Group 13 metal(I) and (II) guanidinate complexes: effect of ligand backbone on metal oxidation state and coordination sphere†‡

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Reactions of lithium salts of the bulky guanidinate and phosphaguanidinate ligands, $[ArNC(ER_2)NAr]^-$ (ER_2 = NPr^i_2 (Priso$^-$), *cis*-$NC_5H_8Me_2$-2,6 (Pipiso$^-$) or $P(C_6H_{11})_2$ (PGiso$^-$); Ar = $C_6H_3Pr^i_2$-2,6), with group 13 metal(I) halides have been carried out. All reactions with TlBr led to monomeric thallium(I) complexes, [Tl{$ArNC(ER_2)NAr$}], in which the ligand chelates the metal in an *N*,arene-fashion. The reactions with InCl led to mixed results and the isolation of the dimeric indium(II) complexes, [{InCl(Priso)}$_2$] and [{InCl(Pipiso)}$_2$], and the monomeric indium(I) species, [In(Pipiso)] and [In(PGiso)]. The ligands of the latter two complexes exhibit differing coordination modes in the solid state, namely *N*,*N*′-chelating and *N*,arene-chelating, respectively. The reactions with "GaI" were less successful and gave only low yields of the poorly characterised gallium(II) complexes, [{GaI(Priso)}$_2$] and [{GaI(Pipiso)}$_2$]. This study has shown that the related ligand, $[ArNC\{N(C_6H_{11})_2\}NAr]^-$ (Giso$^-$) is superior for the stabilisation of group 13 metal(I) complexes. The oxidative additions of I_2 or $SiMe_3I$ to one such complex, [Ga(Giso)], yielded the gallium(III) compounds, [GaI_2(Giso)] and [GaI($SiMe_3$)(Giso)].

Introduction

The low oxidation state chemistry of all the group 13 metals is now well developed.[1–5] In this field sterically bulky amide ligands have proved especially useful for the stabilisation of complexes with the group 13 metals in either the +1, +2 or mixed oxidation states. The vast majority of such complexes are, however, polynuclear. Recent efforts have been directed towards the formation of mononuclear metal(I) amide systems as these possess a stereochemically active singlet lone pair at the metal which can lead to their use as unconventional Lewis bases in the formation of heterometallic species. Although bulky monodentate amides, *e.g.* –N($SiMe_3$)-{$C_6H_3(C_6H_2Me_3$-2,4,6)$_2$-2,6}, have rarely been used to prepare monomeric metal(I) amides,[6] chelating amides, *e.g.* β-diketiminates[7] (as in **1**[8]) and doubly reduced diazabutadienes (as in **2**[9]), are more commonly employed for this task. Complexes **1** and **2** have been described as group 13 analogues of the important *N*-heterocyclic carbene (NHC) class of ligand and their coordination and other chemistry has been widely explored.[2,10]

One of our contributions to this area centres on the use of bulky guanidinates and amidinates as potentially chelating ligands for the formation of group 13 metal(I) amides.[11–15] Preliminary studies have suggested that the metal involved, and subtle changes to the steric and electronic properties of the enlisted ligands, can lead to significant variations in the complex type obtained. For example, when alkali metal salts of the bulky guanidinate ligand, $[ArNC\{N(C_6H_{11})_2\}NAr]^-$ Giso$^-$ (Ar = $C_6H_3Pr^i_2$-2,6), were reacted with metal(I) halides, either *N*,*N*′- or *N*,arene-chelated complexes (**3–5**, respectively) were obtained.[11] Apparently, the larger size of the metal in **5** circumvents *N*,*N*′-chelation by the small bite angle Giso$^-$ ligand in that case. Similar reactions with salts of the less bulky, less N-electron rich amidinate, $[ArNC(Bu^t)NAr]^-$ (Piso$^-$), led to different outcomes, namely the formation of the indium or thallium *N*,arene-chelated complexes, **6** and **7** (which co-crystallise with the free ligand, PisoH), and the dimeric gallium(II) complex, **8**; the latter *via* disproportionation.[12,13] The differences here probably result from the smaller backbone substituent on Piso$^-$ (relative to Giso$^-$) which reduces its propensity to form the *N*,*N*′-chelated isomers of **6** and **7**. In addition, the smaller ligand presumably provides less protection towards disproportionation of the likely gallium(I) intermediate to **8** (*viz.* [Ga(Piso)]), than Giso$^-$ provides for **3**. Considering that **3** and **4** have shown utility as "NHC like" ligands in the formation of novel transition metal complexes,[16] we wished to further explore the effect that the backbone substituent of guanidinate and phosphaguanidinate ligands, $[ArNC(ER_2)NAr]^-$ (E = N or P), has on the nature of

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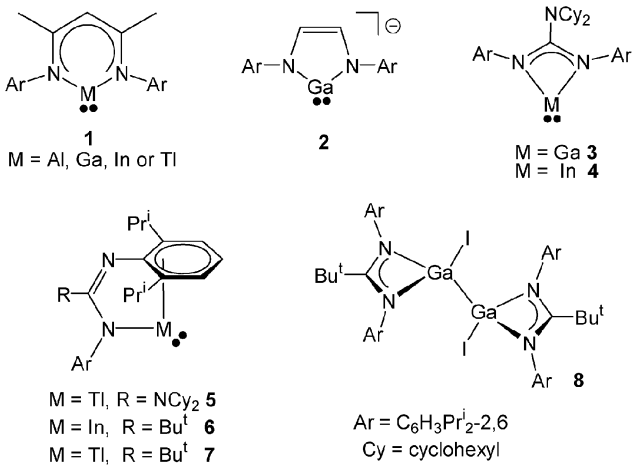
† Dedicated to Professor Jerry Atwood on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Synthesis, spectroscopic and crystallographic data for [InCl{ArNC-(p-C_6H_4Me)NAr}$_2$]·(hexane). ORTEP diagram for **15**. Crystallographic data for compounds **9–16**. CCDC reference number 677872 and 679098–679104. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718799h

their complexes with low oxidation state group 13 centres. The results of this study are reported herein.



Results and discussion

In the early stages of this study a range of amidinate salts, M[ArNC(R)NAr]$^{-}$ (M = Li, Na or K; R = alkyl or aryl), were reacted with indium(I) and gallium(I) halides. Despite the bulky *N*-aryl substituents of the amidinates used, these reactions almost exclusively led to disproportionation and the formation of metal(III) amidinate complexes, *e.g.* [In^{III}Cl{ArNC(*p*-C$_6$H$_4$Me)NAr}$_2$],[17] unless the amidinate backbone substituent was a tertiary alkyl group, *e.g.* as in **6**. As a result, attention shifted to guanidinate ligands that have a similar steric bulk to the Giso^{-} ligand, the stabilising properties of which have already been demonstrated. The ligands chosen for this study are depicted in Fig. 1. Priso^{-} was chosen to examine the effect a slight reduction in guanidinate backbone bulk (relative to Giso^{-}) would have on the outcome of its reactions with group 13 halides. Pipiso^{-} (the steric bulk of which is intermediate between that of Priso^{-} and Giso^{-}) was chosen as it was expected to introduce a degree of asymmetry to its group 13 complexes. PGiso^{-} was chosen as its PCy$_2$ substituent is pyramidal as opposed to the planar NCy$_2$ group of Giso^{-}. Consequently, its P-lone pair cannot participate in delocalised π-bonding within the ligand backbone, as the corresponding *N*-lone pair of Giso^{-} can potentially do.

The reactions of TlBr with lithium salts of Priso^{-}, Pipiso^{-} and PGiso^{-} were carried out and all led to the formation of monomeric complexes, **9–11** (Scheme 1), in which the guanidinate ligand chelates the thallium(I) centre in an *N*,arene-fashion (*cf.* **5** and **7**). The ^{1}H and ^{13}C NMR spectra of **9** and **10** are more symmetrical than expected and exhibit broad, poorly resolved signals. A similar observation was made for the spectra of **5**.[11] In that case it was suggested that a fluxional process was occurring in solution at room temperature in which the thallium centre exchanges between the two *N*-centres of the ligand. It is not known if this occurs *via.* an *N*,*N*-chelated intermediate but the exchange must be a low energy process as the NMR spectra of **5** (and **9** and **10**) remained largely unchanged down to −90 °C. In contrast, the spectra for **11** are well resolved and are consistent with its proposed structure, as has previously been reported to be the case for the amidinate complex, **7**.[12] These differences likely result from the fact that the guanidinate ligands of **5**, **9** and **10** (unlike the amidinate and phosphaguanidinate ligands of **7** and **11**, respectively) have resonance structures possessing two C–NAr single bonds, *viz.* [R$_2$N^{+}=C{C–N^{-}Ar}$_2$], thus facilitating their isomerisation by rotation about these bonds.

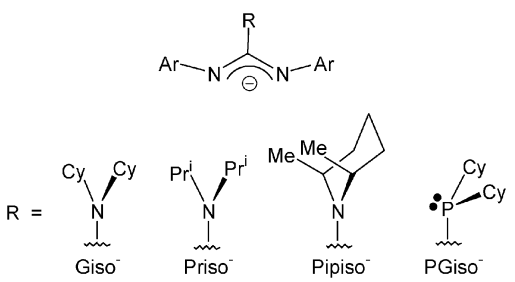
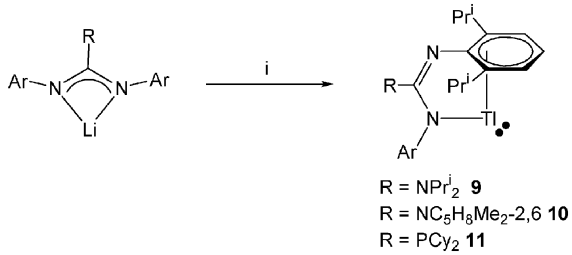


Fig. 1 Ligands used in this study.



Scheme 1 *Reagents*: (i) TlBr, toluene, −LiBr.

The X-ray crystal structures of **9–11** were all determined and their molecular structures are depicted in Fig. 2. Two crystallographically independent molecules were refined in the asymmetric unit of the structure of **10**. As these exhibit very similar metrical parameters, comment on the geometry of only one will be passed here. The thallium centre of each monomeric complex is coordinated in an η^{1}-fashion by the amido centre (N(1)) of its guanidinate ligand. The metal also has an approximately η^{3}-interaction with the aryl substituent of N(2). An examination of the magnitudes of the C(1)–N bond lengths of the guanidinate ligands suggests a low degree of delocalisation over their N$_3$C backbones (see Table 1). As these structures are closely related to those of **5** and **7**, it seems that for thallium(I), *N*,arene-chelation of the metal by the ligand is certainly preferred over *N*,*N*′-chelation, which has previously been exhibited by the smaller gallium(I) and indium(I) centres of **3** and **4**. In addition, in the preparation of all thallium(I) complexes in this study, there has been no evidence of disproportionation processes leading to thallium(II) or (III) complexes. This is in line with the redox stability of thallium(I), relative to that of indium(I) and gallium(I).

The reactions of lithium salts of the guanidinates used in this study with InCl led to more diverse outcomes than those with TlBr. Disproportionation (as evidenced by In metal deposition) occurred in the reaction with Li[Priso] to give a low to moderate yield of the indium(II) dimeric complex, **12**, and a significant amount of the free guanidine, PrisoH (Scheme 2). Disproportionation was also evident in the

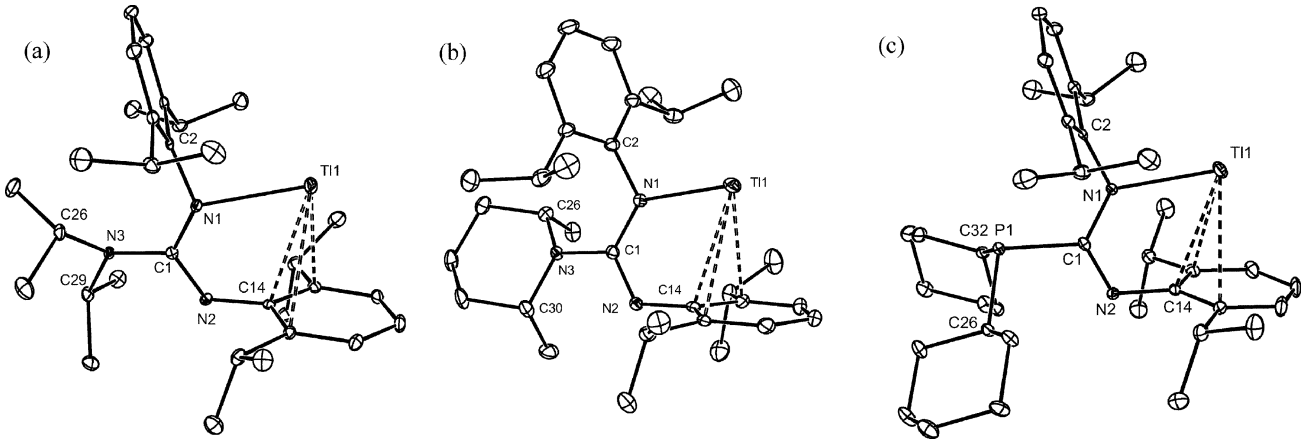


Fig. 2 Molecular structures of (a) **9**, (b) **10** and (c) **11** (25% thermal ellipsoids are shown; hydrogen atoms omitted for sake of clarity).

reaction with Li[Pipiso] which afforded a low yield of the indium(II) complex, **13**, but also the *N*,*N*′-chelated indium(I) complex, **14**. An indium(I) complex, **15**, was the only isolated product from the reaction with Li[PGiso], but in this case it was isolated as the *N*,arene-chelated isomer.

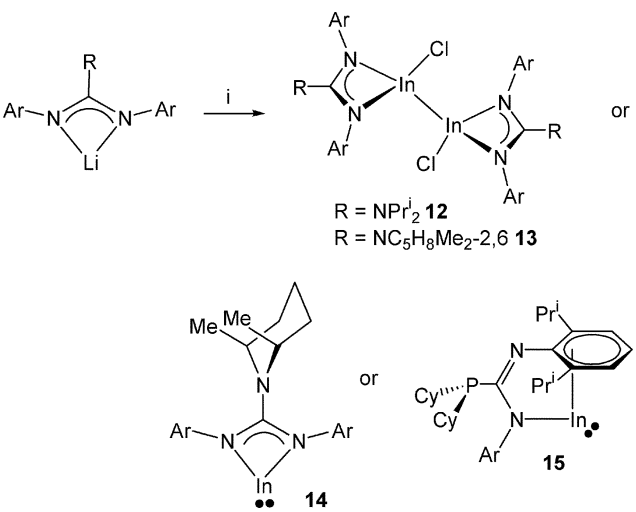
These results highlight the more redox active nature of indium(I) than thallium(I) and show that subtle differences in ligand sterics can have a significant effect on the product formed. Despite what could be considered as only a small difference in the sterics of the Giso$^-$ and Priso$^-$ ligands, the former stabilises the indium(I) complex, **4** (mp 168–169 °C decomp.), whereas the related complex, [In(Priso)], is apparently unstable with respect to disproportionation, to form **12**. The fact that both indium(I) and (II) products were isolated from the reaction involving Pipiso$^-$, which is of intermediate steric bulk, adds weight to this proposal. Interestingly, although PGiso$^-$ appears to have a comparable ability to stabilise indium(I) as does its apparently similarly bulky counterpart, Giso$^-$, it acts as an *N*,arene-chelating ligand in **15** as opposed to the *N*,*N*′-chelating Giso$^-$ ligand in **4**. This could be due to the fact that the P-centre in PGiso$^-$ can only be pyramidal whereas the amino *N*-centre of Giso$^-$ is normally planar. This gives rise to both electronic and spatial differences between the ligands.

The spectroscopic data for **12–15** largely reflect their solid state structures which were all determined by X-ray crystallographic studies. The molecular structures of **12–15** are shown in Fig. 3–5. Two crystallographically independent molecules were refined in the asymmetric unit of the structure of **12**. The geometries of both are similar and so only the metrical parameters for one are included in the caption of Fig. 3. As **15** is isomorphous with **11**, its structure has been included in the supplementary material, though relevant metrical parameters for this compound are included in Table 1. These show the phosphaguanidinate ligand to be effectively localised. The structures of both **12** and **13** reveal them to be dimeric (*cf*. the structure of **8**) with similar In^{II}–In^{II} distances that lie within the normal range[18] and can be compared with related complexes, *e.g.* [{In^{II}Cl[ArNC(H)C(H)NAr]}$_2$] (2.7280(9) Å[19]). In addition, the In-N distances in both complexes are unexceptional (*cf*. 2.168 Å mean in [{In^{II}Cl-[ArNC(H)C(H)NAr]}$_2$][19]) and the atom separations within the coordinated NCN fragments of the complexes are suggestive of significant delocalisation. The backbone amino substituents of the guanidinate ligands are removed from being co-planar with their attached indium heterocycles (dihedral angles between least squares planes: **12** = 27.5, **13** = 32.3° mean) which leads to a lower degree of delocalisation of their *N*-lone pairs into the guanidinate framework than would be expected if they were co-planar. This is manifested by significantly longer bonds from the backbone carbon centres to the amino *N*-atoms than to the metal coordinated nitrogens.

The structure of **14** is very similar to that of **4**. It possesses a two-coordinate indium centre that has no significant inter- or intramolecular interactions. The indium coordinated NCN

Table 1 Selected bond lengths (Å) and angles (°) for **9–11** and **15**

	9	**10**	**11**	**15**
N–M	2.429(2)	2.443(3)	2.417(3)	2.2829(19)
N(1)–C(1)	1.358(4)	1.354(4)	1.348(4)	1.360(3)
N(2)–C(1)	1.319(4)	1.313(5)	1.316(5)	1.305(3)
N(3)–C(1) or P(1)–C(1)	1.402(4)	1.410(4)	1.882(4)	1.885(2)
M–C(14)	2.903(3)	2.916(3)	2.884(4)	2.799(4)
N(1)–C(1)–N(2)	122.4(3)	123.2(3)	123.6(3)	123.52(18)



Scheme 2 *Reagents*: (i) InCl, toluene, –LiCl.

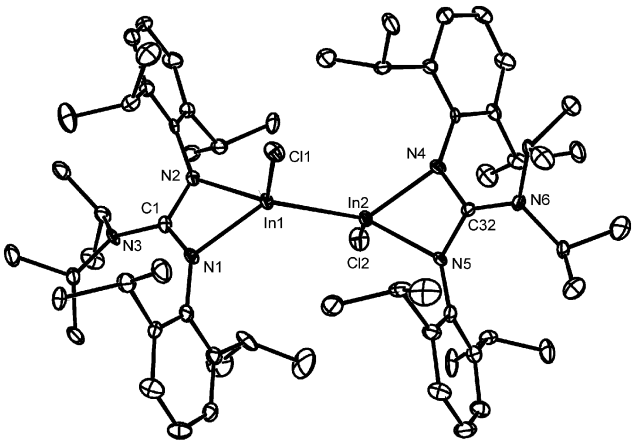


Fig. 3 Molecular structure of **12** (25% thermal ellipsoids are shown; hydrogen atoms omitted for sake of clarity). Selected bond lengths (Å) and angles (°): In(1)–N(2) 2.177(10), In(1)–N(1) 2.194(9), In(1)–Cl(1) 2.392(3), In(1)–In(2) 2.7196(13), N(1)–C(1) 1.316(14), C(1)–N(2) 1.346(14), C(1)–N(3) 1.416(13), In(2)–N(5) 2.171(10), In(2)–N(4) 2.185(9), In(2)–Cl(2) 2.375(3), N(4)–C(32) 1.356(14), N(5)–C(32) 1.371(13), N(6)–C(32) 1.339(14); N(2)–In(1)–N(1) 61.3(3), N(2)–In(1)–Cl(1) 113.3(3), N(1)–In(1)–Cl(1) 106.7(3), N(2)–In(1)–In(2) 121.9(3), N(1)–In(1)–In(2) 129.9(3), Cl(1)–In(1)–In(2) 113.75(9), N(1)–C(1)–N(2) 113.5(10), N(5)–In(2)–N(4) 61.4(3), N(5)–In(2)–Cl(2) 108.8(3), N(4)–In(2)–Cl(2) 113.6(3), N(5)–In(2)–In(1) 125.6(2), N(4)–In(2)–In(1) 118.8(3), Cl(2)–In(2)–In(1) 116.90(10), N(4)–C(32)–N(5) 109.3(9).

fragment is delocalised with C–N distances (1.345(3) Å) that are only slightly shorter than the backbone C–N(amino) separation of 1.375(5) Å. Both the In–N distances of **14** are substantially longer than those in **12** and **13**, as would be expected considering the lower indium oxidation state in the former.

The reactions of lithium salts of the three guanidinates used in this study with "GaI" were carried out using toluene as a solvent. In all cases the reactions led to many products as determined from the ^{1}H NMR spectra of the product mixtures. None of

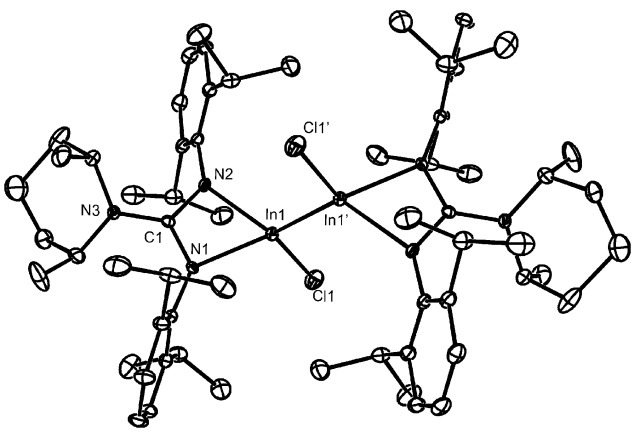


Fig. 4 Molecular structure of **13** (25% thermal ellipsoids are shown; hydrogen atoms omitted for sake of clarity). Selected bond lengths (Å) and angles (°): In(1)–N(1) 2.162(3), In(1)–N(2) 2.173(3), In(1)–Cl(1) 2.3752(12), In(1)–In(1)′ 2.7085(7), N(1)–C(1) 1.344(4), C(1)–N(2) 1.344(5), C(1)–N(3) 1.375(5); N(1)–In(1)–N(2) 61.17(12), N(1)–In(1)–Cl(1) 106.62(10), N(2)–In(1)–Cl(1) 117.87(9), N(1)–In(1)–In(1)′ 127.46(9), N(2)–In(1)–In(1)′ 118.06(8), Cl(1)–In(1)–In(1)′ 115.24(4), N(2)–C(1)–N(1) 110.3(3). Symmetry operation: ′ $-x + 1, -y + 1, -z + 1$.

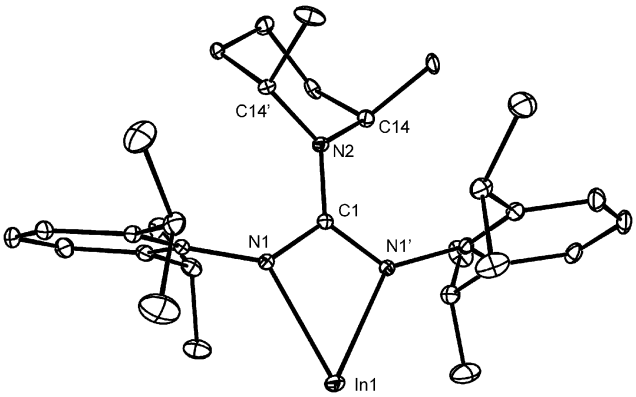
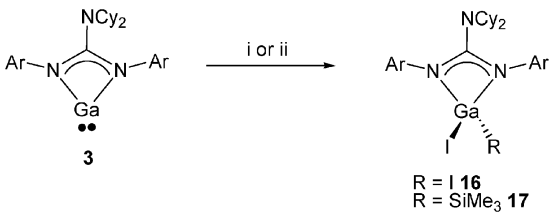


Fig. 5 Molecular structure of **14** (25% thermal ellipsoids are shown; hydrogen atoms omitted for sake of clarity). Selected bond lengths (Å) and angles (°): In(1)–N(1) 2.298(2), N(1)–C(1) 1.345(3), N(2)–C(1) 1.375(5); N(1)–In(1)–N(1)′ 57.90(11), C(1)–N(1)–In(1) 95.24(17), N(1)–C(1)–N(1)′ 111.6(3). Symmetry operation: ′ $-x + 1, y, -z + 3/2$.

these products could be identified in the reaction with Li[PGiso]. The only products identified from the reactions with Li[Priso] and Li[Pipiso] were the dimeric gallium(II) complexes, [{GaI(Priso)}$_2$] (yield <10%, colourless crystals, mp 124–128 °C decomp.) and [{GaI(Pipiso)}$_2$] (yield <10%, colourless crystals, mp 186–188 °C decomp.), which X-ray crystallographic studies proved to be isostructural to **8**, **12** and **13**. However, the quality of the structures proved too low for inclusion here. Moreover, many attempts to crystallise these low yield products free of impurities met with failure and as a result meaningful assignments of their spectroscopic data could not be made. These results do, however, show that the NCy_2 backbone substituent of Giso$^-$ gives that ligand a greater ability to stabilise gallium(I) (as in **3**, mp 158–159 °C[11]) than the other ligands used in this study.

Despite the greater stabilising ability of the Giso$^-$ ligand, the 1 : 1 reaction of its lithium salt with "GaI" gave only a 35% yield of **3** and no other identifiable products.[11] In an attempt to increase the yield of this reaction, Li[Giso] was reacted with 4 equivalents of "GaI" in toluene. However, upon work-up compound **3** was not found to be present in the reaction mixture but instead a low yield (<5%) of the gallium(III) compound, [GaI_2(Giso)] **16**, was formed. It seems likely that this reaction proceeds *via* transfer of iodine from the excess "GaI" to the gallium centre of initially formed [Ga(Giso)] **3**, with concomitant deposition of gallium metal. A rational synthesis of **16** was devised whereby **3** was treated with one equivalent of diiodine which oxidatively added to its gallium(I) centre to give **16** in low yield (Scheme 3). In order to test the generality of oxidative additions to **3**, it was also treated with one equivalent of $SiMe_3I$ which gave a good yield of **17**.



Scheme 3 *Reagents*: (i) I_2, toluene; (ii) $SiMe_3I$, toluene.

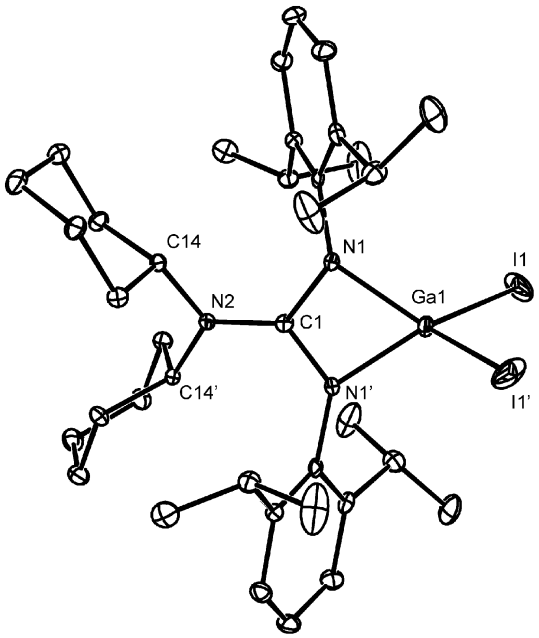


Fig. 6 Molecular structure of **16** (25% thermal ellipsoids are shown; hydrogen atoms omitted for sake of clarity). Selected bond lengths (Å) and angles (°): I(1)–Ga(1) 2.5090(9), Ga(1)–N(1) 1.953(5), N(1)–C(1) 1.372(7); N(1)–Ga(1)–N(1)′ 68.6(3), N(1)–Ga(1)–I(1)′ 123.83(15), N(1)–Ga(1)–I(1) 115.54(15), I(1)′–Ga(1)–I(1) 106.57(6), N(2)–C(1)–N(1)′ 126.7(3). Symmetry operation: ′ $-x + 3/2, -y + 1/2, z$.

Both compounds were spectroscopically characterised and the X-ray crystal structure of **16** obtained (Fig. 6). This shows the complex to be monomeric with a distorted tetrahedral gallium coordination geometry and Ga–I distances in the known range.[18] The geometry of the delocalised Giso$^-$ ligand in **16** is very similar to that in **3**, but its Ga–N bond lengths are substantially shorter, as would be expected for a gallium(III) compound.

Conclusion

In summary, the reactions of two bulky guanidinates (Priso$^-$ and Pipiso$^-$) and one phosphaguanidinate (PGiso$^-$) towards a series of group 13 metal(I) halides have been carried out. The outcomes of these reactions have been compared to those involving a related guanidinate (Giso$^-$). The study shows that subtle changes to the sterics and electronics of the backbone substituent ($-ER_2$) of the general unit, [ArNC(ER_2)NAr]$^-$ (E = N or P), can have a marked effect on the stability, metal oxidation state and ligand coordination mode of the product obtained. The Giso$^-$ ligand is the most adept at stabilising group 13 metal(I) complexes, and complexes in which the metal centre is *N*,*N*′-chelated. 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 section

General considerations

All manipulations were carried out using standard Schlenk and glove box techniques under atmospheres of high purity argon or dinitrogen. Hexane and toluene were distilled over molten potassium metal. 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. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DXP400 spectrometer and were referenced to the resonances of the solvent used. ^{31}P{^{1}H} NMR spectra were recorded on a Jeol Eclipse 300 spectrometer and were referenced to external 85% H_3PO_4. Reproducible microanalyses could not be obtained for several complexes because of their very air and moisture sensitive nature. The ^{1}H NMR spectra for all such complexes indicate that they have bulk purities of >95%. Li[Priso],[15b] Li[Pipiso][20] and [Ga(Giso)][11] were synthesised by variations of literature procedures. PGisoH was prepared by an equivalent procedure to that used to prepare GisoH.[11] All other reagents were used as received.

Preparation of [Tl(*N*,arene-Priso)] 9

TlBr (0.94 g, 3.32 mmol) was added to a cooled slurry of Li[Priso] (1.36 g, 2.89 mmol) in toluene (30 cm^3) at −80 °C. The mixture was warmed to ambient temperature overnight with stirring. It was then filtered and volatiles removed from the filtrate under reduced pressure. The residue was extracted with hexane (40 cm^3), concentrated to *ca.* 12 cm^3 and slow cooled to −30 °C to afford yellow crystals of **9** (yield 1.08 g, 56%); mp 170–172 °C (*ca.* 190 °C decomp.). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.30 (d, very broad, 12 H, CH(CH_3)$_2$), 1.44 (broad d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 1.46 (broad d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 3.65–3.77 (m of overlapping sept, $^3J_{HH}$ = 6.8 Hz, 6 H, C*H*(CH$_3$)$_2$), 6.96–7.04 (m, very broad, 2 H, ArH), 7.22–7.33 (m, 4 H, Ar*H*); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 23.1 (NCH(*C*H$_3$)$_2$), 22.7 (very broad, ArCH(*C*H$_3$)$_2$), 28.3 (very broad, Ar*C*H(CH$_3$)$_2$), 49.0 (N*C*H(CH$_3$)$_2$), 122.5 (very broad, Ar*C*), 125.2 (very broad, Ar*C*), 143.3 (very broad, Ar*C*), 164 (very broad, backbone *C*N$_3$); no other Ar*C* resonances were observed; IR ν/cm^{-1} (Nujol): 1612 (s), 1582 (m), 1256 (m), 1149 (m), 1045 (m), 952 (m), 851 (m), 756 (s); MS (EI 70 eV), *m*/*z* (%): 668.4 (M + H$^+$, 1), 464.5 (PrisoH, 100); accurate MS (EI) calc. for $C_{31}H_{48}N_3{}^{205}$Tl: 668.3665, found: 668.3691.

Preparation of [Tl(*N*,arene-Pipiso)] 10

TlBr (0.78 g, 2.74 mmol) was added to a cooled slurry of Li[Pipiso] (1.10 g, 2.28 mmol) in toluene (30 cm^3) at −80 °C. The mixture was warmed to ambient temperature overnight with stirring. It was then filtered and volatiles removed under reduced pressure. The residue was extracted with hexane (20 cm^3), concentrated to *ca.* 5 cm^3 and slow cooled to −30 °C to afford yellow crystals of **10** (yield 0.98 g, 63%); mp 144–146 °C (*ca.* 170 °C decomp.). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.24–1.53 (m, very broad, 22 H, CH(CH_3)$_2$, NCHCH_3, CH_2), 1.55 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 1.73–1.90 (m, very broad, 2 H, CH_2), 3.73 (m$_c$, 4 H, C*H*(CH$_3$)$_2$), 4.14 (m$_c$, 2 H, NC*H*CH$_3$), 6.93–7.11 (m, very broad, 2 H, Ar*H*), 7.24–7.35 (m, 4 H, Ar*H*); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K):

δ 15.4 (CH_2), 21.8 (CH_3), 23.4 (broad, $CH(CH_3)_2$), 28.3 (broad, $CH(CH_3)_2$), 30.9 (CH_2), 49.0 ($NCHCH_3$), 122.8 (very broad), 124.3 (very broad), 141.0 (very broad), 144.3 (very broad) (Ar*C*), 164.8 (very broad, backbone CN_3); IR ν/cm^{-1} (Nujol): 1615 (m), 1584 (m), 1227 (m), 1193 (m), 1143 (m), 1118 (m), 1018 (m), 907 (m), 770 (m), 757 (m); MS (EI 70 eV), *m*/*z* (%): 679.1 (M^+, 1), 636.1 ($M^+ - {}^i$Pr, 3), 432.3 (PipisoH − Pr^i, 100); accurate MS (EI) calc. for $C_{32}H_{49}N_3Tl_1$ (MH^+): 679.3587 found: 679.3580.

Preparation of [Tl(*N*,arene-PGiso)] 11

Bu^{n}Li (0.65 cm^3 of a 1.6 m solution in hexanes, 1.04 mmol) was added to a solution of PGisoH (0.57 g, 1.02 mmol) in toluene (20 cm^3) at 20 °C and the resultant solution stirred for 1 h. Solid TlBr (0.35 g, 1.22 mmol) was then added to the solution at −80 °C. The mixture was slowly warmed to ambient temperature and stirred overnight. All volatiles were removed under reduced pressure, the residue extracted into hexane (60 cm^3) and filtered. The filtrate was concentrated to *ca.* 15 cm^3 and stored at −30 °C to give light yellow crystals of **11** (yield 0.18 g, 23%); mp 70 °C (decomp.). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.20 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH(C-H_3)$_2$), 1.34 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH(CH_3)$_2$), 1.41 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH(CH_3)$_2$), 1.61 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH(CH_3)$_2$), 1.36–2.28 (m, 20 H, CH_2), 2.40 (m, 2 H, C*H*P), 3.58 (sept, $^3J_{HH}$ = 6.7 Hz, 2 H, C*H*(CH$_3$)$_2$), 3.65 (sept, $^3J_{HH}$ = 6.7 Hz, 2 H, C*H*(CH$_3$)$_2$), 6.90–7.45 (m, 6 H, Ar*H*); ^{31}P NMR (121 MHz, C_6D_6, 298 K): δ 3.3; ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 23.0, 23.5, 25.4, 28.5 (CH(*C*H$_3$)$_2$), 27.2, 28.1, 28.2, 29.4, 33.1 (d, $^2J_{CP}$ = 17.1 Hz) (*C*H$_2$), 27.4, 28.3 (*C*H(CH$_3$)$_2$), 34.7 (d, $^1J_{CP}$ = 22.4 Hz, *C*HP), 123.4, 123.6, 124.3, 127.4, 138.3, 139.2, 144.0, 155.9 (Ar*C*), 170.0 (br, backbone *C*N$_2$); MS (EI 70 eV), *m*/*z* (%): 764.4 (M^+, 5), 721.4 (M^+ − Pr^i, 15), 477.3 (M^+ − Cy$_2$P, 35); IR ν/cm^{-1} (Nujol): 1566 (m), 1336 (m), 1313 (m), 1257 (m), 1178 (m), 914 (m); accurate MS (EI) calc. for $C_{37}H_{56}N_2P^{203}Tl$: 761.3821 ($M - H^+$), found 761.3830; $C_{37}H_{55}N_2PTl$ requires C 58.15, H 7.39, N 3.66%; found C 58.07, H 7.14, N 3.64%.

Preparation of [{InCl(*N*,*N*′-Priso)}$_2$] 12

InCl (0.30 g, 2.00 mmol) was added to a slurry of Li[Priso] (0.80 g, 1.70 mmol) in toluene (25 cm^3) at −80 °C. The mixture was warmed to room temperature and stirred overnight. It was then filtered and all volatiles were removed under reduced pressure. The residue was extracted into hexane (50 cm^3), concentrated to *ca.* 20 cm^3 and slow cooled to −30 °C to give colourless crystals of **12** (yield 0.33 g, 32%); mp 178–180 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.91 (d, $^3J_{HH}$ = 6.8 Hz, 24 H, NCH(CH_3)$_2$), 1.42 (d, $^3J_{HH}$ = 6.8 Hz, 24 H, CH(CH_3)$_2$), 1.28–1.86 (m, very broad, 24 H, CH(CH_3)$_2$), 3.90–4.12 (m of overlapping sept, 12 H, C*H*(CH$_3$)$_2$), 7.03–7.28 (m, 12 H, Ar*H*); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 22.0 (ArCH(*C*H$_3$)$_2$), 22.4 (NCH(*C*H$_3$)$_2$), 26.4 (ArCH(*C*H$_3$)$_2$), 26.7 (Ar*C*H(CH$_3$)$_2$), 49.2 (N*C*H(CH$_3$)$_2$), 122.5, 124.3, 139.2, 143.6 (very broad, Ar*C*), 164.9 (backbone *C*N$_3$); IR ν/cm^{-1} (Nujol): 1611 (s), 1581 (m), 1257 (m), 1154 (m), 1109 (s), 1047 (m), 799 (s), 751 (m); MS (CI), *m*/*z* (%): 462.5 (Priso$^-$ − H, 100).

Preparation of [{InCl(*N*,*N*′-Pipiso)}$_2$] 13 and [In(*N*,*N*′-Pipiso)] 14

InCl (0.33 g, 2.20 mmol) was added to a slurry of Li[Pipiso] (0.92 g, 1.91 mmol) in toluene (30 cm^3) at −80 °C. The mixture was warmed to ambient temperature and stirred over night. It was then filtered and all volatiles were removed under reduced pressure. The residue was extracted into hexane (50 cm^3), concentrated to *ca.* 30 cm^3 and slowly cooled to −30 °C to give colourless crystals of **13**. The supernatant was further concentrated to *ca.* 5 cm^3 to give colourless crystals of **14**. Data for **13**: (yield 0.26 g, 22%), mp 172–173 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.75 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, NCHCH_3), 1.25–1.73 (m, 36 H, CH(CH_3)$_2$, CH_2), 1.47 (d, $^3J_{HH}$ = 6.8 Hz, 24 H, CH(CH_3)$_2$), 3.97 (m$_c$, 12 H, C*H*(CH$_3$)$_2$, NC*H*CH$_3$), 7.05–7.27 (m, 12 H, Ar*H*); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 13.1 (*C*H$_2$), 20.9 (*C*H$_3$), 23.0 (CH(-*C*H$_3$)$_2$), 27.5 (CH(*C*H$_3$)$_2$), 28.0 (*C*H(CH$_3$)$_2$), 29.3 (*C*H$_2$), 48.4 (N*C*HCH$_3$), 122.3, 123.7, 125.5, 140.3, 142.6, 144.7 (Ar*C*), 164.3 (backbone *C*N$_3$); IR ν/cm^{-1} (Nujol): 1616 (m), 1584 (m), 1113 (m), 1076 (m), 1021 (m), 931 (m), 798 (s), 754 (m); MS (EI 70 eV), *m*/*z* (%): 589.3 (M^+, 1), 546.2 (M^+ − Pr^i, 2), 432.3 (PipisoH − Pr^i, 100).

Data for **14**: (yield 0.20 g, 18%); mp 119–121 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.83 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, NCHCH_3), 0.90–1.56 (m, 6 H, CH_2), 1.44 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 1.48 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 3.77 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$), 3.96 (m$_c$, 2 H, NC*H*CH$_3$), 7.13–7.29 (m, 6 H, Ar*H*); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 12.6 (*C*H$_2$), 19.7 (*C*H$_3$), 20.7 (CH(*C*H$_3$)$_2$), 26.6 (CH(*C*H$_3$)$_2$), 26.7 (*C*H(CH$_3$)$_2$), 28.9 (*C*H$_2$), 46.1 (N*C*HCH$_3$), 122.0, 141.3, 142.9 (one Ar*C* resonance not observed), 164.8 (backbone *C*N$_3$); IR ν/cm^{-1} (Nujol): 1616 (m), 1585 (m), 1260 (m), 1110 (m), 1076 (m), 1024 (m), 932 (m), 796 (s), 756 (m); MS (EI 70 eV), *m*/*z* (%): 589.3 (M^+, 1), 546.2 (M^+ − Pr^i, 2), 432.3 (PipisoH − Pr^i, 100); accurate MS (EI) calc. for $C_{32}H_{49}N_3In_1$ (MH^+): 589.2882, found: 589.2877.

Preparation of [In(*N*,arene-PGiso)] 15

Bu^{n}Li (0.82 cm^3 of a 1.6 m solution in hexanes, 1.30 mmol) was added to a solution of Cy$_2$PGisoH (0.72 g, 1.28 mmol) in toluene (20 cm^3) at room temperature, and stirred for 1 h. Solid InCl (0.23 g, 1.54 mmol) was then added to the above solution at −80 °C. The mixture was slowly warmed to room temperature and stirred overnight. All volatiles were removed under reduced pressure, the residue extracted into hexane (60 cm^3) and filtered. The filtrate was concentrated to *ca.* 15 cm^3 and stored at −30 °C to give colourless blocks of **15** (yield 0.25 g, 29%); mp 84 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.38 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.57 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.35–2.21 (m, 20 H, CH_2), 2.37 (m, 2 H, C*H*P), 3.46 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 3.56 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 6.91–7.49 (m, 6 H, Ar*H*); ^{31}P NMR (121.6 MHz, C_6D_6, 298 K): δ 0.1; ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 22.8, 23.5, 25.1, 28.2 (CH(*C*H$_3$)$_2$), 27.8, 28.4 (*C*H(CH$_3$)$_2$), 27.2, 28.1, 28.6, 29.1, 33.0 (d, $^2J_{CP}$ = 16.1 Hz)

Table 2 Crystal data for compounds **9–16**

Compound	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Empirical formula	$C_{31}H_{48}N_3Tl$	$C_{32}H_{48}N_3Tl$	$C_{37}H_{56}N_2PTl$	$C_{62}H_{96}Cl_2In_2N_6$	$C_{64}H_{96}Cl_2In_2N_6$	$C_{32}H_{48}InN_3$	$C_{37}H_{56}InN_2P$	$C_{37}H_{56}GaI_2N_3$
M_r	667.09	679.10	764.18	1225.99	1250.01	589.55	674.63	866.37
T/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Tetragonal
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$C2/c$	P-1	$P4_2/n$
a/Å	14.425(3)	17.940(4)	9.844(5)	14.424(3)	11.518(2)	17.298(4)	9.866(5)	12.5767(18)
b/Å	11.625(2)	17.922(4)	12.034(5)	22.313(5)	19.205(4)	11.948(2)	12.021(5)	12.5767(18)
c/Å	18.247(4)	20.153(4)	16.117(5)	22.538(5)	14.668(3)	15.609(3)	16.135(5)	23.270(5)
α/°	90	90	82.340(5)	116.69(3)	90	90	82.804(5)	90
β/°	104.28(3)	107.01(3)	79.940(5)	97.26(3)	103.02(3)	102.04(3)	80.474(5)	90
γ/°	90	90	68.729(5)	96.81(3)	90	90	68.833(5)	90
V/Å^3	2965.1(10)	6196(2)	1746.7(13)	6301(2)	3161.0(11)	3155.0(11)	1755.4(13)	3680.7(11)
Z	4	8	2	4	2	4	2	4
D_c/Mg m^{-3}	1.494	1.456	1.453	1.292	1.313	1.241	1.276	1.563
μ(Mo-Kα)/mm^{-1}	5.470	5.236	4.696	0.857	0.856	0.772	0.745	2.454
F(000)	1344	2736	776	2568	1308	1240	712	1744
No. reflections collected	11 705	37 199	14 179	40 299	22 412	6276	14 452	5324
No. independent reflns	6130	13 411	7564	21 836	6459	3340	7622	3241
R_{int}	0.0302	0.0542	0.0401	0.0721	0.0631	0.0262	0.0282	0.0450
Final $R1$ ($I > 2\sigma(I)$) and $wR2$ indices (all data)	$R1$ = 0.0269 $wR2$ = 0.0575	$R1$ = 0.0369 $wR2$ = 0.0725	$R1$ = 0.0371 $wR2$ = 0.0748	$R1$ = 0.1049 $wR2$ = 0.2388	$R1$ = 0.0455 $wR2$ = 0.1193	$R1$ = 0.0394 $wR2$ = 0.1098	$R1$ = 0.0326 $wR2$ = 0.0807	$R1$ = 0.0670 $wR2$ = 0.1216

(CH_2), 34.3 (d, $^1J_{CP}$ = 23.1 Hz, CHP); 123.3, 125.3, 128.3, 128.7, 138.7, 139.9, 140.0, 145.2 (ArC), 169.5 (d, $^1J_{CP}$ = 21.2 Hz, backbone CN_2); MS (EI 70 eV), m/z (%): 674 (M^+, 12), 631 ($M^+ - Pr^i$, 33), 477.3 ($M^+ - Cy_2P$, 84); IR ν/cm^{-1} (Nujol): 1565 (m), 1429 (m), 1329 (m), 1286 (m), 1178 (m), 1152 (m), 918 (m), 757 (m); accurate MS (EI) calc. for calc. for $C_{37}H_{55}N_2InP$ ($M - H^+$): 673.3136, found 673.3144; $C_{37}H_{56}N_2InP$ requires C 65.87, H 8.37, N 4.15%; found C 65.61, H 8.45, N 4.29%.

Preparation of [GaI$_2$(Giso)] 16

I_2 (17 mg, 0.07 mmol) was added to a solution of [Ga(Giso)] (40 mg, 0.07 mmol) in toluene (5 cm^3) at −80 °C. The solution was slowly warmed to room temperature overnight with stirring. All volatiles were then removed under reduced pressure and the residue extracted into hexane (10 cm^3) and filtered. The filtrate was slowly cooled to −30 °C affording **16** as a colourless crystalline solid (yield 16 mg, 26%); mp 203–205 °C; ^{1}H NMR (400 MHz, 296 K, C_6D_6) δ 0.82–1.23 (m, 8 H, CH_2), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 1.45 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(CH_3)$_2$), 1.41–1.73 (m, 12 H, CH_2), 3.43 (m, 2 H, CHN), 3.81 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, CH(CH$_3$)$_2$), 7.04–7.42 (m, 6 H, ArH); ^{13}C NMR (100.6 MHz, C_6D_6) δ 21.5 (CH_2), 23.3 (CH(CH_3)$_2$), 225.8 (CH(CH_3)$_2$), 28.3 (CH(CH$_3$)$_2$), 32.7 (CH_2), 34.0 (CH_2), 58.1 (HCN), 123.1, 124.5, 145.3, 145.8 (ArC), 165.7 (CN_3); IR ν/cm^{-1} (Nujol): 1608 (s), 1583 (m), 1258 (m), 1018 (m); MS (EI 70 eV) m/z (%): 866.3 (M^+, 3%), 500.3 (GisoH$^+ - Pr^i$, 100%).

Preparation of [GaI(SiMe$_3$)(Giso)] 17

Me_3SiI (40 μL, 56 mg, 0.28 mmol) was added to a solution of [Ga(Giso)] (0.11 g, 0.18 mmol) in toluene (8 cm^3) at −80 °C. The solution was slowly warmed to room temperature overnight with stirring. All volatiles were then removed under reduced pressure and the residue extracted into hexane (10 cm^3) and filtered. The filtrate was slowly cooled to −30 °C affording **17** as a microcrystalline off-white solid (yield 90 mg, 62%); mp 175–177 °C (decomp.); ^{1}H NMR (400 MHz, 296 K, C_6D_6): δ 0.51 (s, 9 H, Si(CH_3)$_3$), 0.73–0.88 (m, broad, 6 H, CH_2), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.40–1.90 (m, 14 H, CH_2), 1.45 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.60 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 1.63 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(CH_3)$_2$), 3.56 (m$_c$, 2 H, NCH), 3.80 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, CH(CH$_3$)$_2$), 4.27 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, CH(CH$_3$)$_2$), 7.14–7.30 (m, 6 H, ArH); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 298 K): δ 0.2 (Si(CH_3)$_3$), 21.6 (CH(CH_3)$_2$), 22.4 (CH_2), 24.4 (CH_2), 25.9 (CH(CH_3)$_2$), 27.1 (CH(CH_3)$_2$), 27.4 (CH(CH_3)$_2$), 27.6 (CH(CH$_3$)$_2$), 30.8 (CH(CH$_3$)$_2$), 33.5 (CH_2), 58.3 (NCH), 122.4, 124.0, 124.9, 138.8, 143.3, 145.2 (ArC), 164.6 (backbone CN_3); IR ν/cm^{-1} (Nujol): 1611 (m), 1583 (m), 1259 (m), 1176 (m), 1095 (m), 1021 (m), 896 (m), 838 (s), 800 (s), 772 (m), 688 (m); MS (EI 70 eV), m/z (%): 812.3 (M^+ + H, 1), 796.2 (M^+ − Me, 3), 738.3 ($M^+ - SiMe_3$, 1), 684.4 (M^+ − I, 47), 528.3 (GisoH$^+$ − Me, 100); accurate MS (EI) calc. for calc. for $C_{40}H_{64}GaN_3ISi$ (M^+ − H): 810.3165, found: 810.3159.

X-Ray crystallography

Crystals of **9–16** 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)[21] 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 2.

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