Synthesis, characterisation and reactivity of germanium(II) amidinate and guanidinate complexes[†]

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Reactions of lithium salts of the bulky guanidinate ligands, $[ArNC(NR_2)NAr]^-$ (NR₂ = N(C₆H₁₁)₂ (Giso⁻) and *cis*-NC₃H₈Me₂-2,6 (Pipiso⁻); Ar = C₆H₃Prⁱ₂-2,6), with GeCl₂ dioxane afforded the heteroleptic germylenes, [(Giso)GeCl] and [(Pipiso)GeCl], the former of which was structurally characterised. The further reactivity of these and the related complexes, [(Piso)GeCl] and [(Priso)GeCl] (Piso⁻ = [ArNC(Buⁱ)NAr]⁻, Priso⁻ = [ArNC(NPrⁱ₂)NAr]⁻) has been investigated. Salt elimination reactions have yielded the new monomeric complexes, [(Piso)Ge(NPrⁱ₂)] and [(Piso)GeFeCp(CO)₂], whilst a ligand displacement reaction afforded the heterometallic species, [(Piso)Ge(Cl){W(CO)₅}]. Chloride abstraction from [(Priso)GeCl] with GaCl₃ has given the structurally characterised contact ion pair, [(Priso)Ge][GaCl₄]. In addition, the inconclusive outcome of a number of attempts to reduce the germanium halide complexes are discussed.

Introduction

Amidinates and guanidinates have been widely used as ligands to form complexes with metals from across the periodic table.¹ From group 14, the majority of the literature deals with tin(II) amidinate complexes which have found use as, for example, catalysts for the polymerisation of lactide² and the cyclisation of isocyanates.3 In contrast, very few studies of amidinate or guanidinate complexes of Si(II),⁴ Ge(II)^{3,5,6} or Pb(II)^{7,8} have been reported, and no complexes of the type, LGeX (L = amidinate or guanidinate, X = halide), were known prior to our involvement in the field. In a preliminary communication we described the synthesis and structural characterisation of two such monomeric complexes, [(Piso)GeCl] and [(Priso)GeCl],9 which incorporate the bulky Piso⁻ ([ArNC(Bu^t)NAr]⁻, Ar = $C_6H_3Pr^{i_2}$ -2,6) and Priso⁻ ([ArNC(NPrⁱ₂)NAr]⁻) ligands. These complexes were successfully reduced by treatment with potassium metal to give the thermally stable dimeric germanium(I) amides, [{(Piso)Ge}₂] and $[{(Priso)Ge}_2]$, which can be considered as base stabilised amido-germynes (cf. Power's terphenyl substituted digermynes, e.g. $[{(C_6H_3Ar_2-2,6)Ge}_2]^{10})$. The exceptional stability of these complexes derives from the kinetic protection provided by the bulky ligands. In other work, we have employed Piso-, Prisoand related ligands to prepare stable Ga(I),¹¹ As(I),¹² Mg(I)¹³ and lanthanide(II)¹⁴ complexes. It has become clear from these studies that the stabilising properties of these ligands are similar to those of sterically hindered β-diketiminates, e.g. [(ArNCMe)₂CH]⁻

(Nacnac⁻), which have been extensively used for the preparation of low oxidation state metal complexes. $^{\rm 15}$

The β -diketiminate complex of most relevance to this study is [(Nacnac)GeCl]¹⁶ which has been used as a precursor for an impressive array of Ge(II) and Ge(IV) complexes.^{17–19} Following on from our preliminary study, we proposed to extend the range of known LGeX complexes and to explore their further chemistry, drawing comparisons with that of [(Nacnac)GeCl]. The results of our efforts towards this goal are reported here.

Results and discussion

(i) Germanium(II) amidinates

Our initial investigations centred on the use of amidinates related to Piso⁻, but with less bulky backbone substituents, to form complexes of the type, LGeX. To this end Li[Fiso] (Fiso⁻ = [ArNC(H)NAr]⁻) was reacted with GeCl₂·dioxane in a 1 : 1 stoichiometry. However, this reaction led to a moderate yield of [Ge(Fiso)₂], **1**, as the only identifiable product (Scheme 1). Presumably, [(Fiso)GeCl] is initially formed and this reacts with a second equivalent of Li[Fiso] more rapidly than the excess GeCl₂·dioxane can. It is of note that Gibson and co-workers have recently reported that the related 1 : 1 reactions of SnCl₂ with Li[Piso] or Li[ArNC(Me)NAr] led to monomeric [(Piso)SnCl] and a 2 : 3 mixture of [{ArNC(Me)NAr}SnCl] and [Sn{ArNC(Me)NAr}₂], respectively.² The outcomes of the germanium and tin halide reactions indicate that bulky amidinates, *e.g.* Piso⁻, are required to prevent the formation of bis(amidinate) complexes.

The X-ray crystal structure of **1** was determined and its molecular structure is depicted in Fig. 1. This shows it to be isostructural with $[Pb(Fiso)_2]$.⁸ It is monomeric with a four-coordinate germanium centre that has a heavily distorted sawhorse coordination geometry and a stereochemically active lone pair of electrons. As expected, the distances from the axial nitrogens, N(2) and N(4), to Ge(1) are significantly longer than the equatorial N(1)–Ge and N(2)–Ge separations. The geometry

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[†] Electronic supplementary information (ESI) available: ORTEP diagram and metrical parameters for **5** and full crystallographic details for the cocrystallised mixture of [(Priso)GeGa($I_{0.6}$ /Cl_{0.4})(Giso)]. Crystallographic data (excluding structure factors) for the structures of **1**, **3–6**, **8** and [(Priso)GeGa($I_{0.6}$ /Cl_{0.4})(Giso)]. CCDC reference numbers 675662–675668. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b801168k



Scheme 1 Reagents and conditions: (i) Li[Fiso], diethyl ether, -LiCl; (ii) LiNPrⁱ₂, THF, -LiCl; (iii) Na[CpFe(CO)₂], THF, -NaCl; (iv) [W(CO)₅(THF)], THF.



Fig. 1 Molecular structure of 1 (25% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Ge(1)–N(3) 1.994(4), Ge(1)–N(1) 2.008(4), Ge(1)–N(4) 2.258(4), Ge(1)–N(2) 2.293(4), N(1)–C(1) 1.325(6), N(2)–C(1) 1.297(6), N(3)–C(26) 1.326(6), N(4)–C(26 1.308(6), N(3)–Ge(1)–N(1) 102.78(17), N(3)–Ge(1)–N(4) 62.29(16), N(1)–Ge(1)–N(4) 94.51(17), N(3)–Ge(1)–N(2) 91.07(16), N(1)–Ge(1)–N(2) 61.76(17), N(4)–Ge(1)–N(2) 140.57(14), N(2)–C(1)–N(1) 115.9(5), N(4)–C(26)–N(3) 114.1(5).

of the backbone amidinate NCN fragments show them to be effectively delocalised. The structure of **1** is closely related to that of $[Sn{ArNC(Me)NAr}_2]^2$ and $[Ge{Pr^iNC(Me)NPr^i}_2]$.⁵ Interestingly, it differs from those of $[Ge{CyNC(R)NCy}_2]$ (R = Me or Bu^t, Cy = cyclohexyl) which have three-coordinate Ge centres ligated by one chelating, delocalised amidinate and one monodentate, localised amidinate.⁶

The NMR spectral data for 1 differ from those of $[Sn{ArNC(Me)NAr}_2]^2$ in that the latter are consistent with the tin compound retaining its solid state structure in solution

without interconversion of the axial and equatorial N-sites on the NMR timescale at ambient temperature. In contrast, the room-temperature ¹H and ¹³C{¹H} NMR spectra of **1** display broadened signals compatible with four chemically inequivalent sets of methyl groups and two sets of inequivalent methine centres. This suggests a fluxional process is occurring in solution, the speed of which is approximately equal to the NMR timescale. Although the low solubility of **1** in D₈-toluene prevented the resolution of its NMR spectra at lower temperatures, the fluxional process is proposed to involve an exchange of the axial and equatorial nitrogen sites. A similar exchange process has been previously proposed for the less hindered germanium bis(amidinate) complex, [Ge{PrⁱNC(Me)NPrⁱ}₂].⁵

As the germanium amidinate complex, [(Fiso)GeCl], proved inaccessible in our hands, attention turned to the bulkier complex, [(Piso)GeCl], as a precursor for further reactivity studies. The utility of this compound towards salt elimination was tested in its reactions with $Li[NPr_{2}^{i}]$ and $Na[CpFe(CO)_{2}]$. These gave the expected germanium(II) amide, 2, and the Ge-Fe bonded complex, 3, in moderate isolated yields (Scheme 1). Complex 2 is comparable to the related amidinato germanium(II) amide, e.g. $[Ge{Me_3SiNC(Bu^t)NSiMe_3}{N(SiMe_3)_2}]$, and the tin complexes, $[(Piso)Sn(NR_2)]$ (R = Me or SiMe₃),² the latter of which have recently been shown to be effective as lactide polymerisation catalysts. In addition, if comparisons are made with the chemistry of [(Nacnac)GeCl], its treatment with Li[N(SiMe₃)₂] does not lead to [(Nacnac)Ge{N(SiMe₃)₂}], but instead to deprotonation of one Nacnac⁻ methyl substituent.¹⁷ Moreover, there are no known metal functionalised amidinato germanium complexes for comparison with 3.

Given that the germanium lone pair of [(Nacnac)GeOH]¹⁸ has been shown to coordinate to metal fragments, e.g. $Fe(CO)_4$ or CpMn(CO)₂, it seemed that the metal functionalisation of [(Piso)GeCl] could also be achieved by its coordination to related, neutral metal carbonyl fragments. This proved to be the case in its reaction with [W(CO)₅(THF)] which gave the heterometallic system, 4, in good yield (Scheme 1). In a similar fashion, oxidation of [(Nacnac)GeCl] by treatment with elemental chalcogens is known to give the monomeric complexes, [(Nacnac)Ge(=E)Cl] (E = S or Se).¹⁹ In contrast, the reactions of [(Piso)GeCl] with elemental sulfur, selenium or tellerium, gave intractable mixtures of products in our hands. In order to add control to the oxidation of [(Piso)GeCl] with sulfur, the complex was treated with one equivalent of propylene sulfide, a soluble source of the chalcogen. However, again a mixture of products was obtained from this reaction, the only one of which could be isolated (18% yield) was the amidinium salt, [PisoH₂][GeCl₃] 5, which presumably forms due to the presence of adventitious water in the reaction mixture. Subsequently, compound 5 was intentionally synthesised in moderate yield by treating GeCl₂ dioxane with one equivalent of [PisoH₂]Cl.

The NMR spectroscopic data for **2–4** are as would be expected for these complexes retaining their solid state structures in solution. The ¹H and ¹³C{¹H} NMR spectra of each displays four methyl and two methine signals arising from their aryl isopropyl substituents. Similar spectral patterns have been observed for [(Piso)ECI] (E = Ge⁹ or Sn²) and [(Piso)Sn(NR₂)] (R = Me or SiMe₃²) and originate from the tetrahedral geometry of the germanium centres of the complexes, ensuring different chemical environments on either side of the plane of the germanium heterocycle.

Compounds 3-5 were crystallographically characterised and the molecular structures of 3 and 4 are depicted in Figs. 2 and 3, respectively. As the $[GeCl_3]^-$ anion has been structurally characterised on a number of occasions²⁰ and the structure of the amidinium cation, [PisoH₂]⁺, is similar to that of neutral PisoH,²¹ the molecular structure of 5 has been included in the ESI[†] and will not be commented on here. There are two crystallographically independent molecules in the asymmetric unit of 3 that have no significant geometric differences and, therefore, the metric parameters of only one will be discussed. The geometries of the germanium heterocycles of the compounds are similar to each other and to that of [(Piso)GeCl]. Both compounds possess heavily distorted tetrahedral germanium centres, chelated by a delocalised Piso⁻ ligand. The Ge-M distances are in the known ranges²² (Fe-Ge 2.240-2.496 Å, 2.389 Å mean; W-Ge 2.486-2.724 Å, 2.574 Å mean), whilst the Ge-Cl distance in 4 is slightly longer than that in [(Piso)GeCl] (2.174(2) Å).9



Fig. 2 Molecular structure of 3 (25% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Ge(1)–N(1) 2.042(4), Ge(1)–N(2) 2.043(4), Ge(1)–Fe(1) 2.4415(11), Fe(1)–C(35) 1.750(6), Fe(1)–C(36) 1.756(6), N(1)–C(1) 1.341(6), N(2)–C(1) 1.351(6); N(1)–Ge(1)–N(2) 64.19(15), N(1)–Ge(1)–Fe(1) 110.45(11), N(2)–Ge(1)–Fe(1) 111.61(12), C(35)–Fe(1)–C(36) 95.7(3), N(1)–C(1)–N(2) 107.5(4).

(i) Germanium(II) guanidinates

The only guanidinato germanium(II) halide reported in the literature is [(Priso)GeCl] which we have shown to be readily reduced to the dimeric germanium(I) species, [{(Priso)Ge}₂].⁹ We have also demonstrated that [(Priso)GeCl] can participate in a salt elimination reaction with the sterically demanding, anionic gallium(I) heterocyclic complex, [K(tmeda)₂][:Ga{ArNC(H)C(H)NAr}], which yielded the monomeric germanium(II) gallyl complex, [(Priso)GeGa{ArNC(H)C(H)NAr}].²³ In order to extend guanidinato germanium(II) chemistry, it was seen as desirable to



Fig. 3 Molecular structure of 4 (25% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): W(1)–Ge(1) 2.5564(6), Ge(1)–N(1) 1.961(3), Ge(1)–N(2) 1.978(3), Ge(1)–Cl(1) 2.2091(10), N(1)–C(1) 1.352(4), C(1)–N(2) 1.340(4), N(1)–Ge(1)–N(2) 66.42(12), N(1)–Ge(1)–Cl(1) 100.64(9), N(2)–Ge(1)–Cl(1) 95.93(9), N(1)–Ge(1)–W(1) 132.01(9), N(2)–Ge(1)–W(1) 138.78(8), Cl(1)–Ge(1)–W(1) 111.86(3), N(2)–C(1)–N(1) 106.5(3).

extend the available range of guanidinato germanium halides. To this end, two bulky guanidinate salts, Li[Giso] and Li[Pipiso] (Giso⁻ = [ArNC(NCy₂)NAr]⁻; Pipiso⁻ = [ArNC(*cis*-2,6-Me₂C₅H₈N)NAr]⁻) were reacted with GeCl₂·dioxane in 1 : 1 stoichiometries. Both reactions yielded the desired products, **6** and 7 respectively, in good yields (Scheme 2). It is of note that the tin analogues of these complexes have been recently reported.²⁴



Scheme 2 *Reagents and conditions:* (i) Li[Giso] or Li[Pipiso], THF, -LiCl; (ii) GaCl₃, toluene.

The NMR spectra of the complexes are similar to those of [(Giso)SnCl] and [(Pipiso)SnCl],²⁴ and like those of [(Priso)GeCl]⁹ exhibit four methyl and two methine signals arising from their aryl isopropyl substituents. This pattern is consistent with the solid state structure of **6** (Fig. 4) which was determined by an X-ray crystallographic study. The molecule is monomeric and possesses a heavily distorted pyramidal germanium centre



Hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Ge(1)-N(1) 1.993(3), Ge(1)-N(2) 2.003(3), Ge(1)-Cl(1) 2.245(2), N(1)-C(1) 1.363(5), C(1)-N(2) 1.342(5), C(1)-N(3) 1.360(5); N(1)-Ge(1)-N(2) 65.76(13), N(1)-Ge(1)-Cl(1) 102.01(13), N(2)-Ge(1)-Cl(1) 99.84(12), N(2)-C(1)-N(3) 127.1(3), N(2)-C(1)-N(1) 106.6(3), N(3)-C(1)-N(1) 126.2(4).

N1

 $(\sum \text{ angles} = 267.6^\circ, cf. 263.5^\circ \text{ for } [(\text{Priso})\text{GeCl}]) \text{ that is coordi$ nated by a delocalised guanidinate ligand. The Ge-Cl distance for the compound is close to those seen for [(Priso)GeCl] (2.252(4) Å) but both are significantly greater than that for the amidinate complex, [(Piso)GeCl] (2.174(2) Å). A possible explanation for this observation arises from the fact that guanidinate ligands are more N-electron rich than amidinates. This would lead to more electron density being placed on the Ge centres of 6 and [(Priso)GeCl] relative to that of [(Piso)GeCl], thus weakening the Ge-Cl bonds of the guanidinate complexes. In contrast to 6, it is of note that the structure of the lead analogue of this compound, $[{(Giso)Pb(\mu -$ Cl)₂], has been recently reported to be a chloride bridged dimer.⁸

Preliminary efforts have been made to study the further chemistry of [(Giso)GeCl] and [(Pipiso)GeCl]. Their reduction over potassium mirrors in toluene led to deep green solutions in both cases. Although no crystalline or pure materials could be isolated from these reactions, the colours of the reaction mixtures are similar to that of toluene solutions of $[{(Priso)Ge}_2]$.⁹ This suggests that related Ge(I) species were formed in the reductions, though no other evidence for this proposition was forthcoming. The reduction of [(Giso)GeCl] with [AlH₃(NMe₃)] was also attempted, with the expectation that the corresponding terminal hydride complex, [(Giso)GeH], would be formed. This seemed reasonable as [(Nacnac)GeH] has recently been reported to be formed in the reaction of [(Nacnac)GeCl] with [AlH₃(NMe₃)].²⁵ However, the reaction proceeded via a transmetallation process to give a co-crystallised guanidinate aluminium hydride/halide mixture, [(Giso)AlH_xCl_{2-x}], as determined by an X-ray crystallographic study. The outcome of the germanium in this reaction is not known. A number of other reductions of [(L)GeCl] (L = Priso⁻, Giso⁻ or Pipiso⁻) with various reagents were attempted with largely inconclusive results.²⁶

In addition to reduction of guanidinato germanium chloride complexes, we are interested in abstraction of chloride from them to give cations of the type, [(guanidinate)Ge]⁺. If achievable, these would be isoelectronic to the gallium(I) heterocycle, [(Giso)Ga:], we reported in 2006.¹¹ A comparison of the structural aspects of the two complex types would be of significant interest. A similar study has compared the [(Nacnac)Ge]+ cation with the monomeric gallium(I) heterocycle, [(Nacnac)Ga:], with the conclusion that there is partial π -delocalisation over the whole heterocycle of the cation, which also has shorter, and apparently stronger, E-N bonds than the neutral heterocycle.27

In an attempt to access the target heterocycles, toluene solutions of [(Giso)GeCl] or [(Priso)GeCl], were treated with the chloride abstraction agent, Na[B{ $C_6H_3(CF_3)_2$ -3,5}]]. No reaction occurred in either case, probably due to the low solubility of $Na[B{C_6H_3(CF_3)_2-3,5}_4]$ in toluene. Attention shifted to the use of toluene soluble GaCl₃ as a chloride abstraction agent. When toluene solutions of both germylene precursors were treated with GaCl₃, colourless precipitates formed, though only that from the [(Priso)GeCl] reaction had sufficient solubility to be recrystallised in a pure form. Subsequent analyses proved this to be the contact ion pair, 8 (Scheme 2), which was formed in high yield.

The ¹H and ¹³C{¹H} NMR spectra (D_8 -THF) of 8 are not as symmetrical as would be expected if the [(Priso)Ge]+ was uncoordinated in solution. For example, the ¹H NMR spectrum exhibits four broad aryl isopropyl methyl signals and two aryl isopropyl methine resonances. Consistent with this is the presence of six aryl carbon resonances in the ${}^{13}C{}^{1}H$ NMR spectrum of the compound. It is possible that the lower than expected symmetry of these spectra is due to either a persistent cationanion interaction in solution, or the germanium centre of an ion separated [(Priso)Ge]⁺ cation being coordinated by one molecule of THF, leading to a pyramidal geometry at that centre.

The molecular structure of 8 (Fig. 5) shows it to exist as a contact ion pair with a Ge \cdots Cl interaction that is *ca.* 0.28 Å longer than the Ge-Cl distance in [(Priso)GeCl], but within the known range for Ge-Cl bonds.²² This interaction should therefore be considered as relatively strong, as additionally evidenced by the fact that the bridging Ga–Cl bond is ca. 0.1 Å longer than the three terminal Ga–Cl bonds. The C_3N ligand backbone of the cation of 8 appears to be largely delocalised, as is the case with [(Priso)GeCl]. In addition, its Ge-N bond lengths and N-Ge-N angle are not significantly different to those of [(Priso)GeCl] (1.954 Å (mean) and 67.22(12)° Å, respectively). They are, however, markedly shorter and more obtuse, respectively, than the Ga-N distances and N-Ga-N angle of the isoelectronic gallium(1) heterocycle, [(Giso)Ga:] (2.091 Å mean and 63.77(7)°).¹¹ These differences are likely to be predominantly a result of the smaller radius of Ge (1.22 Å) than Ga (1.25 Å).²⁸ The probable greater positive charge on the Ge centre in 8 than the Ga centre in [(Giso)Ga:] may also lead to a more pronounced E-N interaction in the former. Similar arguments have been put forward to explain the structural differences between [(Nacnac)Ge]+ and [(Nacnac)Ga:].27

Conclusion

In summary, two new heteroleptic germylenes, [(Giso)GeCl] and [(Pipiso)GeCl], have been prepared and one shown to be monomeric by an X-ray crystallographic study. A preliminary



Fig. 5 Molecular structure of 8 (25% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Ge(1)–N(1) 1.9477(18), Ge(1)–N(2) 1.9552(18), Ge(1)–Cl(1) 2.5333(9), Ga(1)–Cl(4) 2.1406(8), Ga(1)–Cl(3) 2.1451(11), Ga(1)–Cl(2) 2.1590(8), Ga(1)–Cl(1) 2.2613(8), N(1)–C(1) 1.359(3), C(1)–N(3) 1.344(3), C(1)–N(2) 1.377(3); N(1)–Ge(1)–N(2) 67.47(7), N(1)–Ge(1)–Cl(1) 95.20(6), N(2)–Ge(1)–Cl(1) 92.55(5), Ga(1)–Cl(1)–Ge(1) 105.80(3), N(3)–C(1)–N(1) 128.52(19), N(3)–C(1)–N(2) 126.7(2), N(1)–C(1)–N(2) 104.76(18).

study of the reactivity of these and two related complexes, [(Piso)GeCl] and [(Priso)GeCl], has been carried out. Salt elimination reactions have yielded the new monomeric complexes, [(Piso)Ge(NPrⁱ₂)] and [(Piso)GeFeCp(CO)₂]. A neutral ligand displacement reaction afforded the heterometallic species, [(Piso)Ge(Cl){W(CO)₅}], whilst a chloride abstraction reaction gave the contact ion pair, [(Priso)Ge][GaCl₄], the cation of which is isoelectronic to the previously reported gallium(1) heterocycle, [(Giso)Ga:]. Studies continue in our laboratory on the use of bulky guanidinates to prepare stable complexes containing low oxidation state metal centres from across the periodic table.

Experimental

General considerations

All manipulations were carried out using standard Schlenk and glove box techniques under atmospheres of high purity argon or dinitrogen. Hexane, toluene and THF were distilled over molten potassium metal, diethyl ether was distilled over Na/K alloy, whilst dichloromethane was distilled over CaH₂. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Mass spectra were recorded at the EPSRC National Mass Spectrometric Service at Swansea University. Microanalyses were obtained from Medac Ltd. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. ¹H and ¹³C{¹H} NMR spectra were recorded on either Bruker DXP400 or Jeol Eclipse 300 spectrometers and were referenced to the resonances of the solvent used. FisoH,²⁹ Li[Giso],¹¹ Li[Pipiso],²⁴ [(Piso)GeCl],⁹ [(Priso)GeCl],⁹ GeCl₂-dioxane³⁰

 $[W(CO)_5(THF)]^{31}$ were synthesised by variations of literature procedures. [PisoH₂]Cl was prepared by treating PisoH with 3M HCl followed by rigorous drying of the salt *in vacuo*. All other reagents were used as received.

Preparation of [Ge(Fiso)₂] 1. BuⁿLi (1.10 cm³ of a 1.6 M solution in hexanes, 1.76 mmol) was added to a solution of FisoH (0.62 g, 1.70 mmol) in diethyl ether (20 cm³) at 20 °C and the solution stirred overnight. This was then added at -80 °C to a slurry of GeCl₂·dioxane (0.42 g, 1.81 mmol) in diethyl ether (20 cm³) over 5 min. The resultant mixture was warmed to room temperature over 4 h. Volatiles were removed in vacuo and the residue extracted into toluene (30 cm³) and cooled to 4 °C yielding 1 as colourless crystals (0.29 g, 41%). Mp 255–257 °C (280 °C rapid decomp.). ¹H NMR (400 MHz, C₆D₆, 298 K): δ 1.10-1.40 (overlapping m, 48 H, CH(CH₃)₂), 3.40–3.70 (overlapping m, 8 H, CH(CH₃)₂), 7.00–7.38 (m, 12 H, Ar–H), 7.60 (s, 2 H, CH); ¹³C NMR (100.6 MHz, C₆D₆, 298 K): δ 23.1, 23.8, 24.2, 24.8 (CH(CH₃)₂), 28.5, 28.9 (CH(CH₃)₂), 123.7, 123.9, 127.7, 137.2, 141.6, 144.0 (Ar-C), 160.1 (NCN); MS (APCI) m/z (%): 365 (FisoH₂⁺, 100); IR ν/cm^{-1} (Nujol): 1668 (m), 1634 (m), 1593 (m), 1558 (m), 1261 (s), 1186 (m), 1098 (s), 1057 (m), 956 (m), 769 (m), 754 (m).

Preparation of [(Piso)GeNPr¹₂] 2. To a solution of [(Piso)GeCl] (0.25 g, 0.47 mmol) in THF (30 cm³) at -78 °C was added a solution of Li[NPrⁱ₂] (0.05 g, 0.47 mmol) in THF (10 cm³) over 5 min. The resultant colourless solution was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo and the residue extracted with hexane (15 cm³). Filtration, concentration and cooling to -50 °C overnight yielded colourless crystals of 2 (0.12 g, 42%). Mp 138–140 °C; ¹H NMR (400 MHz, C_6D_6 , 298 K): δ 0.68 (s, 9 H, Bu^t), 0.85 (d, ${}^3J_{HH} = 6.7$ Hz, 6 H, $CH(CH_3)_2$), 0.94 (d, ${}^{3}J_{HH} = 6.7$ Hz, 6 H, $CH(CH_3)_2$), 0.98 (d, ${}^{3}J_{\rm HH} = 6.7$ Hz, 6 H, CH(CH₃)₂), 1.05 (d, ${}^{3}J_{\rm HH} = 6.7$ Hz, 6 H, $CH(CH_{3})_{2}$), 1.10 (d, ${}^{3}J_{HH} = 6.8$ Hz, 12 H, $NCH(CH_{3})_{2}$), 3.25 (sept, ${}^{3}J_{HH} = 6.8$ Hz, 2 H, NCH(CH₃)₂), 3.40 (sept, ${}^{3}J_{HH} = 6.7$ Hz, 2 H, $CH(CH_3)_2$), 3.68 (sept, ${}^{3}J_{HH} = 6.7$ Hz, 2H, $CH(CH_3)_2$), 6.75-6.86 (m, 6 H, Ar-H); ¹³C NMR (75 MHz, C₆D₆, 298 K): δ 21.4 (NCH(CH₃)₂), 23.4 (CH(CH₃)₂), 24.1 (CH(CH₃)₂), 27.4 (CH(CH₃)₂), 28.2 (CH(CH₃)₂), 28.6 (CH(CH₃)₂), 28.7 (CH(CH₃)₂), 29.1 (NCH(CH₃)₂), 29.9 (C(CH₃)₃), 42.1 (C(CH₃)₃), 123.0, 124.0, 124.8, 138.3, 141.0, 142.0 (Ar-C), 166.5 (NCN); IR v/cm⁻¹ (Nujol): 1652 (s), 1616 (s), 1585 (s), 1321 (s), 1258 (s), 1042 (m), 933 (m); MS (APCI) m/z (%): 593 (M⁺, 100), 493 (M⁺ – NPrⁱ₂, 90), 421 (PisoH⁺, 100). Elemental analysis: C₃₅H₅₇N₃Ge requires: C 70.95, H 9.70, N 7.09. Found: C 70.69, H 9.41, N 6.86%.

Preparation of [(Piso)GeFeCp(CO)₂] **3.** To a solution of [(Piso)GeCl] (0.30 g, 0.57 mmol) in THF (15 cm³) was added a solution of Na[CpFe(CO)₂] (0.11 g, 0.57 mmol) in THF (15 cm³) at $-78 \degree$ C over 5 min. The resultant red solution was warmed to 20 °C and stirred overnight. Volatiles were removed *in vacuo* and the residue extracted with hexane (10 cm³). Filtration, concentration and cooling to $-30 \degree$ C overnight yielded red crystals of **3** (0.21 g, 56%). Mp 120–150 °C; ¹H NMR (400 MHz, C₆D₆, 298 K): δ 0.82 (s, 9H, Bu¹), 1.15 (d, ³J_{HH} = 6.8 Hz, 6 H, CH(CH₃)₂), 1.20 (d, ³J_{HH} = 6.8 Hz, 6 H, CH(CH₃)₂), 1.21 (d, ³J_{HH} = 6.8 Hz, 6 H, CH(CH₃)₂), 3.49 (sept, ³J_{HH} = 6.8 Hz, 2 H, CH(CH₃)₂), 3.90 (s, 5H, CpH), 3.97 (sept, ³J_{HH} = 6.8 Hz, 2 H, CH(CH₃)₂),

6.86–6.92 (m, 6 H, Ar-*H*); ¹³C NMR (75 MHz, C₆D₆, 298 K): δ 22.9 (CH(*C*H₃)₂), 23.4 (CH(*C*H₃)₂), 27.4 (CH(*C*H₃)₂), 28.0 (CH(*C*H₃)₂), 28.7 (CH(CH₃)₂), 29.2 (CH(CH₃)₂), 29.4 (C(*C*H₃)₃), 41.9 (*C*(CH₃)₃), 84.5 (*C*₅H₅), 123.5, 124.1, 126.1, 140.5, 144.1, 145.4 (Ar–*C*), 165.0 (N*C*N), 216.5 (*C*O); IR *ν*/cm⁻¹ (Nujol): 1964 (CO str, s), 1921 (CO str, s), 1315 (s), 1253 (s), 969 (m); MS (EI) *m*/*z* (%): 666 (M⁺, 6), 493 (PisoGe⁺, 42), 421 (PisoH⁺, 100); accurate MS (EI) calc. for C₃₆H₄₈N₂GeFeO₂: 666.2320, found 666.2328. Elemental analysis: C₃₆H₄₈N₂GeFeO₂ requires: C 64.61, H 7.23, N 4.18. Found: C 64.36, H 7.15, N 4.33%.

Preparation of [(Piso)Ge(Cl){W(CO)₅}] 4. To a solution of [(Piso)GeCl] (0.30 g, 0.57 mmol) in THF (10 cm³) was added a solution of [W(CO)₅(THF)] (0.23 g, 0.57 mmol) in THF (40 cm³) at -78 °C over 5 min. The resultant colourless solution was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo and the residue extracted with hexane (15 cm³). Filtration, concentration and cooling to -30 °C overnight yielded colourless crystals of 4 (0.27 g, 56%). Mp 138-142 °C; ¹H NMR (400 MHz, C₆D₆, 298 K): δ 0.48 (s, 9 H, Bu^t), 0.96 (d, ${}^{3}J_{\rm HH} = 6.8$ Hz, 6 H, CH(CH₃)₂), 1.01 (d, ${}^{3}J_{\rm HH} = 6.8$ Hz, 6 H, $CH(CH_3)_2$), 1.09 (d, ${}^{3}J_{HH} = 6.8$ Hz, 6 H, $CH(CH_3)_2$), 1.23 (d, ${}^{3}J_{\rm HH} = 6.8$ Hz, 6 H, CH(CH₃)₂), 3.35 (sept, ${}^{3}J_{\rm HH} = 6.8$ Hz, 2 H, $CH(CH_3)_2$), 3.82 (sept, ${}^{3}J_{HH} = 6.8$ Hz, 2 H, $CH(CH_3)_2$), 6.72–6.80 (m, 6 H, Ar–H); ¹³C NMR (75 MHz, C₆D₆, 298 K): δ 22.2 (CH(CH₃)₂), 23.6 (CH(CH₃)₂), 27.7 (CH(CH₃)₂), 28.4 (CH(CH₃)₂), 28.9 (CH(CH₃)₂), 29.1 (CH(CH₃)₂), 29.4 (C(CH₃)₃), 41.9 (C(CH₃)₃), 124.1, 124.7, 125.6, 135.8, 146.3, 146.8 (Ar-C), 185.1 (NCN), 196.0 (CO); IR v/cm⁻¹ (Nujol): 2073 (CO str, s), 1978 (CO str, s), 1948 (CO str, s), 1318 (s), 1260 (s), 1208 (m), 1185 (s), 933 (m); MS (APCI) m/z (%): 815 (M⁺ – Cl, 25), 421 (PisoH⁺, 100). Elemental analysis: C₃₄H₄₃N₂GeClO₅ requires: C 47.95, H 5.09, N 3.29. Found: C 46.96, H 5.14, N 3.19%.

Preparation of [PisoH₂][GeCl₃] 5. To a solution of [PisoH₂]Cl (0.25 g, 0.55 mmol) in THF (20 cm³) was added a solution of GeCl₂·dioxane (0.13 g, 0.55 mmol) in THF (20 cm³) at -78 °C over 5 min. The resultant pale yellow solution was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo and the residue extracted with dichloromethane (5 cm³). Filtration and layering with hexane yielded pale yellow crystals of 5 (0.15 g, 46%). Mp 194–196 °C; ¹H NMR (400 MHz, C₆D₆, 298 K): δ 0.99 (d, ${}^{3}J_{\text{HH}} = 6.8$ Hz, 6 H, CH(CH₃)₂), 1.30 (d, ${}^{3}J_{\rm HH} = 6.8$ Hz, 6 H, CH(CH₃)₂), 1.31 (d, ${}^{3}J_{\rm HH} = 6.8$ Hz, 6 H, CH(CH₃)₂), 1.33 (d, ${}^{3}J_{HH} = 6.8$ Hz, 6 H, CH(CH₃)₂), 1.44 (s, 9 H, Bu^t), 2.86 (2 × overlapping sept, ${}^{3}J_{\rm HH} = 6.8$ Hz, 4 H, CH(CH₃)₂), 5.20 (s, 1 H, CNH), 7.08–7.52 (m, 6 H, Ar– H), 9.60 (s, 1 H, CNH); ¹³C NMR (75 MHz, C₆D₆, 298 K): δ 22.2 (CH(CH₃)₂), 22.5 (CH(CH₃)₂), 25.8 (CH(CH₃)₂), 26.1 (CH(CH₃)₂), 29.1 (CH(CH₃)₂), 29.6 (CH(CH₃)₂), 29.8 (C(CH₃)₃), 40.1 (C(CH₃)₃), 124.7, 125.6, 125.8, 129.6, 131.3, 132.3, 145.6, 146.7 (Ar-C), 175.2 (NCN); IR v/cm⁻¹ (Nujol): 3265 (br, N-H str), 1260 (s), 1095 (m), 802 (m); MS (APCI) m/z (%): 421 (PisoH⁺, 100). Elemental analysis: C₂₉H₄₅Cl₃GeN₂ requires: C 57.99, H 7.55, N 4.66. Found: C 57.68, H 7.38, N 4.48%.

Preparation of [(Giso)GeCl] 6. A solution of Li[Giso] (1.20 g, 2.18 mmol) in THF (20 cm³) was added to a solution of GeCl₂·dioxane (0.54 g, 2.34 mmol) in THF (10 cm³) at -80 °C. The resultant mixture was warmed to room temperature over 4 h and

stirred for a further 2 h. All volatiles were removed in vacuo and the residue extracted into hexane (40 cm³). The extract was concentrated to *ca*. 12 cm³ and slowly cooled to -30 °C to give colourless crystals of 6 (1.07 g, 75%). Mp 198-200 °C; ¹H NMR (400 MHz, 296 K, C_6D_6): δ 0.73–0.90 (m, 6 H, CH_2), 1.21–1.90 (m, 14 H, CH_2), 1.38 (d, ${}^{3}J_{HH} = 6.8$ Hz, 6 H, $CH(CH_3)_2$), 1.45 (d, ${}^{3}J_{HH} = 6.8$ Hz, 6 H, CH(CH₃)₂), 1.53 (d, ${}^{3}J_{HH} = 6.8$ Hz, 6 H, $CH(CH_3)_2$, 1.66 (d, ${}^{3}J_{HH} = 6.8$ Hz, 6 H, $CH(CH_3)_2$), 3.70 (m_c, 2 H, NCH), 3.72 (sept, ${}^{3}J_{HH} = 6.8$ Hz, 2 H, CH(CH₃)₂), 4.17 (sept, ${}^{3}J_{HH} = 6.8 \text{ Hz}, 2 \text{ H}, CH(CH_{3})_{2}$), 7.13–7.29 (m, 6 H, Ar–H); ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ 21.3 (CH(CH₃)₂), 22.1 (CH₂), 24.0 (CH₂), 25.5 (CH(CH₃)₂), 27.2 (CH(CH₃)₂), 27.4 (CH(CH₃)₂), 27.6 (CH(CH₃)₂), 27.8 (CH(CH₃)₂), 33.1 (CH₂), 57.1 (NCH), 122.3, 123.4, 125.1, 137.3, 143.3, 145.9 (Ar-C), 161.2 (backbone CN_3); IR ν/cm^{-1} (Nujol): 1612 (s), 1582 (m), 1162 (m), 1094 (m), 1018 (m), 894 (m), 797 (m); MS (EI 70 eV), m/z (%): 651.3 (M⁺, 3), 616.4 (M⁺ - Cl, 2), 544 (GisoH⁺, 33); accurate MS (EI) calc. for $C_{37}H_{56}ClGeN_3$: 651.3369, found: 651.3374.

Preparation of [(Pipiso)GeCl] 7. A solution of Li[Pipiso] (1.00 g, 2.08 mmol) in THF (20 cm³) was added to a solution of GeCl₂·dioxane (0.51 g, 2.24 mmol) in THF (10 cm³) at -80 °C. The resultant mixture was warmed to room temperature over 4 h and stirred for a further 2 h. All volatiles were removed in vacuo and the residue extracted into hexane (40 cm^3). The extract was concentrated to ca. 12 cm³ and slowly cooled to -30 °C to give colourless crystals of 7 (0.93 g, 77%). Mp 195– 197 °C (decomp.); ¹H NMR (400 MHz, C₆D₆, 298 K): δ 0.83 (d, ${}^{3}J_{\text{HH}} = 7.1$ Hz, 6 H, NCHCH₃), 0.90–1.71 (m, 6 H, CH₂), 1.37 $(d, {}^{3}J_{HH} = 6.8 \text{ Hz}, 6 \text{ H}, CH(CH_{3})_{2}), 1.40 (d, {}^{3}J_{HH} = 6.8 \text{ Hz},$ 6 H, CH(CH₃)₂), 1.44 (d, ${}^{3}J_{HH} = 6.8$ Hz, 6 H, CH(CH₃)₂), 1.62 (d, ${}^{3}J_{HH} = 6.8$ Hz, 6 H, CH(CH₃)₂), 3.62 (sept, ${}^{3}J_{HH} =$ 6.8 Hz, 2 H, CH(CH₃)₂), 3.91 (m_c, 2 H, NCHCH₃), 4.22 (sept, ${}^{3}J_{\rm HH} = 6.8$ Hz, 2 H, CH(CH₃)₂), 7.11–7.28 (m, 6 H, Ar–H); ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ 11.9 (CH₂), 19.8 (CH₃), 21.7 (CH(CH₃)₂), 22.3 (CH(CH₃)₂), 26.6 (CH(CH₃)₂), 26.8 (CH(CH₃)₂), 27.2 (CH(CH₃)₂), 27.6 (CH(CH₃)₂), 28.2 (CH₂), 46.3 (NCHCH₃), 122.3, 123.5, 125.4, 136.9, 143.7, 146.1 (Ar-C), 160.2 (backbone CN₃); IR v/cm⁻¹ (Nujol): 1613 (m), 1577 (m), 1116 (m), 1080 (m), 1054 (m), 801 (s), 759 (s), 666 (m); MS (EI 70 eV), m/z (%): 583.1 (M⁺, 7), 548.2 (M⁺ - Cl, 6), 540.1 (M⁺ - Prⁱ, 7), 475.3 (PipisoH⁺, 5), 432.3 (PipisoH⁺ - Prⁱ, 100); Accurate MS (EI) calc. for C₃₂H₄₈ClN₃Ge: 583.2743, found: 583.2748.

Preparation of [(Priso)Ge][GaCl₄] 8. A solution of GaCl₃ (0.11 g, 0.61 mmol) in toluene (6 cm³) was added to a solution of [(Priso)GeCl] (0.35 g, 0.61 mmol) in toluene (15 cm³) at -50 °C over 5 min. A white crystalline precipitate immediately formed. The resultant suspension was warmed to room temperature, stirred for 2 h and the colourless product was filtered off. X-Ray quality crystals of **8** were obtained by cooling a saturated toluene solution of the compound to 4 °C (0.40 g, 88%). Mp *ca.* 230 °C (decomp.); ¹H NMR (400 MHz, THF-d₈, 298 K): δ 1.06 (d, ³J_{HH} = 6.8 Hz, 12 H, NCH(CH₃)₂), 1.35 (2 x overlapping v br d, 12 H, ArCH(CH₃)₂), 1.42 (br d, ³J_{HH} = 6.8 Hz, 6 H, ArCH(CH₃)₂), 1.48 (br d, ³J_{HH} = 6.8 Hz, 2 H, CH(CH₃)₂), 3.87 (br sept, ³J_{HH} = 6.8 Hz, 2 H, CH(CH₃)₂), 4.05 (sept, ³J_{HH} = 6.8 Hz, 2 H, NCH(CH₃)₂), 7.19–7.31 (m, 6 H, ArC-H); ¹³C{¹H} NMR (100.6 MHz, THF-d₈, 298 K): δ

3–6 and 8

Compound	1	3	4	5	6	8
Empirical formula	C ₅₀ H ₇₀ GeN ₄	C ₃₆ H ₄₈ FeGeN ₂ O ₂	C ₃₄ H ₄₃ ClGeN ₂ O ₅ W	C ₂₉ H ₄₅ Cl ₃ GeN ₂	C ₃₇ H ₅₆ ClGeN ₃	C ₃₁ H ₄₈ Cl ₄ GaGeN ₃
$M_{\rm r}$	799.69	669.20	851.59	600.61	650.89	746.83
T/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_{1}/c$
a/Å	10.697(2)	22.080(4)	10.592(2)	10.665(2)	10.586(2)	16.025(3)
b/Å	15.758(3)	16.626(5)	16.684(3)	18.049(4)	18.950(4)	12.550(3)
c/Å	27.692(6)	19.551(5)	21.013(4)	17.156(3)	18.311(4)	19.558(4)
β/°	91.22(3)	109.60(1)	101.67(3)	102.93(3)	103.50(3)	110.87(3)
$V/Å^3$	4666.7(16)	6761(3)	3636.6(13)	3218.7(11)	3571.9(11)	3675.4(13)
Ζ	4	8	4	4	4	4
$D_{\rm c}/{\rm Mg}~{\rm m}^{-3}$	1.138	1.315	1.555	1.239	1.210	1.350
μ (Mo-K α)/mm ⁻¹	0.692	1.351	4.100	1.220	0.961	1.865
F(000)	1720	2816	1696	1264	1392	1544
No. reflections collected	28378	48937	26171	18619	34978	15624
No. independent reflns (R_{int})	8212 (0.1827)	13741 (0.0576)	7377 (0.0613)	6527 (0.0900)	6257 (0.0895)	8003 (0.0311)
Final $R1$ ($I > 2\sigma(I)$) and	R1 = 0.0840 wR2 =	R1 = 0.0675	R1 = 0.0335 wR2 =	R1 = 0.0572	R1 = 0.0724	R1 = 0.0353
wR2 indices (all data)	0.1501	wR2 = 0.01418	0.0788	wR2 = 0.1294	wR2 = 0.1621	wR2 = 0.0746

21.2 (NCH(CH₃)₂), 21.8 (ArCH(CH₃)₂), 25.2 (ArCH(CH₃)₂), 26.0 (ArCH(CH₃)₂), 26.4 (ArCH(CH₃)₂), 26.7 (ArCH(CH₃)₂), 47.3 (NCH(CH₃)₂), 122.0, 122.8, 124.6, 136.4, 143.0, 145.2 (Ar–*C*), 161.0 (backbone *C*N₃), N.B. one ArCH(*C*H₃)₂ resonance obscured by solvent resonance; IR ν /cm⁻¹ (Nujol): 1603 (s), 1538 (m), 1261 (m), 1170 (m), 1105 (m), 805 (m), 759 (m); MS (EI), *m*/*z* (%): 420.4 (PrisoH⁺, 100).

X-Ray crystallography

Crystals of 1, 3–6 and 8 suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)³² using all unique data. Hydrogen atoms have been included in calculated positions (riding model) for all structures. Crystal data, details of data collections and refinement are given in Table 1.

CCDC reference numbers 675662-675668.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b801168k

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- 26 It is of note that the attempted reduction of a co-crystallised mixture, [(Priso)GeCl_{0.4}/I_{0.6}], with the gallium(1) heterocycle, [(Giso)Ga:],¹¹ led instead to an oxidative insertion reaction and the formation of the germanium gallyl complex mixture, [(Priso)GeGa(I_{0.6}/Cl_{0.4})(Giso)]. Details of the crystallographic characterisation of this mixture are included in the ESI†.
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