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Gallium tri-chloride derivatives of the sterically demanding pyridines 2,6-$Ar_2C_6H_3N$ (Ar = 2,4,6-$Me_3C_6H_2$ or 2,4,6-$Pr^i_3C_6H_2$)

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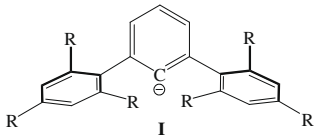
ABSTRACT

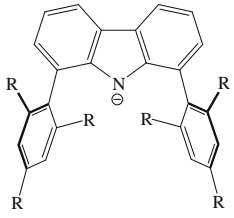
The sterically demanding pyridines 2,6-$Ar_2C_6H_3N$ [Ar = 2,4,6-$Me_3C_6H_2$ (**1**) or 2,4,6-$Pr^i_3C_6H_2$ (**2**)] were prepared by a palladium catalysed Kumada C–C coupling reaction in high yield. Pyridine **1** reacted with one equivalent of $GaCl_3$ to afford the tetra-chloro gallate–pyridinium ion pair complex $[GaCl_4]^-[2,6\text{-}(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3NH]^+$ (**3**). Contrastingly, pyridine **2** reacted with one equivalent of $GaCl_3$ to afford the anticipated donor-acceptor complex $[GaCl_3\{2,6\text{-}(2,4,6\text{-}Pr^i_3C_6H_2)_2C_6H_3N\}]$ (**4**). Complexes **1**–**4** have been characterised variously by single crystal X-ray diffraction, NMR, CHN, and mass spectrometry.

1. Introduction

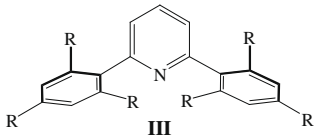
In recent years a 'renaissance' in main group chemistry has taken place which has been mainly driven by the pursuit of p-block elements in low-oxidation states exhibiting novel coordination motifs [1]. Arguably, the greatest progress to date has been made with the group 13 elements, almost all of which can now be isolated in oxidation states I and II in addition to III [2].



I



II



III

Situated half way down group 13 and immediately neighbouring the transition metal series, gallium occupies a unique place in the periodic table which enables it above all other group 13 elements to frequently adopt I, II, and III oxidation states [3]. One ligand class which has proven exceptionally well suited to supporting low valent gallium [4] and landmark multiply bonded transition metal compounds [5] is the anionic terphenyl ligand class (**I**) pioneered by Robinson and Power [4,6]. Emerging more recently, Aldridge introduced bulky anionic carbazole ligands (**II**) as a supporting ligand class for gallium [7]. Ligands of type **II** might be regarded as the anionic N-analogue of terphenyls, but since the central ring topology is different the cone angle of carbazoles with sterically demanding aryl substituents far exceeds a terphenyl with the same aryl substituents. Sterically demanding pyridines such as **III** are topologically similar to terphenyls, but since the coordinating centre is nitrogen rather than carbon the ligand is neutral, and thus ligands of type **III** represent a complimentary ligand class to **I** and **II**.

The use of ligands of type **III** in low valent gallium chemistry is appealing because the neutral nature of the pyridine ligand frees up a valency which would otherwise be unavailable with a terphenyl. However, despite the versatility and widespread application of terphenyls, we were surprised to find that sterically demanding pyridines of type **III** have not yet been applied to gallium chemistry, and structurally characterised mono-pyridine adducts of gallium tri-halides are limited to a handful of examples reported by Schmidbaur et al. [8,9]. Furthermore, reports of structurally characterised sterically demanding pyridine ligands of type **III** are apparently limited to a sole report by Bosch detailing the synthesis of a 2,6-di-mesityl-pyridine and its use in the preparation of a cationic silver(I) complex [10]. With this in mind, and with a view to comparing terphenyls with topologically similar

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sterically demanding pyridines, we have prepared two sterically demanding pyridines and investigated their coordination behaviour towards gallium tri-chloride with the intention of using the resultant complexes as precursors to low valent gallium chemistry.

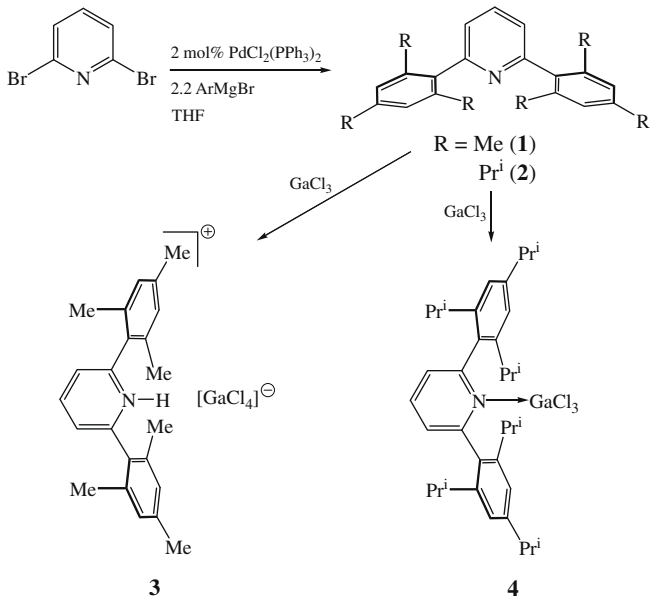
2. Results and discussion

2.1. Synthesis of *1* and *2*

The two ligands employed in this study, 2,6-$Ar_2C_6H_3N$ [Ar = 2,4,6-$Me_3C_6H_2$ (**1**) or 2,4,6-$Pr^i_3C_6H_2$ (**2**)], were prepared by a straightforward, palladium catalysed Kumada coupling reaction. Pyridine **1** was prepared as described previously, but we found that neither CuI or $NHEt_2$ were required as previously indicated [10] (Scheme 1). Pyridine **2** was found to precipitate from the reaction mixture during cooling to room temperature following reflux; cooling the solution further to 0 °C resulted in the isolation of **2** in high yield following filtration and drying, which renders the preparation of **2** very convenient and straightforward. The ^1H and ^{13}C NMR spectra of **2** were clean and as expected; in particular, the inequivalent nature of the *ortho-iso*-propyl methyl groups was confirmed by the observation of two doublets in the ^1H NMR spectrum in addition to the *para-iso*-propyl methyl group doublet. The ^{31}P NMR spectrum of **2** exhibited no resonances in the range ±300 ppm which confirmed that no phosphine-containing products co-precipitated with **2**. The identity of **2** was confirmed by ES–MS which exhibited a single peak at *m/z* 483 corresponding to $\mathbf{2}\cdot H^+$.

2.2. Synthesis of *3* and *4*

Reactions of **1** and **2** with gallium tri-chloride apparently take two very different courses despite both ligands being spectroscopically and analytically pure. The reaction of **1** with one equivalent of gallium tri-chloride reproducibly afforded the tetra-chloro gallate–pyridinium ion pair complex $[GaCl_4]^-[2,6\text{-}(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3NH]^+$ (**3**) in high crystalline yield. It is thought that **1**, whilst sterically demanding, is not sterically demanding enough to prevent further reaction leading to **3**. Support for this suggestion is given by the fact two of **1** were shown to easily coordinate to a silver(I) cation, so there is clearly accessible space around gallium in the putative complex $[GaCl_3\{2,6\text{-}(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3N\}]$ for dimerisation to occur, which might be an expected pre-requisite for chloride transfer to proceed. However, the fact that $GaCl_3$ more often than not reacts from the ionic form $[GaCl_2]^+[GaCl_4]^-$ cannot be excluded as a possible explanation in part for the formation of **3** [8b] and $GaCl_3$ partially exists as a dimer in toluene. Although all the usual routine precautions were taken, and the parallel synthesis of **4** was always straightforward, we cannot exclude the possibility that the incorporated proton of the pyridinium component of **3** results from adventitious moisture rather than from solvent. Intermediates were not observed when the experiment was monitored by ^1H NMR spectroscopy. In contrast, the reaction of **2** with gallium tri-chloride proceeded as anticipated to give the donor-acceptor complex $[GaCl_3\{2,6\text{-}(2,4,6\text{-}Pr^i_3C_6H_2)_2C_6H_3N\}]$ (**4**) in high crystalline yield. The straightforward reaction to give **4** compared to **3** can be directly attributed to the greater sterically demanding nature of **2** compared to **1**. Spectroscopic and analytical data for **3** and **4** were found to be consistent with the proposed formulations.



Scheme 1. Synthesis of **1**–**4**.

2.3. Structural characterisation of *1*

Colourless single crystals of **1** were obtained by slow evaporation of a hexane solution of **1**. The molecular structure of **1** is illustrated in Fig. 1 and selected bond lengths are listed in Table 1. The asymmetric unit was found to contain two independent half molecules that are very similar to each other and each resides over a crystallographic two-fold rotation axis. The observed bond lengths are unremarkable, and the steric bulk of the mesityl groups prevents them adopting a co-planar arrangement with the pyridine ring to maximise conjugation; instead the mesityl rings are approximately orthogonal to the pyridine ring and the angles between the planes defined by the mesityl and pyridine rings were found to be 112°.

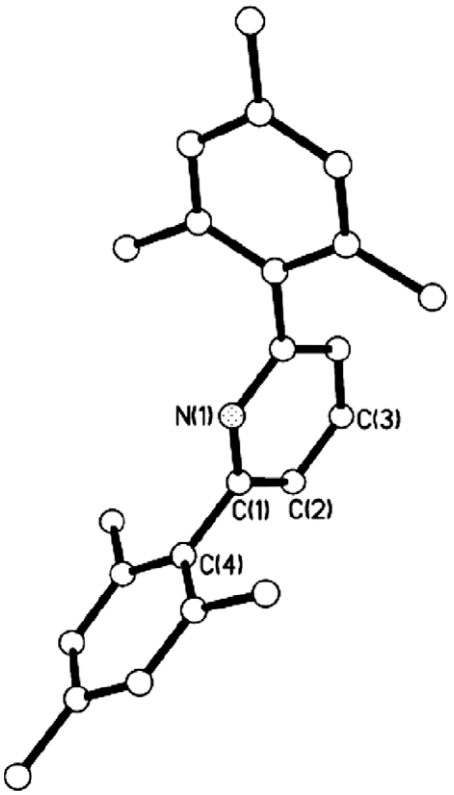


Fig. 1. Molecular structure of one of the two unique molecules of **1** in the asymmetric unit. The other molecule is very similar. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths and angles for **1**–**4**.

1			
N(1)–C(1)	1.347(2)	C(1)–C(2)	1.385(3)
C(2)–C(3)	1.372(2)	C(1)–C(4)	1.487(2)
2			
N(1)–C(1)	1.342(5)	C(1)–C(2)	1.375(7)
C(2)–C(3)	1.390(6)	C(1)–C(4)	1.515(6)
3			
N(1)–C(1)	1.359(3)	N(1)–C(5)	1.354(3)
C(1)–C(2)	1.381(3)	C(2)–C(3)	1.384(3)
C(3)–C(4)	1.385(3)	C(4)–C(5)	1.378(3)
C(1)–C(6)	1.489(3)	C(5)–C(15)	1.496(3)
Ga(1)–Cl(1)	2.1579(7)	Ga(1)–Cl(2)	2.1550(7)
Ga(1)–Cl(3)	2.1572(7)	Ga(1)–Cl(4)	2.1992(7)
Cl(2)–Ga(1)–Cl(3)	109.79(3)	Cl(2)–Ga(1)–Cl(1)	112.04(4)
Cl(3)–Ga(1)–Cl(1)	111.35(3)	Cl(2)–Ga(1)–Cl(4)	107.46(3)
Cl(3)–Ga(1)–Cl(4)	106.08(3)	Cl(1)–Ga(1)–Cl(4)	109.86(3)
4			
N(1)–C(1)	1.371(2)	N(1)–C(5)	1.371(2)
C(1)–C(2)	1.389(3)	C(2)–C(3)	1.382(3)
C(3)–C(4)	1.378(3)	C(4)–C(5)	1.386(3)
C(1)–C(6)	1.488(3)	C(5)–C(21)	1.501(3)
Ga(1)–N(1)	2.0563(15)	Ga(1)–Cl(1)	2.1530(6)
Ga(1)–Cl(2)	2.1598(6)	Ga(1)–Cl(3)	2.1725(6)
N(1)–Ga(1)–Cl(1)	119.86(5)	N(1)–Ga(1)–Cl(2)	113.97(5)
Cl(1)–Ga(1)–Cl(2)	104.28(2)	N(1)–Ga(1)–Cl(3)	97.96(4)
Cl(1)–Ga(1)–Cl(3)	108.21(2)	Cl(2)–Ga(1)–Cl(3)	112.59(2)

2.4. Structural characterisation of **2**

Thin colourless needles of **2** were obtained by slow cooling of a saturated solution of **2** in THF. The molecular structure of **2** is illustrated in Fig. 2 and selected bond lengths are listed in Table 1. The asymmetric unit is composed of one half molecule of **2** which resides over a crystallographic two-fold rotation axis. The observed bond lengths in **2** are unremarkable, but it is worth noting that the C_{α}–C_{ispo} bond lengths are unsurprisingly longer in **2** compared to **1** due to the greater steric demand of the aryl group in **2** compared to **1**. The greater steric bulk of the aryl groups in **2** enforces a stricter orthogonal arrangement of the aryl rings with respect to the pyridine ring, compared to **1**, with the angles between the planes defined by the aryl and pyridine rings now measured at 94°.

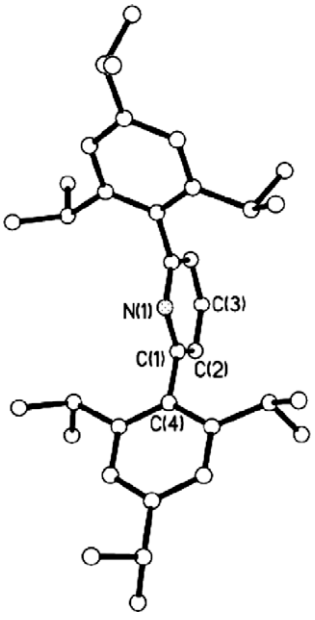


Fig. 2. Molecular structure of **2**. Hydrogen atoms are omitted for clarity.

2.5. Structural characterisation of **3**

Colourless crystals of **3** were grown from a saturated toluene solution at −30 °C. The molecular structure of **3** is illustrated in Fig. 3 and selected bond lengths and angles are listed in Table 1. The tetra-chloro gallate–pyridinium complex **3** crystallises as an ion pair with no intermolecular contacts. In the solid state the **1**·H^+ and $GaCl_4^-$ fragments were found to be associated together by a H(1A)···Cl(4) hydrogen bond measuring 2.405(3) Å, which compares well to the Cl···H hydrogen bonding distance range of 2.124–2.273 Å observed in the complex $[HB(NCHCHCBu^tNH)_3Cl]^+[AlCl_4]^-$ [11]. The presence of the hydrogen bond is supported by inspection of the Ga–Cl bond lengths which fall into two distinct groups: 2.1550(7)–2.1579(7) Å for Ga(1)–Cl(1), Ga(1)–Cl(2), and Ga(1)–Cl(3) which are terminal, and 2.1992(7) Å for Ga(1)–Cl(4) which bridges to the pyridinium proton. Interestingly, the short range of Ga–Cl bond lengths is slightly below the sum of the covalent radii for gallium and chlorine (2.24 Å) [12], but this range is inline with the range of observed Ga–Cl bond lengths in the tetrachloro gallate anion fragments in $[GaCl_2(4\text{-}RC_5H_4N)_4]^+[GaCl_4]^-$ (R = H or Me) [13].

2.6. Structural characterisation of **4**

Cooling of a saturated solution of **4** in toluene to 5 °C resulted in the formation of colourless crystals. The molecular structure of **4** is illustrated in Fig. 4 and selected bond lengths and angles are listed in Table 1. Complex **4** crystallises as a monomeric, solvent-free, donor–acceptor complex. The gallium centre adopts a distorted tetrahedral geometry. The sterically demanding nature of ligand **2** is apparent from the fact that although the gallium coordinates straight on to the N-centre with respect to the Ga(1)–N(1)–C(1) and Ga(1)–N(1)–C(5) angles, which are essentially equal, the gallium centre does not coordinate to the N-centre in the plane of the pyridine ring; instead, the gallium centre pitches out of the plane by 16°. In terphenyl analogues, the gallium centre in $[Ar^*GaCl_2]$ [Ar^* = 2,6-(2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$] coordinates straight on and in the aryl plane [14], but in dimeric $[\{Ar^*GaCl_2\}_2]$ the gallium centre coordinates ~4° out of the aryl plane [15] and in $[Ar^*GaCl_2(Py)]$ (Py = C_5H_5N) the gallium centre coordinates out of the aryl plane by ~8° [16]. The corresponding germanium complex $[Ar^*GeCl_3]$ is

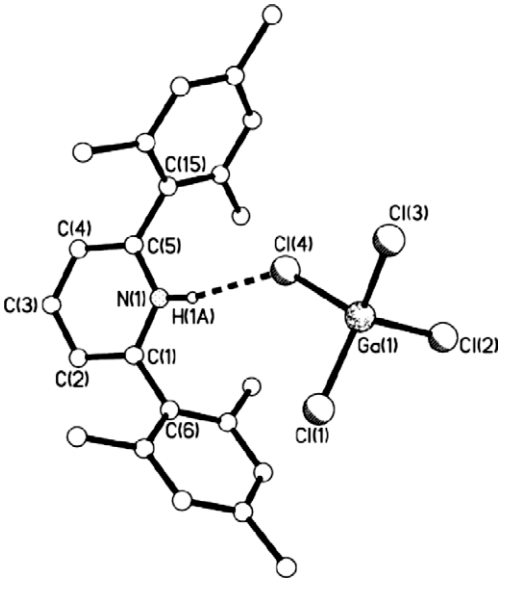


Fig. 3. Molecular structure of **3**. Carbon-bound hydrogen atoms are omitted for clarity.

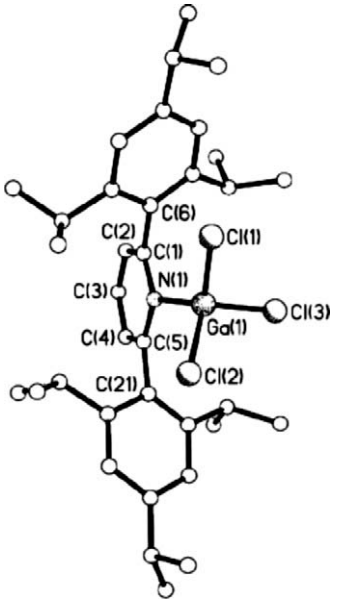


Fig. 4. Molecular structure of **4**. Hydrogen atoms are omitted for clarity.

not structurally available for comparison, but the silicon analogue [Ar*SiCl$_3$] has been structurally characterised and the Si centre was found to bend ~4° out of the aryl plane [17]. The sterically demanding nature of **2** is further underscored by the fact the Ga(1)–N(1) bond length of 2.0563(15) Å is significantly longer than the Ga–N bond length of 1.968(1) Å observed in the sterically undemanding complex [(3,5-Me$_2$C$_6$H$_3$N)GaCl$_3$] [8b], although this does not take account of the undoubtedly different nucleophilicities of the two pyridine ligands due to the different ring substituents. However, the Ga–Cl bond distances cover the range 2.1530(6)–2.1598(6) Å, which is comparable to the range of 2.152–2.161 Å observed in [(3,5-Me$_2$C$_6$H$_3$N)GaCl$_3$] [8b].

3. Conclusions

The sterically demanding pyridines 2,6-Ar$_2$C$_6$H$_3$N [Ar = 2,4,6-Me$_3$C$_6$H$_2$ (**1**) or 2,4,6-Pr$^i_3$C$_6$H$_2$ (**2**)] were prepared by a palladium catalysed Kumada C–C coupling reaction in high yield. Pyridine **1** reacted with one equivalent of GaCl$_3$ to afford the tetra-chloro gallate–pyridinium ion pair complex [GaCl$_4$]$^-$[2,6-(2,4,6-Me$_3$C$_6$H$_2$)$_2$-C$_6$H$_3$NH]$^+$ (**3**). Contrastingly, pyridine **2** reacted with one equivalent of GaCl$_3$ to afford the anticipated monomeric, donor-acceptor complex [GaCl$_3${2,6-(2,4,6-Pr$^i_3$C$_6$H$_2$)$_2$C$_6$H$_3$N}] (**4**). We are currently studying the utility of **4** in preparing gallium complexes with novel bonding and low-oxidation states by reduction, halide abstraction, and salt metathesis reactions.

4. Experimental

4.1. General

All manipulations were carried out using Schlenk or Glove Box techniques under an atmosphere of dry nitrogen. Solvents were dried by passage through activated alumina, degassed, and stored over potassium mirrors with the exception of THF which was stored over activated 4 Å molecular sieves. Deuterated benzene was distilled from potassium, degassed by three freeze-pump-thaw cycles and stored under nitrogen. Complex **1** and 2,4,6-Pr$^i_3$C$_6$H$_2$MgBr were prepared according to published procedures [10,18]. All other reagents were used as supplied.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DPX 400 spectrometer operating at 400.2 and 100.6 MHz, respectively; chemical shifts are quoted in ppm and are relative to TMS. Elemental microanalyses were carried out by Mr Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK.

4.2. Synthesis of 2,6-(2,4,6-Pr$^i_3$C$_6$H$_2$)$_2$C$_6$H$_3$N (*2*)

2,4,6-Pr$^i_3$C$_6$H$_2$MgBr (30 ml of a 1.0 M solution in THF) was added dropwise over 15 min to a cold (−10 °C) mixture of 2,6-dibromopyridine (3.23 g, 13.6 mmol) and PdCl$_2$(PPh$_3$)$_2$ (0.02 g, 2 mol%) in THF (30 ml). The mixture was refluxed for 12 h, then cooled to 0 °C resulting in precipitation of a white solid. The solid was filtered and washed with THF (3 × 20 ml) then dried in vacuo. Yield: 5.94 g, 90%. *Anal.* Calc. for C$_{35}$H$_{49}$N: C, 86.90; H, 10.21; N, 2.90. Found: C, 86.12; H, 9.89; N, 2.75%. ^{1}H NMR (CDCl$_3$): δ 1.13 (d, $^3J_{HH}$ = 6.80 Hz, 12H, *ortho*-Pr^i–Me), 1.15 (d, $^3J_{HH}$ = 6.80 Hz, 12H, *ortho*-Pr^i–Me), 1.28 (d, $^3J_{HH}$ = 7.20 Hz, 12H, *para*-Pr^i–Me), 2.61 (sept, $^3J_{HH}$ = 6.80 Hz, 4H, *ortho*-Pr^i–CH), 2.94 (sept, $^3J_{HH}$ = 7.20 Hz, 2H, *para*-Pr^i–CH), 7.05 (s, 4H, *meta*-CH), 7.29 (d, $^3J_{HH}$ = 7.20 Hz, 2H, β-CH), 7.78 (t, $^3J_{HH}$ = 7.20 Hz, 1H, γ-CH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 23.63 (*ortho*-Pr^i–Me), 24.14 (*ortho*-Pr^i–Me), 24.57 (*para*-Pr^i–Me), 30.45 (*ortho*-Pr^i–CH), 30.94 (*para*-Pr^i–CH), 120.44 (*meta*-C), 122.87 (*para*-C), 135.22 (β-C), 136.79 (γ-C), 146.06 (*ortho*-C), 148.55 (α-C), 159.99 (*ipso*-C). (MS/ES) *m/z*: 483 **2**·H$^+$.

4.3. Synthesis of [GaCl$_4$]$^-$[2,6-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$NH]$^+$ (*3*)

Toluene (40 ml) was added to a cold (−78 °C) mixture of GaCl$_3$ (0.35 g, 2.00 mmol) and **1** (0.63 g, 2.00 mmol). The solution was allowed to warm to room temperature and was stirred for 1 h. The solution was concentrated to incipient crystallisation, gently warmed to afford a clear yellow solution, and stored at −30 °C overnight to afford colourless crystals of **3**. Yield: 0.55 g, 70%. *Anal.* Calc. for C$_{23}$H$_{26}$Cl$_4$GaN: C, 52.32; H, 4.96; N, 2.65. Found: C, 52.02; H, 4.93; N, 2.62%. ^{1}H NMR (C$_6$D$_6$): δ 1.61 (s, br, 1H, NH), 2.20 (s, 12H, *ortho*-Me), 2.25 (s, 6H, *para*-Me), 6.57 (d, $^3J_{HH}$ = 7.60 Hz, 2H, β-CH), 6.92 (s, 4H, *meta*-CH), 7.06 (t, $^3J_{HH}$ = 7.60 Hz, 1H, γ-CH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 20.94 (*para*-Me), 21.10 (*ortho*-Me), 128.37 (β-C), 129.09 (*meta*-CH), 132.98 (γ-C), 137.75 (*para*-C), 141.87 (*ortho*-C), 142.21 (α-C), 162.65 (*ipso*-C).

4.4. Synthesis of [GaCl$_3${2,6-(2,4,6-Pr$^i_3$C$_6$H$_2$)$_2$C$_6$H$_3$N}] (*4*)

Toluene (40 ml) was added to a cold (−78 °C) mixture of GaCl$_3$ (0.35 g, 2.00 mmol) and **2** (0.97 g, 2.00 mmol). The solution was allowed to warm to room temperature and was stirred for 1 hour. The solution was concentrated to incipient crystallisation, gently warmed to afford a clear yellow solution, and stored at 5 °C overnight to afford colourless crystals of **4**. Yield: 0.99 g, 75%. *Anal.* Calc. for C$_{35}$H$_{49}$Cl$_3$GaN: C, 63.71; H, 7.48; N, 2.12. Found: C, 63.66; H, 7.41; N, 2.12%. ^{1}H NMR (C$_6$D$_6$): δ 1.10 (d, $^3J_{HH}$ = 6.80 Hz, 12H, *ortho*-Pr^i–Me), 1.34 (d, $^3J_{HH}$ = 7.20 Hz, 12H, *para*-Pr^i–Me), 1.67 (d, $^3J_{HH}$ = 6.80 Hz, 12H, *ortho*-Pr^i–Me), 2.83 (sept, $^3J_{HH}$ = 6.80 Hz, 4H, *ortho*-Pr^i–CH), 2.95 (sept, $^3J_{HH}$ = 7.20 Hz, 2H, *para*-Pr^i–CH), 7.05 (t, $^3J_{HH}$ = 7.60 Hz, 1H, γ-CH), 7.19 (d, $^3J_{HH}$ = 7.60 Hz, 2H, β-CH), 7.33 (s, 4H, *meta*-CH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 23.22 (*ortho*-Pr^i–Me), 23.83 (*ortho*-Pr^i–Me), 25.52 (*para*-Pr^i–Me), 31.74 (*ortho*-Pr^i–CH), 34.68 (*para*-Pr^i–CH), 121.90 (*meta*-C), 129.53 (*para*-C), 131.46 (β-C), 139.74 (γ-C), 147.64 (*ortho*-C), 152.16 (α-C), 162.26 (*ipso*-C).

4.5. X-ray crystallography

Crystal data for compounds **1**–**4** are given in Table 2, and further details of the structure determinations are in the Supplementary information. Bond lengths and angles are listed in Table 1. Crystals

Table 2
Crystallographic data for **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{23}H_{25}N$	$C_{39}H_{57}NO$	$C_{23}H_{26}Cl_4GaN$	$C_{40.69}H_{55.50}Cl_3GaN$
Formula weight	315.44	555.86	527.97	734.68
Crystal size (mm)	0.60 × 0.30 × 0.13	0.10 × 0.01 × 0.01	0.66 × 0.42 × 0.24	0.65 × 0.17 × 0.12
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12$	$P2_12_12$	$P2_1/c$	$P2_1/c$
a (Å)	12.5029(14)	16.186(12)	15.1484(9)	9.4085(5)
b (Å)	15.5217(17)	17.624(13)	9.3622(6)	13.7328(7)
c (Å)	9.8273(11)	6.017(5)	17.7322(10)	30.4233(16)
β (°)			99.622(2)	92.891(2)
V (Å^3)	1907.1(4)	1716(2)	2479.4(3)	3925.8(4)
Z	4	2	4	4
T (K)	150	28	150	150
ρ_{calc} (g cm^{-3})	1.099	1.076	1.414	1.243
μ (mm^{-1})	0.063	0.062	1.551	0.933
Number of reflections measured	13 894	11 914	12 418	28 503
Number of unique reflections, R_{int}	3361, 0.053	3014, 0.080	4339, 0.0160	6912, 0.0290
Number of reflections with $F^2 > 2\sigma(F^2)$	2179	2246	4021	5781
Transmission coefficient range	0.96–0.98	0.97–0.98	0.42–0.70	0.56–0.88
R, R_w[a] ($F^2 > 2\sigma$)	0.0378, 0.0824	0.0834, 0.1020	0.0330, 0.0353	0.0303, 0.0378
R, R_w[a] (all data)	0.0777, 0.0885	0.2270, 0.2420	0.0901, 0.0918	0.0805, 0.0832
S[a]	0.937	1.090	1.050	1.060
Parameters	226	191	271	361
Maximum, minimum difference map (e Å^{-3})	0.120, −0.110	0.470, −0.580	0.960, −0.690	0.370, −0.270

[a] Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o 2)^2]^{1/2}$; $S = [\Sigma w(F_o^2 - F_c^2)^2/(\text{no. data} - \text{no. params})]^{1/2}$ for all data.

were examined on a Bruker APEX CCD area detector diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) or on a Bruker APEX2 CCD area detector using silicon111-monochromated synchrotron radiation (λ = 0.6946 Å). Intensities were integrated from a sphere of data recorded on narrow (0.3°) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Semi-empirical absorption corrections were applied, based on symmetry-equivalent and repeat reflections. The structures were solved by direct methods and were refined by least-squares methods on all unique F^2 values, with anisotropic displacement parameters, and with constrained riding hydrogen geometries; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom. The largest features in final difference syntheses were close to heavy atoms. The Flack parameters for **1** and **2** refined to 0(4) and −9(10) (not reliably determined). Highly disordered solvent molecules of crystallisation in **1** and **4** could not be modelled and were treated with the Platon SQUEEZE procedure [19]. Programs were Bruker AXS SMART (control) and SAINT (integration) [20], and SHELXTL for structure solution, refinement, and molecular graphics [21].

Supplementary information

CCDC 728403, 728404, 728405 and 728406 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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