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A digermylene (LGe^I–Ge^{I}L) on an N-heterocyclic carbene–fluorenyl hybrid ligand (L) and its oxidation by TEMPO and Ph$_2$E$_2$ (E = S, Se)

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A hybrid N-heterocyclic carbene (NHC)–fluorenyl ligand (L) supported Ge^{II}Cl complex ([LGeCl]; **1**) has been made from GeCl$_2$(dioxane) and [LK]$_n$. Compound **1** is reduced by Jones' Mg$^I_2$ dimer [(^{Mes}NacnacMg)$_2$] (^{Mes}Nacnac = [{(Mes)NCMe}$_2$CH]$^-$; Mes = 2,4,6-Me$_3$-C$_6$H$_2$) to give the digermylene [LGe^I–Ge^{I}L] (**2**) with a *gauche*-bent conformation. Compound **2** is oxidized by TEMPO (2,2,6,6-tetramethylpiperidinyloxy) and Ph$_2$E$_2$ (E = S, Se) to give [LGe(TEMPO)] (**3**) and [LGeEPh] (E = S (**4**), Se (**5**)), respectively. Overoxidation of **2** by Ph$_2$Se$_2$ to give a mixed-valent trinuclear species [{(PhSe)$_2$Ge^{II}}$_2$(μ-L)$_2$Ge^{IV}(SePh)$_2$] (**6**) is also noted. Besides, precursor **1** is converted into [LGeMe] (**7**) and [LGeOSiPh$_3$] (**8**) by treating it with MeMgBr and KOSiPh$_3$, respectively. However, none of these compounds leads to a desired [LGeH] species. Also, interestingly, Cl-abstraction from **1** by AgSbF$_6$ fails and it rather forms a 2 : 1 adduct [(LGeCl)$_2$Ag][SbF$_6$] (**9**).

Introduction

The low-valent/low-oxidation state chemistry of the p-block elements, especially that of the heavier ones, has seen a remarkable rise in the recent past.[1] Ancillary ligand-supported digermylenes are one such class of compounds[2] receiving attention as the Ge^I–Ge^I single-bonded analogues of the relatively rarer but more reactive digermynes (Ge^I≡Ge^I).[3]

As highlighted in Fig. 1, various monoanionic and typically bidentate ligand types have been used to furnish digermylenes (**A–H**)[4] with *trans*- to *gauche*-bent conformations. In **G**[4i] and **H**,[4j] the ligands bridge between the two Ge^I centers to give a butterfly-like appearance. The digermylene **I** has a rare eclipsed geometry achieved with the help of two K$^+$ ions.[5] **J** is a dicationic digermylene,[6] while **K** is an unsymmetrical one with two different ligands.[7]

N-heterocyclic carbenes (NHCs) are also ubiquitous ligands in the low-valent main group domain.[8] However, their uses in digermylenes are limited (Fig. 1). For instance, the NHCs in **L** are external Lewis bases. A bis(NHC)-borate supports a [Ge$^I_2$]$^{2+}$ in **M**[9] like **J**. **N** is an NHC-ligated sila-bis-λ^3-germirane.[10] A CAAC-based digermylene is also possible [CAAC: cyclic(alkyl)(amino)carbene].[11] Lewis base coordination can also convert a digermyne into a digermylene.[12]

Despite such ligand-driven stability and the decent numbers, reactivity-wise, digermylenes remain somewhat underexplored compared to digermynes.[13] Among the few cases studied, both **C** and a variant of **A** oxidatively add PhN═NPh by cleaving their Ge^I–Ge^I bonds but form (CO)$_4$Fe ← Ge^I–Ge^I → Fe(CO)$_4$ type Lewis adducts in reacting with Fe$_2$(CO)$_9$.[14] **C** also reacts with excess sulfur to give a Ge-analogue of a dithiocarboxylic acid anhydride.[4d] **D** adds CO$_2$ to its Ge^I–Ge^I motif reversibly and also oxidatively adds PhC≡CPh and C$_6$F$_5$-F.[4e] **F** is further reduced by KC$_8$ to a K-germylidenide with a formal Ge^0.[4h] **H** and B(C$_6$F$_5$)$_3$ together induce ring-opening of THF.[4j] A few monodentate bulky anilides furnish pseudo-digermylenes by circumventing the Ge^I–Ge^I multiple bonding through *N* → Ge^I π-donation,[15] although they react mostly like the digermynes. Hence, further exploration of digermylenes, especially towards controlled oxidation of Ge^I to Ge^{II}, would be a worthy proposition and may potentially lead to Ge^I/Ge^{II} redox catalysis. Performing this on an NHC-based ligand support would be even more compelling.

Danopoulos' (CH$_2$)$_2$-linked NHC–fluorenyl hybrid ligand [Flu-(CH$_2$)$_2$-NHC^{Dipp}]$^-$ (L; Dipp = 2,6-^{i}Pr$_2$-C$_6$H$_3$) has been successful in d- and f-block chemistry.[16] We have lately applied it to divalent main group metals like Zn, Mg, Ca, and Sr.[17] Given the relevance of NHCs in stabilizing low-valent main group species, we employ here the same L on Ge and report the digermylene [LGe^I–Ge^{I}L] and its oxidation by TEMPO and

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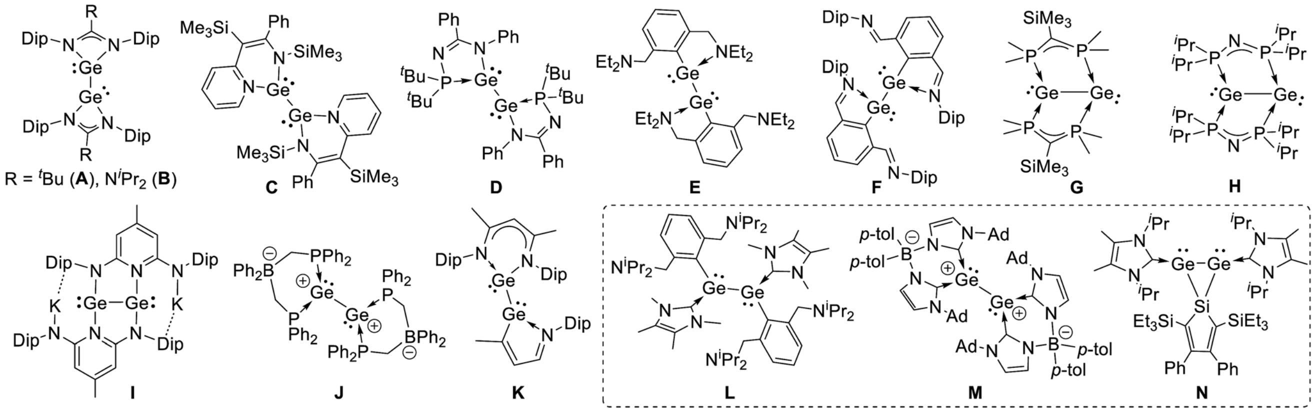


Fig. 1 Digermylenes (**A**–**N**) supported by ancillary ligands including a few based on NHCs. Dip = 2,6-^{i}Pr$_2$-C$_6$H$_3$; *p*-tol = 4-Me-C$_6$H$_4$; Ad = adamantyl.

Ph$_2$E$_2$ (E = S, Se). In addition, a compound [LGeH] is sought but found to be elusive. A Cl-abstraction from [LGeCl] by AgSbF$_6$ also fails and surprisingly leads to their 2 : 1 adduct instead.

Results and discussion

[LK]$_n$ [17b] and GeCl$_2$(dioxane) at a 1 : 1 ratio in THF give [LGeCl] (**1** (89%); Scheme 1) as a colorless monomeric solid as shown by X-ray diffraction (Fig. 2). The fluorenyl is σ-bonded to the Ge$^{\mathrm{II}}$ center, which, with a stereogenic lone pair, adopts a distorted trigonal pyramidal geometry. **1** is THF-soluble but insoluble in benzene. Its ^{1}H NMR spectrum in a 2 : 1 C$_6$D$_6$/THF-d_8 solvent mixture shows the characteristic resonances of L within their expected regions. The ^{13}C NMR C_{NHC} signal is observed at δ 172.7 ppm.

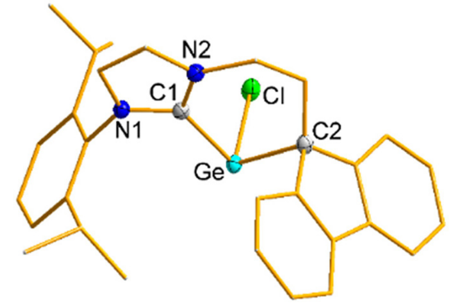


Fig. 2 Molecular structure of **1**. Ellipsoids are set at the 50% probability level. H atoms are omitted for clarity. Selected distances (Å): Ge–C1 2.0574(14), Ge–C2 2.0939(20), and Ge–Cl 2.3223(5).

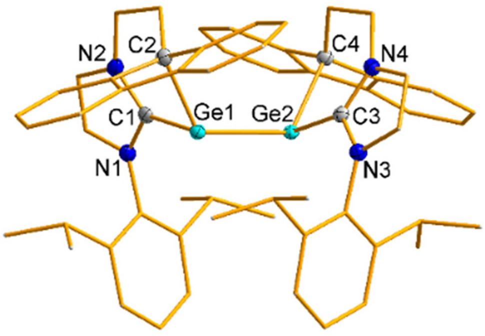
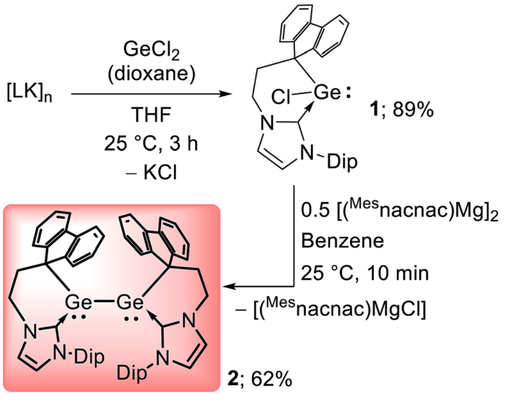


Fig. 3 Molecular structure of **2**. Ellipsoids are set at the 50% probability level. H atoms are omitted for clarity. Selected distances (Å): Ge–Ge 2.5730(4), Ge1–C1 2.0301(17), G2–C3 2.0244(17), Ge1–C2 2.1606(20), and Ge2–C4 2.1710(17).

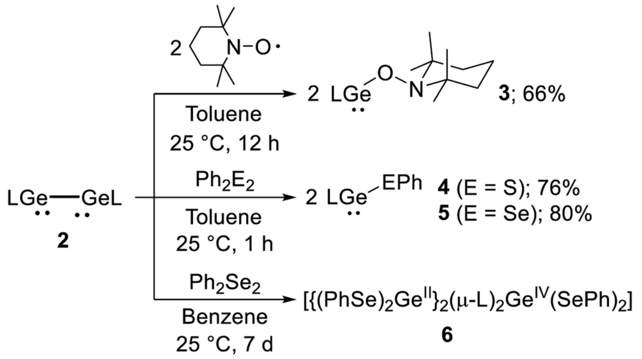


Scheme 1 Synthesis of [LGeCl] (**1**) and its reduction to [LGe$^{\mathrm{I}}$–Ge$^{\mathrm{I}}$L] (**2**).

Reducing **1** using Jones' Mg$^{\mathrm{I}}_2$ dimer [(${}^{\mathrm{Mes}}$NacnacMg)$_2$] (${}^{\mathrm{Mes}}$Nacnac = [{(Mes)NCMe}$_2$CH]$^-$; Mes = 2,4,6-Me$_3$-C$_6$H$_2$)[18] in benzene gives the desired digermylene [LGe$^{\mathrm{I}}$–Ge$^{\mathrm{I}}$L] (**2** (62%); Scheme 1) as a red solid with a *gauche*-bent conformation as authenticated by X-ray crystallography (Fig. 3). The L → Ge bite angles are nearly the same (~ 88.5°). While the torsion angle ∠C$_{\mathrm{NHC}}$–Ge1–Ge2–C$_{\mathrm{NHC}}$ is 156.4°, that of ∠C2–Ge1–Ge2–C4 is recorded as 27.5°. The Ge$^{\mathrm{I}}$–Ge$^{\mathrm{I}}$ bond distance (2.5726(4) Å) is comparable to that of other digermylenes. Notably, the C_{Flu}–Ge and C$_{\mathrm{NHC}}$–Ge distances are slightly different at the two Ge$^{\mathrm{I}}$ centers. However, the ^{1}H NMR spectrum of **2** in C$_6$D$_6$ shows the two ligands as chemically equivalent in solution. The ^{13}C NMR C_{NHC} signal appears at δ 185.4 ppm.

Compound **2** has been optimized at the M06-2X/def2-SVP level of theory in the gas phase (Fig. 4). The Ge$^{\mathrm{I}}$–Ge$^{\mathrm{I}}$ bond length in the DFT-optimized structure (2.55 Å) is in good agreement with that determined in the solid state (2.57 Å). The Kohn–Sham orbitals calculated at the M06-2X/def2-TZVP//M06-2X/def2-SVP level indicate that the HOMO is localized on the Ge$^{\mathrm{I}}$–Ge$^{\mathrm{I}}$ σ bond, formed by the overlap of their p orbitals. The HOMO-1 is essentially derived from the Ge-lone pairs. An NBO analysis at the same level of theory shows a Wiberg bond index of 0.960 for the Ge$^{\mathrm{I}}$–Ge$^{\mathrm{I}}$ motif. Each Ge center lends 87.8% of its p-orbital character (s: 11.8%) to the Ge$^{\mathrm{I}}$–Ge$^{\mathrm{I}}$ bond, while the lone pairs have more of the s-orbital character (s: 67.0%, p: 33.0%). The LUMO is ligand-based, lying on the fluorenyls. A reasonably high HOMO–LUMO gap (4.61 eV) reflects the stability of **2**, while the same gap between the HOMO and the HOMO-1 is only 0.77 eV, suggesting that the Ge–Ge bond and the Ge-centered lone pairs can compete in reactivity. The calculated natural charge on each Ge$^{\mathrm{I}}$ center is 0.377, while that on each $C_{\mathrm{fluorenyl}}$ and C_{NHC} are −0.397 and 0.161, respectively. The homolytic bond dissociation energy of the Ge$^{\mathrm{I}}$–Ge$^{\mathrm{I}}$ bond in **2** is calculated to be 37.7 kcal mol^{-1}. The red color of **2** might originate from the $S_1 \leftarrow S_0$ transition at around 540 nm (see the SI).

TEMPO is a common 1e$^-$ oxidant in synthetic chemistry.[19] However, given the rarity of Ge$^{\mathrm{I}}$ → Ge$^{\mathrm{II}}$ oxidation by TEMPO,[20] **2** when reacted with TEMPO in a 1 : 2 ratio furnishes [LGe(TEMPO)] (**3** (66%); Scheme 2) as a colorless monomeric solid, as confirmed by X-ray crystallography (Fig. 5). **2** and TEMPO in a 1 : 1 ratio still gives **3** with 0.5 equiv. of **2** remaining unreacted. As observed in **1** and **2**, the fluorenyl in **3** is also σ-bonded to the Ge$^{\mathrm{II}}$ center. Like **1**, **3** is also THF-soluble but benzene-insoluble and its NMR spectra are recorded using a 1 : 2 C_6D_6/THF-d_8 mixture. The ^{13}C NMR C_{NHC} signal is seen at δ 176.4 ppm.



Scheme 2 Reactivity of **2** towards oxidation by TEMPO and Ph_2E_2 (E = S, Se).

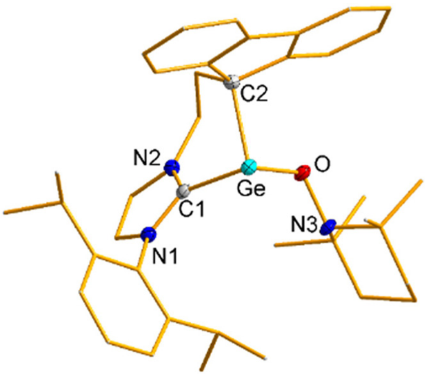


Fig. 5 Molecular structure of **3**. Ellipsoids are set at the 50% probability level. H atoms are omitted for clarity. Selected distances (Å): Ge–C1 2.071(3), Ge–C2 2.116(3) Ge–O 1.8798(19), and O–N3 1.451(3).

Oxidative addition of RE–ER (R = an organyl, E = S, Se) to low-valent metal centers is a mild and efficient route to achieve heavier chalcogenides at the metal's higher oxidation states.[21] While this has been reported for Ge$^{\mathrm{II}}$ → Ge$^{\mathrm{IV}}$,[22] a controlled oxidation of the Ge$^{\mathrm{I}}$–Ge$^{\mathrm{I}}$ bond to yield two Ge$^{\mathrm{II}}$ centers is rare. Reacting **2** with Ph_2E_2 in a 1 : 1 ratio gives [LGeEPh] (E = S (**4**; 76%); Se (**5**; 80%); Scheme 2) as colorless solids. Both are THF-soluble but insoluble in benzene and have similar NMR spectroscopic footprints recorded in a 1 : 1 mixture of C_6D_6/THF-d_8. The ^{13}C NMR C_{NHC} signals appear at δ 173.0 and 173.7 ppm, respectively, for **4** and **5**. **4** is additionally verified by X-ray diffraction as a monomer (Fig. S18), although the data quality is not satisfactory. Notably, a crystallization attempt from **1** with an excess (3 equiv.) of Ph_2Se_2 in benzene at room temperature reacting over a week gives a complex mixture and suggests possible overoxidation. Indeed, a few single crystals of the mixed-valent trinuclear $\mathrm{Ge}^{\mathrm{II}}_2\mathrm{Ge}^{\mathrm{IV}}$ complex

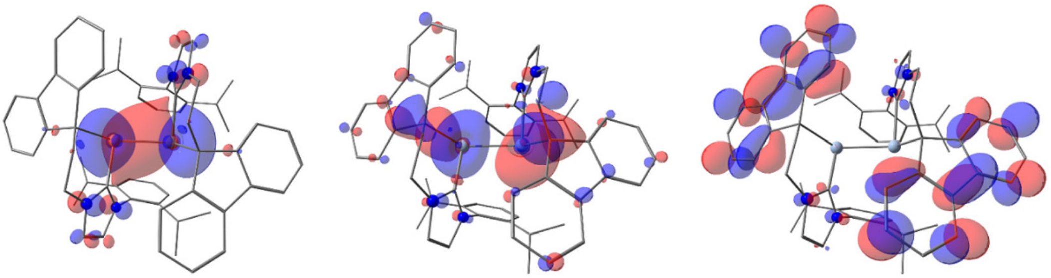
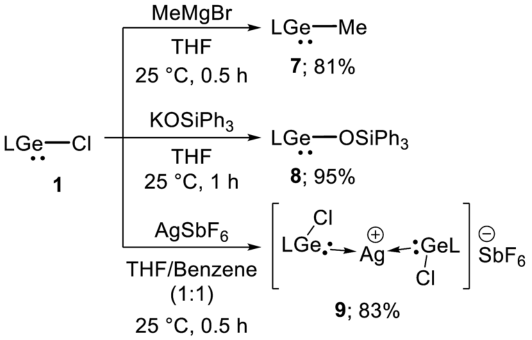


Fig. 4 DFT-optimized HOMO (left), HOMO-1 (middle), and LUMO (right) of **2** (iso-value = 0.030).

[{(PhSe)$_2$Ge^{II}}$_2$(μ-L)$_2$Ge^{IV}(SePh)$_2$] (**6**; Scheme 2) are obtained from the crystallization attempts and only identified by X-ray crystallography (Fig. 6). While the Ge^{IV} center is at the middle and σ-bonded to two fluorenyls of the two bridging L units, the two Ge^{II} centers at the sides exhibit dative coordination from the NHC sidearm. Each Ge center has two terminal SePh groups as well.

Given the values of main group metal hydrides and the well-established precedence of heteroleptic Ge^{II} hydrides,[23] isolating a complex [LGeH] has been attempted but remains unsuccessful. A Cl/H exchange between **1** and hydride sources such as LiAlH$_4$, LiHBEt$_3$, and MH (M = Li–K) gives intractable mixtures in all cases. To test the alternative Ge^{II}–(R/OR)/H–(Si/B) metathesis,[15b,23i] **1** is first treated with MeMgBr and KOSiPh$_3$ to obtain [LGeMe] (**7**; 81%) and [LGeOSiPh$_3$] (**8**, 95%), respectively (Scheme 3). The ^{13}C NMR C_{NHC} signals appear at δ 181.5 and 175.6 ppm, respectively, for **7** and **8**. Complex **8** is also structurally verified by X-ray crystallography (Fig. 7). The bond connectivity in **7** is also confirmed similarly (Fig. S19), but the X-ray data quality is low. However, none of these derivatives on treating with HBpin or PhSiH$_3$ gives a pure GeH species. The hydrogenation of **2** is also not clean.[15b] Notably, [(NHC)ArGeH$_3$] (Ar = 2,6-Trip$_2$C$_6$H$_3$, Trip = 2,4,6-^{i}Pr$_3$-C$_6$H$_2$) is dehydrogenated with an extra equivalent of the NHC to give [(NHC)ArGeH].[23l] A reaction of [{(Dipp)N(^{t}Bu)}GeO^{t}Bu] with HBpin gives [{(Dipp)N(^{t}Bu)}GeH]$_4$, which is then monomerized by NHC coordination[15b].

NHC-stabilized [RGe^{II}(NHC)]$^+$ (R = alkyl, aryl, amide, aryloxide, boryl, W(CO)$_3$(C$_5$Me$_5$)) cations are also of interest due to their Lewis ambiphilicity and ability to activate small molecules.[24] They are usually made by halide (X) abstraction from [(NHC)GeRX] using M[WCA] (M = Na, Li, Ag; WCA: weakly coordinating anion). Surprisingly, no Cl-abstraction results from **1** by either AgSbF$_6$ or Na[{B(3,5-(CF$_3$)$_2$-C$_6$H$_3$}$_4$)] in THF or bromobenzene. **1** and AgSbF$_6$ preferably form a 2 : 1 Lewis adduct as [{(L)GeCl}$_2$Ag]SbF$_6$ (**9** (83%); Scheme 3). The ligand likely pushes the Lewis basicity of the Ge^{II} lone pair to prevail over the potential Cl-abstraction. Cationic **9** is soluble in THF but not in benzene. Notably, its ^{1}H NMR spectrum in THF-d_8 shows two closely spaced set of ligand resonances suggesting discrimination between the two LGeCl units. This could also be due to the existence of two diastereomers in solution as the two Ge^{II} centers bonded to the Ag would be chiral. The two ^{13}C NMR C_{NHC} signals are observed close together at δ 160.3 and 160.1 ppm, respectively. **9** is structurally confirmed by X-ray diffraction (Fig. S20), but the data quality is again unsatisfactory. Such halide abstraction can depend on the conditions applied. For instance, Aldridge's L′GeBr (L′ = an NHC-tethered amide) is Br-abstracted by LiAl[OC(CF$_3$)$_3$]$_4$ in haloarenes to give [L′Ge]Al[OC(CF$_3$)$_3$]$_4$.[24d] However, the same process in benzene gives [(L′Ge)$_2$(μ-Br)]Al[OC(CF$_3$)$_3$]$_4$ by incomplete Br-abstraction. Only a few [Ge^{II}–Ag–Ge^{II}]$^+$ motifs are known.[25]



Scheme 3 Syntheses and reactivity of LGeCl (**1**) and LGe–GeL (**2**).

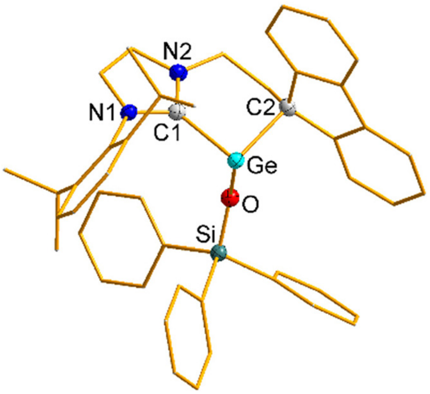


Fig. 7 Molecular structure of **8**. Ellipsoids are set at the 50% probability level. H atoms are omitted for clarity. Selected distances (Å): Ge–C1 2.0889(17), Ge–C2 2.1048(17), and Ge–O 1.8593(12).

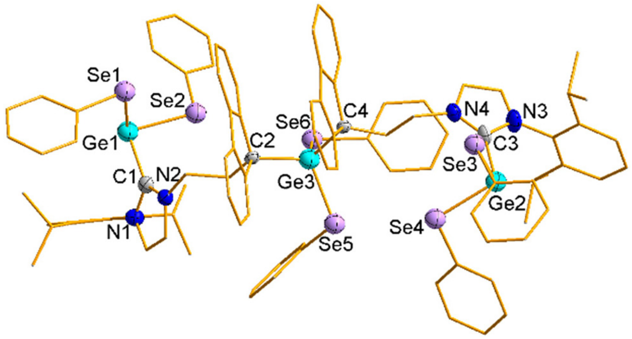


Fig. 6 Molecular structure of **6**. Ellipsoids are set at the 50% probability level. H atoms are omitted for clarity. Selected distances (Å): Ge1–C1 2.104(3), Ge2–C3 2.079(3), Ge3–C2 2.024(2), Ge3–C4 2.019(2), G1–Se1 2.469(5), Ge1–Se2 2.465(5), Ge2–Se3 2.453(4), Ge2–Se4 2.477(4), Ge3–Se5 2.400(3), and Ge3–Se6 2.387(3).

Conclusions

In conclusion, we have isolated a digermylene on a fluorenyl–NHC hybrid ligand L and explored its preliminary reactivity towards controlled oxidation. Attempts to form [LGeH] and [LGe]$^+$ were also made from the precursor [LGeCl] but these remain unsuccessful so far. Instead, the Cl-abstraction attempt results in an unusual adduct formation. We are currently focusing on establishing Ge^I/Ge^{II}-based redox catalytic cycles.

Experimental

General considerations

All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or inside a glovebox, unless otherwise indicated. Prior to use, glassware was dried overnight at 130 °C and solvents were dried, distilled and degassed using standard methods. [LK]$_n$ [17b] and [^{Mes}NacnacMg]$_2$ [26] were prepared by following literature procedures. GeCl$_2$(dioxane) was purchased from Sigma and MeMgBr was purchased from TCI. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on either a Jeol (JNM ECZL-400S, 400 MHz) or Bruker (Avance NEO or Avance III, both 500 MHz) spectrometer at ambient temperature, unless otherwise mentioned. Chemical shifts (δ ppm) in the ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the residual signals of the deuterated solvents.[27] Abbreviations for NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), p (pentate), and br (broad). X-ray data were recorded on either a Rigaku Synergy i XtaLAB or a Bruker D8 diffractometer. The diffraction data are reported in crystallographic information files (cif) accompanying this document and also deposited at the Cambridge Crystallographic Data Centre, under the deposition numbers 2480685 (**1**), 2480687 (**2**), 2480688 (**3**), 2480686 (**6**), and 2480683 (**8**).

[LGeCl] (1). A 3 mL THF solution of [LK]$_n$ (0.459 g, 1.000 mmol) was added dropwise to a 1 mL THF solution of GeCl$_2$(dioxane) (0.232 g, 1.000 mmol). The reaction mixture was stirred for 3 h. The resulting colorless solution was filtered through Celite and the volatiles were removed from the filtrate under reduced pressure. The white residue thus obtained was washed with hexane (3 × 2 mL) followed by benzene (2 × 2 mL) before drying under vacuum to obtain **1** (0.472 g, 0.894 mmol, 89%) as a white solid.

^{1}H NMR (400 MHz, 2 : 1 C$_6$D$_6$/THF-d_8 mixture): δ 8.27 (d, J = 7.7 Hz, 1H, ArH), 7.91 (d, J = 7.6 Hz, 1H, ArH), 7.83 (d, J = 7.5 Hz, 1H, ArH), 7.37–7.33 (m, 1H, ArH), 7.26–7.23 (m, 2H, ArH), 7.12–7.05 (m, 2H, ArH), 7.01–6.98 (m, 1H, ArH), 6.86–6.83 (m, 1H, ArH), 6.69 (d, J = 7.8 Hz, 1H, ArH), 6.56 (t, J = 1.6 Hz, 1H, NCH), 6.39 (t, J = 1.6 Hz, 1H, NCH), 4.22–4.08 (m, 2H, CH_2), 3.92–3.88 (m, 1H, CH_2), 2.76 (p, J = 6.8 Hz, 1H, CH(CH$_3$)$_2$), 2.32 (p, J = 6.7 Hz, 1H, CH(CH$_3$)$_2$), 2.14–2.09 (m, 1H, CH_2), 1.38 (d, J = 6.7 Hz, 3H, CH(CH_3)$_2$), 0.98–0.94 (m, 6H, CH (CH_3)$_2$), 0.78 (d, J = 6.8 Hz, 3H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (126 MHz, 2 : 1 C$_6$D$_6$/THF-d_8 mixture): δ 172.7 (NCN), 152.3 (Ar, C), 147.1 (Ar, C), 146.9 (Ar, C), 145.6 (Ar, C), 140.6 (Ar, C), 137.3 (Ar, C), 132.6 (Ar, C), 131.1 (Ar, C), 126.7 (Ar, C), 125.6 (Ar, C), 124.6 (Ar, C), 124.2 (Ar, C), 124.1 (Ar, C), 123.7 (Ar, C), 122.3 (Ar, C), 122.2 (Ar, C), 121.1 (Ar, C), 119.8 (Ar, C), 54.3(fluorenyl–C), 49.3 (CH$_2$), 29.0 (CH$_2$), 28.7(CH$_2$), 27.7, 26.0, 25.4, 23.3, 23.1. Elemental analysis for C$_{30}$H$_{31}$N$_2$ClGe: calcd C, 68.29; H, 5.92; N, 5.31; found C, 67.93; H, 5.88; N, 5.29.

[LGe–GeL] (2). To a 1 mL benzene suspension of **1** (0.100 g, 0.0.189 mmol), a 2 mL benzene solution of [{(^{Mes}Nacnac)Mg}$_2$] (0.067 g, 0.095 mmol) was added dropwise under constant stirring, during which the reaction color turned from yellow to dark red. Resting the mixture for 10 min led to a colorless precipitate, which was filtered off. Concentrating the red filtrate to <1 mL and keeping it undisturbed for 12 h at room temperature produced red crystals of **2** (0.060 g, 0.059 mmol, 62%).

^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.81–7.72 (m, 4H, ArH), 7.43–7.38 (m, 2H, ArH), 7.05–6.90 (m, 10H, ArH), 6.76–6.4 (m, 6H, ArH), 6.53–6.46 (m, 4H, NCH), 4.68–4.46 (m, 4H, CH_2), 4.22–4.10 (m, 2H, CH_2), 2.53–2.46 (m, 2H, CH_2), 2.29–2.20 (m, 2H, CH(CH$_3$)$_2$), 1.14–1.06 (m, 2H, CH(CH$_3$)$_2$), 0.76–0.66 (m, 12H, CH(CH_3)$_2$), 0.58–0.47 (m, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$): δ 185.4 (NCN), 155.2 (Ar, C), 152.2 (Ar, C), 146.4 (Ar, C), 145.7 (Ar, C), 138.7 (Ar, C), 138.1 (Ar, C), 134.4 (Ar, C), 129.1 (Ar, C), 125.3 (Ar, C), 125.0 (Ar, C), 124.3 (Ar, C), 123.5 (Ar, C), 123.2 (Ar, C), 122.8 (Ar, C), 122.7 (Ar, C), 122.5 (Ar, C), 121.8 (Ar, C), 121.4 (Ar, C), 120.1 (Ar, C), 119.7 (Ar, C), 55.0 (fluorenyl–C), 49.4 (CH$_2$), 33.5 (CH$_2$), 28.9, 28.2, 27.4, 24.8, 23.3, 22.2. Elemental analysis for C$_{60}$H$_{62}$N$_4$Ge$_2$: calcd C, 73.20; H, 6.35; N, 5.69; found C, 72.97; H, 6.43; N, 5.75.

[LGe(TEMPO)] (3). A 3 mL toluene solution of TEMPO (0.016 g, 0.102 mmol) was added dropwise to a 1 mL toluene suspension of **2** (0.050 g, 0.051 mmol). The reaction mixture was stirred for 12 h before removing the volatiles under reduced pressure. The residue was first washed with cold toluene (3 × 2 mL) followed by hexane (3 × 2 mL) before drying under vacuum to obtain **3** (0.043 g, 0.059 mmol, 66%) as a colorless solid.

^{1}H NMR (400 MHz, 1 : 2 C$_6$D$_6$/THF-d_8): δ 8.18 (d, J = 7.7 Hz, 1H, ArH), 7.94–7.86 (m, 2H, ArH), 7.41–7.31 (m, 1H, ArH), 7.24–7.19 (m, 3H, ArH), 7.17–7.15 (m, 1H, ArH), 7.14–7.12 (m, 2H, ArH), 7.10–7.06 (m, 2H, ArH), 6.99–6.92 (m, 1H, NCH), 6.46–6.39 (m, 1H, NCH), 4.80–4.70 (m, 1H), 4.50–4.42 (m, 1H, CH_2), 4.14–4.00 (m, 1H, CH_2), 2.78–2.68 (m, 1H, CH(CH$_3$)$_2$), 2.46–2.29 (m, 2H, CH(CH$_3$)$_2$, CH_2), 1.38 (d, J = 7.00 Hz, 6H), 1.31–1.19 (m, 6H), 1.13 (d, J = 6.76 Hz, 3H), 0.95–0.79 (m, 9H), 0.55 (d, J = 6.7 Hz, 3H), 0.25–0.13 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, 1 : 2 C$_6$D$_6$/THF-d_8): δ 176.4 (NCN), 153.9 (Ar, C), 150.7 (Ar, C), 145.6 (Ar, C), 145.3 (Ar, C), 139.0 (Ar, C), 136.6 (Ar, C), 133.4 (Ar, C), 129.9 (Ar, C), 124.7 (Ar, C), 124.7 (Ar, C), 124.2 (Ar, C), 124.1 (Ar, C), 123.9 (Ar, C), 123.5 (Ar, C), 122.4 (Ar, C), 122.4 (Ar, C), 121.2 (Ar, C), 120.5 (Ar, C), 119.8 (Ar, C), 119.0 (Ar, C), 59.6 (fluorenyl–C), 49.8 (CH$_2$), 40.2, 31.5, 28.6, 27.8, 20.8, 17.4, 13.6. Elemental analysis for C$_{39}$H$_{49}$N$_3$OGe: calcd C, 72.24; H, 7.62; N, 6.48; found C, 71.78; H, 7.79; N, 6.33.

[LGeSPh] (4). A 1 mL toluene solution of Ph$_2$S$_2$ (0.010 g, 0.046 mmol) was added dropwise to a 1 mL toluene suspension of **2** (0.045 g, 0.046 mmol), during which the color of the reaction mixture turned from red to yellow. A white precipitate was slowly deposited within 1 h of storing the reaction mixture undisturbed. The precipitate was collected by filtration, washed with cold toluene (3 × 2 mL), and dried under vacuum to give **4** (0.042 g, 0.035 mmol, 76%) as a colorless solid.

^{1}H NMR (500 MHz, 1 : 1 C_6D_6/THF-d_8): *δ* 8.15 (d, *J* = 7.4 Hz, 1H, Ar*H*), 7.94 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.84 (d, *J* = 6.7 Hz, 1H, Ar*H*), 7.25–7.10 (m, 8H, Ar*H*), 7.03–6.99 (m, 3H, Ar*H*), 6.81 (d, *J* = 7.7, 1H, NC*H*), 6.77–6.71 (m, 3H, NC*H*, Ar*H*), 4.57–4.50 (m, 1H, C*H*$_2$), 4.38–4.34 (m, 1H, C*H*$_2$), 4.05–3.98 (m, 1H, C*H*$_2$), 2.85 (p, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 2.47 (p, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 2.38–2.34 (m, 1H, C*H*$_2$), 2.24 (Tol), 1.31 (d, *J* = 6.7 Hz, 3H, CH(C*H*$_3$)$_2$), 1.11 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 1.03 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 0.84 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (126 MHz, 1 : 1 C_6D_6/THF-d_8): *δ* 173.0 (NCN), 152.5 (Ar, *C*), 149.6 (Ar, *C*), 147.0 (Ar, *C*), 146.0 (Ar, *C*), 143.5 (Ar, *C*), 139.9 (Ar, *C*), 137.5 (Ar, *C*), 133.2 (Ar, *C*), 132.2 (Ar, *C*), 131.1 (Ar, *C*), 128.6 (Ar, *C*), 127.8 (Ar, *C*), 126.6 (Ar, *C*), 125.8 (Ar, *C*), 125.4 (Ar, *C*), 124.6 (Ar, *C*), 124.5 (Ar, *C*), 124.2 (Ar, *C*), 124.1 (Ar, *C*), 123.3 (Ar, *C*), 123.3 (Ar, *C*), 123.1 (Ar, *C*), 122.3 (Ar, *C*), 120.9 (Ar, *C*), 119.8 (Ar, *C*), 53.2 (fluorenyl–*C*), 49.5 (*C*H$_2$), 29.5, 29.4, 29.3, 26.3, 25.6, 23.4, 22.9. Elemental analysis for $C_{36}H_{36}N_2SGe$: calcd C, 71.90; H, 6.03; N, 4.66; found C, 71.23; H, 6.15; N, 4.73.

[LGeSePh] (5). Following a similar procedure to that for **4**, Ph_2Se_2 (0.014 g, 0.046) and **2** (0.045 g, 0.046 mmol) were reacted to obtain **5** (0.047 g, 0.037 mmol, 80%) as a colorless solid.

^{1}H NMR (400 MHz, 1 : 1 C_6D_6/THF-d_8): *δ* 8.33–8.25 (m, 1H, Ar*H*), 7.88 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.79 (dd, *J* = 5.3, 3.5 Hz, 1H, Ar*H*), 7.23–7.19 (m, 4H, Ar*H*), 7.12–7.04 (m, 2H, Ar*H*), 7.02–6.92 (m, 2H, Ar*H*), 6.90–6.86 (m, 2H, Ar*H*), 6.75–6.63 (m, 5H, Ar*H*), 4.34–4.26 (m, 1H, C*H*$_2$), 4.03–3.98 (m, 1H, C*H*$_2$), 3.96–3.87 (m, 1H, C*H*$_2$), 2.82 (p, *J* = 6.7 Hz, 1H, C*H*(CH$_3$)$_2$), 2.49–2.37 (m, 1H, C*H*(CH$_3$)$_2$), 2.32–2.27 (m, 1H, C*H*$_2$), 1.35 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.02 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 0.93 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 0.79 (d, *J* = 7.1 Hz, 3H, CH (C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz, 1 : 1 C_6D_6/THF-d_8): *δ* 173.7 (NCN), 152.1 (Ar, *C*), 149.3 (Ar, *C*), 146.6 (Ar, *C*), 145.6 (Ar, *C*), 141.5 (Ar, *C*), 139.9 (Ar, *C*), 137.2 (Ar, *C*), 135.6 (Ar, *C*), 135.1 (Ar, *C*), 134.0 (Ar, *C*), 132.8 (Ar, *C*), 131.0 (Ar, *C*), 128.6 (Ar, *C*), 126.5 (Ar, *C*), 125.5 (Ar, *C*), 125.1 (Ar, *C*), 124.9 (Ar, *C*), 124.5 (Ar, *C*), 124.3 (Ar, *C*), 124.2 (Ar, *C*), 124.0 (Ar, *C*), 123.0 (Ar, *C*), 122.6 (Ar, *C*), 122.1 (Ar, *C*), 120.9 (Ar, *C*), 119.8 (Ar, *C*), 53.0 (fluorenyl–*C*), 49.3 (*C*H$_2$), 26.1, 25.4, 25.3, 23.2, 22.6, 51.6, 49.2, 30.1, 29.1, 29.1, 26.3, 25.5, 23.5, 22.6. ^{77}Se NMR: 204.7. Elemental analysis for $C_{36}H_{36}N_2SeGe$: calcd C, 66.70; H, 5.60; N, 4.32; found C, 66.09; H, 5.78; N, 4.44.

[{(PhSe)$_2$Ge^{II}}$_2$(μ-L)$_2$Ge^{IV}(SePh)$_2$] (6). A 3 mL benzene solution of Ph_2Se_2 (0.067 g, 0.215 mmol) was added dropwise to a 3 mL benzene suspension of **2** (0.070 g, 0.071 mmol). The reaction mixture was stirred for 1 h before storing undisturbed for crystallization for a week, from which a few colorless crystals of **6** were obtained.

[LGeMe] (7). A 0.19 mL heptane solution of MeMgBr (0.190 mmol) was added dropwise to a 2 mL THF solution of **1** (0.100 g, 0.190 mmol). Stirring the reaction mixture for 30 min gave an orange suspension, which was filtered. Removing the volatiles from the filtrate under reduced pressure followed by washing the residue with hexane (3 × 2 mL) and drying under vacuum gave **7** (0. 080 g, 0.153 mmol, 81%) as an orange solid.

^{1}H NMR (500 MHz, 2 : 1 C_6D_6/THF-d_8): *δ* 7.79–7.74 (m, 2H, Ar*H*), 7.52 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.22 (t, *J* = 7.6 Hz, 1H, Ar*H*), 7.12 (t, *J* = 6.8 Hz, 3H, Ar*H*), 7.04 (t, *J* = 7.2 Hz, 1H, Ar*H*), 7.00 (d, *J* = 7.8 Hz, 1H, Ar*H*), 6.97–6.95 (m, 2H, Ar*H*), 6.91–6.84 (m, 2H, Ar*H*), 4.39–4.34 (m, 1H, C*H*$_2$), 4.21–4.14 (m, 1H, C*H*$_2$), 3.07–3.01 (m, 1H, C*H*$_2$), 2.66 (p, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 2.49 (p, *J* = 6.7 Hz, 1H, C*H*(CH$_3$)$_2$), 2.39–2.33 (m, 1H, C*H*$_2$), 1.21 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 1.06 (d, *J* = 6.8 Hz, 3H, CH (C*H*$_3$)$_2$), 1.02 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 0.92 (d, *J* = 4.8 Hz, 3H, CH(C*H*$_3$)$_2$) −1.03 (d, *J* = 6.5 Hz, 3H, Ge–*Me*). ^{13}C{^{1}H} NMR (126 MHz, 2 : 1 C_6D_6/THF-d_8): *δ* 181.5 (NCN), 155.9 (Ar, *C*), 154.4 (Ar, *C*), 147.1 (Ar, *C*), 146.9 (Ar, *C*), 139.1 (Ar, *C*), 138.1 (Ar, *C*), 134.5 (Ar, *C*), 131.1 (Ar, *C*), 126.5 (Ar, *C*), 126.2 (Ar, *C*), 125 (Ar, *C*), 124.4 (Ar, *C*), 124.3 (Ar, *C*), 123.8 (Ar, *C*), 123.3 (Ar, *C*), 123.1 (Ar, *C*), 122.7 (Ar, *C*), 122.5 (Ar, *C*), 120.5 (Ar, *C*), 120.0 (Ar, *C*), 68.5, 67.7, 51.5 (fluorenyl–*C*), 49.9 (*C*H$_2$), 33.9 (*C*H$_2$), 29.5, 29.2, 26.8, 26.4, 26.1, 25.3, 23.7, 23, 1.8 (Ge–*Me*). Elemental analysis for $C_{31}H_{34}N_2Ge$: calcd C, 73.40; H, 6.76; N, 5.52; found C, 73.10; H, 6.67; N, 5.59.

[LGeOSiPh$_3$] (8). A 1.5 mL THF solution of **1** (0.100 g, 0.189 mmol) was added to a 0.5 mL THF suspension of KOSiPh$_3$ (0.059 g, 0.189 mmol) and stirred for 1 h, during which the reaction mixture became turbid. It was then filtered, and the filtrate was concentrated to dryness under reduced pressure. The residue thus obtained was washed with hexane (3 × 2 mL) before drying under vacuum to obtain **8** (0.138 g, 0.180 mmol, 95%) as a colorless solid.

^{1}H NMR (400 MHz, C_6D_6): *δ* 7.97 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.91 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.77 (dd, *J* = 7.9, 1.4 Hz, 10H, Ar*H* 7.62 (dd, *J* = 8.0, 1.4 Hz, 5H, Ar*H*), 7.29–7.25 (m, 2H, Ar*H*), 7.14–7.12 (m, 3H, Ar*H*), 6.99–6.87 (m, 2H, Ar*H*), 6.83 (dd, *J* = 7.8, 1.4 Hz, 1H, Ar*H*), 6.53 (d, *J* = 7.6 Hz, 1H, Ar*H*), 6.34 (d, *J* = 1.8 Hz, 1H, NC*H*), 6.15 (d, *J* = 1.7 Hz, 1H, NC*H*), 4.19–4.07 (m, 1H, C*H*$_2$), 4.08–3.89 (m, 2H, C*H*$_2$), 2.49 (p, *J* = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 2.30–2.14 (m, 2H, C*H*$_2$, C*H*(CH$_3$)$_2$), 0.93 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$)), 0.74 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 0.28 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): *δ* 175.6 (NCN), 152.8 (Ar, *C*), 148.8 (Ar, *C*), 145.9 (Ar, *C*), 145.7 (Ar, *C*), 140.8 (Ar, *C*), 140.2 (Ar, *C*), 139.7 (Ar, *C*), 136.9 (Ar, *C*), 136.1 (Ar, *C*), 135.8 (Ar, *C*), 133.5 (Ar, *C*), 130.7 (Ar, *C*), 129.4 (Ar, *C*), 128.5 (Ar, *C*), 127.6 (Ar, *C*), 126.8 (Ar, *C*), 124.9 (Ar, *C*), 124.5 (Ar, *C*), 124.4 (Ar, *C*), 124.3 (Ar, *C*), 123.6 (Ar, *C*), 123.5 (Ar, *C*), 121.8 (Ar, *C*), 120.9 (Ar, *C*), 120.6 (Ar, *C*), 119.7 (Ar, *C*), 57.8(fluorenyl–*C*), 49.5 (*C*H$_2$), 29.1, 28.6, 27.2, 25.7, 25.5, 22.6, 22.0. Elemental analysis for $C_{48}H_{46}N_2OSiGe$: calcd C, 75.11; H, 6.04; N, 3.65; found C, 74.75; H, 6.16; N, 3.78.

[(LGeCl)$_2$Ag][SbF$_6$] (9). A 1 mL THF solution of AgSbF$_6$ (0.012 g, 0.048 mmol) was added dropwise to a 1 mL benzene suspension of **1** (0.050 g, 0.095 mmol) and stirred for 1 h. A colorless crystalline solid was deposited overnight, which was collected by filtration, washed with toluene (3 × 2 mL) and dried under vacuum to yield **9** (0.056 g, 0.039 mmol, 83%).

^{1}H NMR (400 MHz, THF-d_8): *δ* 8.02–7.91 (m, 3H, Ar*H*), 7.89–7.82 (m, 6H, Ar*H*), 7.75–7.71 (m, 2H, Ar*H*), 7.58–7.31 (m, 6H, Ar*H*), 7.32–7.19 (m, 1H, Ar*H*), 7.18–7.01 (m, 4H, Ar*H*), 6.71 (d, *J* = 7.7 Hz, 1H, Ar*H*), 6.69–6.60 (m, 2H, Ar*H*), 6.56–6.52 (m, 1H, Ar*H*), 6.19 (d, *J* = 7.8 Hz, 1H, Ar*H*), 4.78–4.60 (m, 4H, C*H*$_2$), 2.54 (p, *J* = 6.7 Hz, 1H, C*H*(CH$_3$)$_2$), 2.40 (p, *J* = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 2.05–1.80 (m, 4H, C*H*$_2$, C*H*(CH$_3$)$_2$), 1.71–1.62 (m, 2H, C*H*$_2$, C*H*(CH$_3$)$_2$), 1.26–1.19 (m, 6H, CH(C*H*$_3$)$_2$), 1.04–0.98 (m, 6H, CH(C*H*$_3$)$_2$), 0.87–0.83 (m, 6H, CH(C*H*$_3$)$_2$), 0.25 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 0.08 (d, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C {^{1}H} NMR (101 MHz, THF-*d*$_8$): *δ* 160.3 (NCN), 160.1 (NCN), 150.1 (Ar, *C*), 149.8 (Ar, *C*), 146.4 (Ar, *C*), 146.4 (Ar, *C*), 146.0 (Ar, *C*), 145.7 (Ar, *C*), 145.1 (Ar, *C*), 144.6 (Ar, *C*), 141.1 (Ar, *C*), 140.6 (Ar, *C*), 139.7 (Ar, *C*), 139.6 (Ar, *C*), 133.7 (Ar, *C*), 132.6 (Ar, *C*), 130.9 (Ar, *C*), 130.8 (Ar, *C*), 128.8 (Ar, *C*), 128.7 (Ar, *C*), 127.6 (Ar, *C*), 127.6 (Ar, *C*), 127.5 (Ar, *C*), 127.4 (Ar, *C*), 127.2 (Ar, *C*), 127.2 (Ar, *C*), 126.6 (Ar, *C*), 125.6 (Ar, *C*), 125.5 (Ar, *C*), 125.2 (Ar, *C*), 125.1 (Ar, *C*), 125.0 (Ar, *C*), 125.0 (Ar, *C*), 124.8 (Ar, *C*), 124.4 (Ar, *C*), 123.6 (Ar, *C*), 123.3 (Ar, *C*), 121.9 (Ar, *C*), 121.7 (Ar, *C*), 121.0 (Ar, *C*), 120.9 (Ar, *C*), 50.9 (fluorenyl–*C*), 50.7(fluorenyl–*C*), 48.9 (*C*H$_2$), 29.7, 29.3, 29.1, 29.1, 28.9, 26.2, 26.2, 26.1, 24.2, 23.0, 22.8. Elemental analysis for $C_{60}H_{62}N_4Cl_2F_6SbAgGe_2$: calcd C, 51.51; H, 4.47; N, 4.01; found C, 51.08; H, 4.66; N, 3.94.

Conflicts of interest

There are no conflicts to declare.

Data availability

Supplementary information (SI): synthetic description of all compounds reported. Spectroscopic data and crystallographic data. See DOI: https://doi.org/10.1039/d5dt02074c.

CCDC 2480685 (**1**), 2480687 (**2**), 2480688 (**3**), 2480686 (**6**) and 2480683 (**8**) contain the supplementary crystallographic data for this paper.[28a–e]

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