine-stabilized germymylidene cations, featuring tethered amido substituents have been isolated for the first time and shown definitively to be two-coordinate in the solid state by X-ray crystallography. The presence of the strongly Lewis acidic cationic germanium centre and proximal amide function allows for facile cleavage of protic E–H bonds in cooperative (1,2-) fashion (exemplified by the N–H bond in carbazole), leading to the formation of a tethered secondary amine donor bound to a three-coordinate Ge centre. By analogy with chemistry reported for neutral stannylene and germanylide systems, and consistent with structural results which imply that addition of the components of the E–H bond happen at one face of the Ge–N linkage, we propose that this chemistry proceeds via coordination of the substrate at the highly electrophilic germanium centre, followed by proton migration (i.e. intramolecular deprotonation) involving the nearby amide group. Such a sequence is consistent with the idea that substrate coordination via the π orbital at germanium markedly reduces the extent of N-to-Ge π donation from the amide, thereby enhancing the basicity of the proximal N-group. As such, the presence of the highly Lewis acidic site in cations of this sort is key to cooperative activation of the substrate across the germanium-nitrogen bond. Differences in the regiochemistry of N–H addition compared to other GeII systems (1,2- vs. 1,1- single site) or 1,4-addition, for example, can then be rationalized on the basis of the location of the most accessible basic site within an initially formed amine adduct. Consistent with these hypotheses, we find that the HOMO of the model adduct 3-NH3 (at −9.18 eV/−886 kJ mol⁻¹) is characterized as the amide lone pair: this orbital is elevated significantly from its counterpart in the free cation 3 (the HOMO-2 at −10.22 eV/−986 kJ mol⁻¹). The germanium-centred lone pair in the adduct 3-NH3 is found in the HOMO−1 (at −9.44 eV/−911 kJ mol⁻¹) (see ESI†).

Experimental

General considerations

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon. Toluene and hexane were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent using a commercially available Braun SPS and stored over potassium; fluorobenzene and bromobenzene were dried by refluxing over CaH2 and stored over molecular sieves. Benzene-d6 was dried using a potassium mirror and bromobenzene-d3, dried using CaH2 and stored over molecular sieves. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. NMR spectra were measured on Bruker Avance III HD Nanobay or Bruker AVII spectrometers operating at 400 or 500 MHz, respectively (for ¹H measurements); ¹H and ¹³C NMR spectra were referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances and are reported relative to tetramethylsilane. ¹⁹F and ²⁷Al NMR spectra were referenced with respect to CFCl₃, and [Al(H₂O)₆]³⁺, respectively. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were carried out at London Metropolitan University. Protoi-ligands ([L¹]H₂)Br and ([L²]H)Br, and metal precursors Ge[N(SiMe₃)₂]₂, Li[Al(OC(CF₃)₃)_4], Li[Al(OCCF₃)]₄, and Al(H₂O)₆ were prepared via literature methods. Li(L²) was prepared from (L²)H and “BuLi as described in the ESI†.

DFT calculations

All computational work reported here was carried out using density functional theory (DFT) within the Gaussian16 (Revision C.01) program package. Geometry optimizations were performed with the PBE1PBE exchange correlation functional, using the Def2-TZVP basis set with an ultrafine integration grid and Grimme’s empirical dispersion correction (GD3B). The nature of stationary points found (minimum) was confirmed by full frequency calculations (no imaginary frequencies).

Crystallography

Single-crystal X-ray diffraction data for all compounds were collected using an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on MiTeGen Micromount loops and quench-cooled using an Oxford Cryosystems open flow N₂ cooling device. Data were collected at 150 K using mirror monochromated Cu Kα radiation (λ = 1.5418 Å; Oxford Diffraction Supernova). Data collected were processed using the CrystAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrystAlisPro). Equivalent reflections were merged and diffraction patterns processed with the CrystAlisPro suite. Structure were solved ab initio from the integrated intensities using SHELXT and refined on F² using SHELXL with the graphical interface Olex2 or X-Seed. Full details are given in the supplementary deposited CIF files (CCDC 1952091–1952095, 1952097 and 2005217–2005219†).

Syntheses of novel compounds

([L¹]GeBr) (1). To a mixture of ([L¹]H₂)Br (600 mg, 1.64 mmol) and Ge[N(SiMe₃)₂]₂ (644 mg, 1.64 mmol) was added toluene...
(15 mL) at −78 °C. The reaction mixture was warmed to room temperature and then heated to 80 °C for 2 d, over which time a colourless solution was formed. Volatiles were removed in vacuo, and 1 was isolated as a pale yellow powder. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in THF layered with hexane and stored at room temperature. Yield: 709 mg, 99%. 1H NMR (400 MHz, benzene-d6, 298 K): δH 1.42 (9H, s, 2Bu), 2.00 (3H, s, para CH3 of Mes), 2.06 (6H, br s, ortho CH3 of Mes), 3.43 (4H, br s, CH2), 5.89 (1H, br d, imidazolylidene backbone CH), 6.12 (1H, br d, imidazolylidene backbone CH), 6.68 (2H, s, CH of Mes). 13C{1H} NMR (126 MHz, benzene-d6, 298 K): δC 129.3 (mesitylene C). JH-H = 6.2 Hz, CH of Dipp), 1.40 (3H, d, 3JHH = 6.2 Hz, CH3 of Dipp), 2.79 (1H, q, 3JHH = 16.5 Hz, CH3), 3.97 (1H, q, 3JHH = 16.2 Hz, CH of Dipp), 3.35 (1H, d, 3JHH = 15.5 Hz, methylene CH3), 6.24 (1H, br m, phenyl backbone CH), 6.61 (1H, br m, phenyl backbone CH), 6.68 (1H, br m, phenyl backbone CH), 6.72−6.93 (10H, overlapping m, PPh2 phenyl CH and Dipp CH), 7.06 (2H, br m, PPh2), 7.28 (2H, br m, PPh2).

11C{1H} NMR (126 MHz, benzene-d6, 298 K): δC 24.6 (CH3 of Dipp), 26.3 (CH3 of Dipp), 28.9 (CH of Dipp), 59.8 (d, 3JCP = 10.6 Hz, methylene C), 124.0 (Dipp para C), 124.3 (Dipp ortho C), 124.3 (phenyl backbone C), 126.3 (Dipp meta C), 127.7 (d, 3JCP = 5.6 Hz, phenyl backbone C), 129.3 (d, 3JCP = 9.8 Hz, PPh2), 129.6 (d, 3JCP = 8.9 Hz, phenyl backbone C), 131.3 (d, 3JCP = 2.0 Hz, PPh2), 131.4 (d, 3JCP = 1.8 Hz, PPh2), 134.4 (d, 3JCP = 10.3 Hz, phenyl backbone C), 147.6 (d, 3JCP = 8.2 Hz, phenyl backbone C), 148.9 (d, 3JCP = 12.8 Hz, phenyl backbone C), 149.1 (Dipp ipso C). 31P NMR (104 MHz, benzene-d6, 298 K): δp −24.4 (s). Elemental microanalysis: calc. for C18H26BrGeN3: C 49.48%, H 6.00%, N 9.62%. Meas. C 49.54%, H 5.82%, N 9.53%. Crystallographic data: C18H26BrGeN3, M̅ = 436.92, monoclinic, P21/n, α = 111.357(1)°, β = 90.475(3)°, γ = 90.475(3)°, V = 1371.34(9) Å³, Z = 2, ρc = 1.535 g cm⁻³, T = 150 K, μ(CuKα) = 3.105 mm⁻¹, λ = 1.54184 Å, Rf = 0.0250 for 5273 observed unique reflections [I > 2σ(I)], wR2 = 0.0883 for all 4070 unique reflections. Max. and min. residual electron densities 0.50, −0.25 e Å⁻³. CCDC 1952092.†

[(L2)GeAl[OC(CF3)3]3]2 (2). To a mixture of Li[(L2)Ge] (750 mg, 1.64 mmol) and GeC6F5-dioxane (379 mg, 1.64 mmol) was added tolune (15 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for 12 h, over which time a yellow solution was formed. Volatiles were removed in vacuo and compound 2 was isolated as a yellow oil. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in toluene layered with hexane and stored at −30 °C to give 2 as a pale yellow crystalline solid. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in toluene layered with hexane and stored at −30 °C. Yield: 610 mg, 67%. 1H NMR (400 MHz, benzene-d6, 298 K): δH 1.01 (6H, br d, CH1 of Dipp), 1.25 (6H, br, CH3 of Dipp), 3.50 (2H, br sept, CH of Dipp), 4.76 (2H, br m, methylene CH2), 6.66 (1H, br m, phenyl backbone CH), 6.84 (1H, br m, phenyl backbone CH), 6.89 (1H, br m, phenyl backbone CH), 6.95−7.15 (10H, m, aromatic H of PPh2, phenyl CH and Dipp CH), 7.42 (4H, br m, PPh2). 1H NMR (400 MHz, toluene-d8, 193 K): δH 0.46 (3H, d, 3JHH = 6.2 Hz, CH3 of Dipp), 1.02 (3H, d, 3JHH = 6.2 Hz, CH3 of Dipp), 1.40 (3H, d, 3JHH = 6.2 Hz, CH3 of Dipp), 1.45 (3H, d, 3JHH = 6.2 Hz, CH3 of Dipp), 2.79 (1H, q, 3JHH = 16.5 Hz, CH3), 3.35 (1H, d, 3JHH = 15.5 Hz, CH3), 3.97 (1H, q, 3JHH = 16.2 Hz, CH of Dipp), 3.35 (1H, d, 3JHH = 15.5 Hz, methylene CH3), 6.24 (1H, br m, phenyl backbone CH), 6.61 (1H, br m, phenyl backbone CH), 6.68 (1H, br m, phenyl backbone CH), 6.72−6.93 (10H, overlapping m, PPh2 phenyl CH and Dipp CH), 7.06 (2H, br m, PPh2), 7.28 (2H, br m, PPh2).

11C{1H} NMR (126 MHz, benzene-d6, 298 K): δC 24.6 (CH3 of Dipp), 26.3 (CH3 of Dipp), 28.9 (CH of Dipp), 59.8 (d, 3JCP = 10.6 Hz, methylene C), 124.0 (Dipp para C), 124.3 (Dipp ortho C), 124.3 (phenyl backbone C), 126.3 (Dipp meta C), 127.7 (d, 3JCP = 5.6 Hz, phenyl backbone C), 129.3 (d, 3JCP = 9.8 Hz, PPh2), 129.6 (d, 3JCP = 8.9 Hz, phenyl backbone C), 131.3 (d, 3JCP = 2.0 Hz, PPh2), 131.4 (d, 3JCP = 1.8 Hz, PPh2), 134.4 (d, 3JCP = 10.3 Hz, phenyl backbone C), 147.6 (d, 3JCP = 8.2 Hz, phenyl backbone C), 148.9 (d, 3JCP = 12.8 Hz, phenyl backbone C), 149.1 (Dipp ipso C). 31P NMR (104 MHz, benzene-d6, 298 K): δp −74.6. 27Al NMR (104 MHz, benzene-d6, 298 K): δC 35.4. Crystallographic data: Cs4H2AlF6Ge4O16, M̅ = 1324.15, monoclinic, P21/n, a = 10.5246(1), b = 18.4838(3), c = 24.2497(3) Å, β = 98.747(1)°, V = 4662.54(11) Å³, Z = 4, ρc = 1.886 g cm⁻³, T = 150 K, μ(CuKα) = 0.938, for 7840 observed unique reflections [I > 2σ(I)], wR2 = 0.2713 for all 9656 unique reflections. Max. and min. residual electron densities 2.04, −1.52 e Å⁻³. CCDC 1952094.†

[(L2)GeAl[OC(CF3)3]3]2 (4). To a mixture of (L2)GeC6F5 (200 mg, 0.36 mmol) and Li[Al(OC(CF3)3)3]2 (474 mg, 0.36 mmol) was added bromobenzene (15 mL) at room temperature. The reaction mixture was stirred for 12 h, over which time a yellow solution and a white precipitate formed. The reaction mixture was filtered and volatiles removed in vacuo to obtain compound 4 as a yellow oil. Single crystals suitable for X-ray crystallography were obtained from a concentrated solution in bromobenzene layered with hexane and stored at −30 °C. Yield: 153 mg, 29%. 1H NMR (400 MHz, bromobenzene-d6, 298 K):
The reaction mixture was stirred overnight, over which time a 0.23 mmol) was added benzene (10 mL) at room temperature. 1H NMR (376 MHz, bromobenzene-d5, 298 K): δH = 3.93 (9H, s, "Bu), 0.69 (3H, s, "Bu), 0.91 (6H, d, 3JHH = 1.8 Hz, Dipp CH3). 13C{1H} NMR (126 MHz, bromobenzene-d5, 298 K): δC = 35.08%, H 2.83%, N 4.81%; meas. C 35.7% (3H, s, "Bu), 0.69 (3H, s, "Bu), 0.91 (6H, d, 3JHH = 1.8 Hz, Dipp CH3). 13C{1H} NMR (126 MHz, bromobenzene-d5, 298 K): δC = 35.08%, H 2.83%, N 4.81%; meas. C 35.19%, H 2.97%, N 4.46%. Elemental microanalysis: calc. for C51H49AlBrF46Ge2N6O4:C 37.88%, H 2.61%, N 0.94%; meas. C 37.87%, H 2.61%, N 0.90%. 19F NMR (376 MHz, bromobenzene-d5, 298 K): δF = -103.24 (CF3 of C(CF3)3), 117.3 (d, 1JCP = 44.4 Hz, phenyl backbone C), 119.0 (d, 1JCP = 52.3 Hz, PPh2), 125.1 ( phenyl backbone C), 130.1 (PPh2), 130.4 (PPh3), 130.7 (d, 1JCP = 11.6 Hz, phenyl backbone CH), 133.7 (d, 1JCP = 11.3 Hz, PPh3). 134.0 (Dipp C), 134.2 (d, 1JCP = 2.6 Hz, phenyl backbone C), 134.5 (Dipp C), 141.6 (d, 1JCP = 11.1 Hz, phenyl backbone C), 142.6 (d, 1JCP = 27.7 Hz, Dipp C), 145.6 (Dipp ipso C).
Conflicts of interest

There are no conflicts to declare.

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