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# The reactivity of gallium(I) and indium(I) halides towards bipyridines, terpyridines, imino-substituted pyridines and bis(imino)acenaphthenes

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"GaI" reacts with 2,2′-bipyridine (bipy) to give salts of composition [Ga(bipy)$_3$][I]$_3$, [{(bipy)$_2$Ga}$_2$(μ-OH)$_2$]$_2$[Ga$_2$I$_6$][I]$_6$ or [{(bipy)$_2$Ga}$_2$(μ-OH)$_2$][I]$_4$, depending upon the reaction conditions. "GaI" also reacts with 4′-phenyl-2,2′:6′,2″-terpyridine (Phterpy) to give the salt [GaI$_2$(Phterpy)][I]. When "GaI" is treated with the imino-substituted pyridines RN=C(H)Py, Py = 2-pyridyl, R = Ar (C$_6$H$_3$Pr$^i_2$-2,6) or Bu$^t$, a reductive coupling of the C=N functionality occurs to give the diamido-digallium(III) complexes [{I$_2$Ga[η$^2$-(Py)(NR)C(H)]}$_2$]. In contrast, InCl reacts with ArN=C(H)Py to give an adduct, [InCl$_3$(THF){η$^2$-ArN=C(H)Py}], *via* disproportionation of the metal halide. Similarly, the reaction of the bis(imino)pyridine, 2,6-{ArN=C(Me)}$_2$(NC$_5$H$_3$), bimpy, with "GaI" affords the salt [GaI$_2$(bimpy)][GaI$_4$]. Finally, the reaction of bis(2,6-diisopropylphenylimino)acenaphthene (ArBIAN) with "GaI" leads to a paramagnetic Ga(III) complex [GaI$_2$(ArBIAN)$^•$]. The X-ray crystal structures of all prepared complexes are reported.

## Introduction

In the past five years there has been much interest in the chemistry of metastable aluminium(I) and gallium(I) halide complexes [{MX(L)}$_n$] (M = Al, Ga; X = halide; L = ether, amine or phosphine), which can only be synthesised in specially designed reactors.[1] The further chemistry of these species has been widely explored and shown to give rise to an array of remarkable sub-oxidation state complexes.[2] An alternative to these reactor generated halide complexes is available with "GaI" which has been reported by Green *et al.*[3] to be simply formed by sonicating gallium metal with 0.5 equivalents of I$_2$. Although its formulation has not been definitely established, its reactivity has indicated that it can be used as a source of Ga(I). We have begun to explore the synthetic potential of "GaI", for example in its reactions with diazabutadienes (DAB) which lead to paramagnetic Ga(II) and Ga(III) complexes of the type [{(DAB$^•$)GaI}$_2$] and [GaI$_2$(DAB$^•$)]. Both of these complexes are readily reduced to novel anionic Ga(I) N-heterocyclic carbene analogues, *e.g.* [K(TMEDA)][:Ga{N(Ar)CH}$_2$], Ar = C$_6$H$_3$Pr$^i_2$-2,6,[4] the further chemistry of which is proving fruitful.[5] In addition, we have also observed that "GaI" reacts with primary and secondary amines, secondary phosphines or N-heterocyclic carbenes to give a variety of Ga(II) iodide complexes *via* disproportionation reactions.[6] It is noteworthy that others have seen similar reactivity with tertiary amines,[7] phosphines[8] and arsines.[9] In the present study we have expanded on this work by examining the reactivity of several unsaturated bi- and tridentate N-donor ligands towards "GaI" and InCl in the hope of preparing new complexes that could be used as precursors to group 13 N-heterocyclic carbene analogues. In all cases, disproportionation and formation of M(III) complexes occurred, though considerable variations in reactivity and complex type formed were observed for the ligand classes investigated. The results of this study are presented herein.

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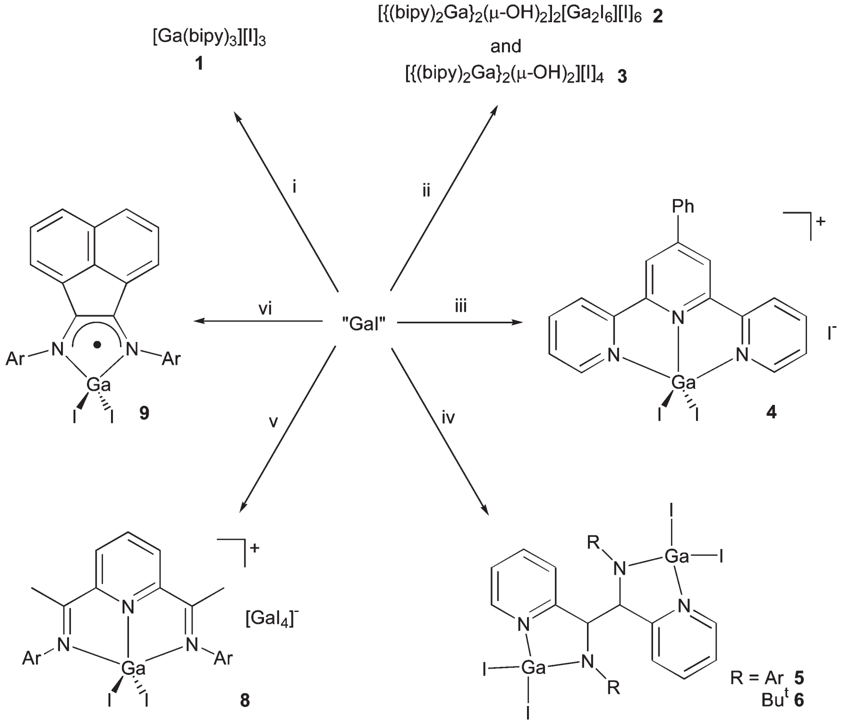
## Results and discussion

The reaction of "GaI" with one equivalent of 2,2′-bipyridine (bipy) in toluene unexpectedly led to the high yield formation of the salt [Ga(bipy)$_3$][I]$_3$, **1**, after recrystallisation from acetonitrile (Scheme 1). This reaction proceeds *via* a disproportionation process as evidenced by the deposition of considerable gallium metal from the reaction mixture. The spectroscopic data for **1** are consistent with its formulation and an X-ray crystal structural analysis of the compound was carried out to confirm this. The structure of the cationic component of **1** is depicted in Fig. 1 (see Table 1) and, surprisingly, represents the first structurally authenticated example of a homoleptic bipyridine complex of any group 13 element. The geometry around the gallium centre is distorted octahedral, with an average Ga–N bond length of 2.063 Å. This value is in the normal range for bipy complexes of gallium(III).[10] The three iodide anions do not display any short contacts with the cation or themselves. It is noteworthy that the complex crystallises in the chiral space group, *Pna*2$_1$, and in the crystal selected for the X-ray experiment the cation exists as its Λ-isomer.

In the first attempted preparation of **1**, two salts containing hydroxy-bridged digallium(III) tetracations, *viz.* [{(bipy)$_2$Ga}$_2$(μ-OH)$_2$]$_2$[Ga$_2$I$_6$][I]$_6$ **2** and [{(bipy)$_2$Ga}$_2$(μ-OH)$_2$][I]$_4$ **3**, were formed in low yields as yellow crystalline solids which were manually separated from orange **1**. Both compounds presumably form as a result of hydrolysis arising from contamination of the solvent or bipy starting material with water (Scheme 1). It is noteworthy that **2** is a rare example of a complex containing gallium atoms in mixed oxidation states, *i.e.* Ga(III) in the cation and Ga(II) in the [Ga$_2$I$_6$]$^{2-}$ dianion. The spectroscopic features of both complexes are very similar and support their formulations. Most significantly, broad absorptions at 3420 cm$^{-1}$ in their IR spectra, and singlet peaks at $\delta$ 2.05 ppm in their $^1$H NMR spectra can be assigned to the bridging hydroxy groups. The proton NMR resonances can be compared to those observed for other hydroxy-bridged gallium dimers, *e.g.* $\delta$ 1.79 ppm for [{[(Me$_3$Si)$_2$CH]$_2$Ga(μ-OH)}$_2$].[11]

Crystals of **2** and **3** suitable for X-ray diffraction were obtained from acetonitrile solutions. The structures of the cations in each are identical within experimental error and thus only that for **2** will be discussed here (Fig. 2, see Table 1). The geometry around the gallium atoms is distorted octahedral and



**Scheme 1** *Reagents and conditions*: i, bipy, toluene, $-$Ga; ii, bipy/$H_2O$, toluene, $-$Ga; iii, Phterpy, toluene, $-$Ga; iv, $Bu^tN{=}C(H)Py$, toluene, $-$Ga; v, bimpy, toluene, $-$Ga; vi, ArBIAN, toluene, $-$Ga.

the average Ga–N bond length, 2.078 Å, is similar to that observed for **1** and *cis*-$[(bipy)_2GaCl_2][GaCl_4]$ [2.103 Å av.].[12] There are no significant differences in the lengths of the Ga–N bonds that are *trans* to a nitrogen or oxygen atom. Moreover, the Ga–O bond lengths at 1.940 Å (av.) and Ga–O–Ga angles at 102.9° (av.) are similar to other hydroxy-bridged gallium(III) compounds reported in the literature, *e.g.* 1.949(2) Å and 99.6(1)° respectively for $[\{(Mes)_2Ga\}_2(\mu\text{-}OH)_2]$.[13] The metric parameters of the $[Ga_2I_6]^{2-}$ counter ion are almost identical to those seen for $[PPh_3H][Ga_2I_6]$.[14] It is interesting to note that one Raman spectroscopic study has suggested that the "GaI" starting material used in the formation of **2** exists as $[Ga]_2^+[Ga_2I_6]^{2-}$ and thus contains this dianion.[15]

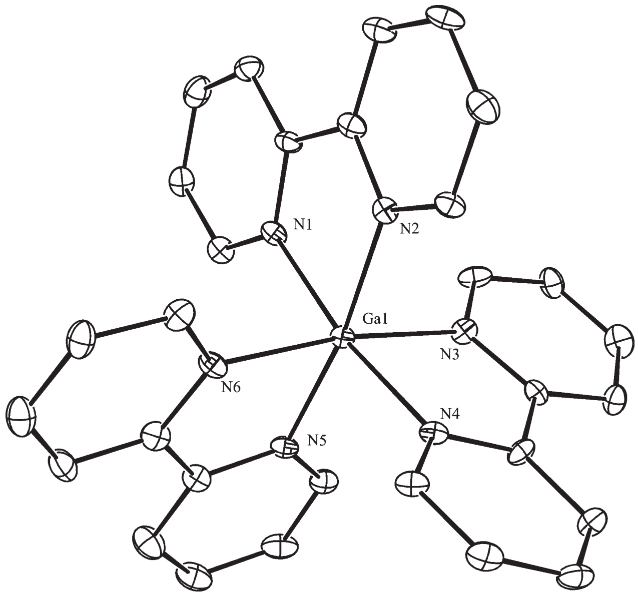


**Fig. 1** Structure of the cationic component of **1**. Selected bond lengths (Å) and angles (°): Ga(1)–N(1) 2.070(6), Ga(1)–N(2) 2.056(5), Ga(1)–N(3) 2.062(6), Ga(1)–N(4) 2.053(6), Ga(1)–N(5) 2.071(5), Ga(1)–N(6) 2.069(6); N(1)–Ga(1)–N(2) 80.1(2), N(1)–Ga(1)–N(3) 93.92(19), N(1)–Ga(1)–N(4) 171.4(2), N(1)–Ga(1)–N(5) 93.7(2), N(1)–Ga(1)–N(6) 91.5(2), N(2)–Ga(1)–N(3) 91.3(2), N(2)–Ga(1)–N(4) 94.2(2), N(2)–Ga(1)–N(5) 172.3(3), N(2)–Ga(1)–N(6) 95.6(2), N(3)–Ga(1)–N(4) 79.8(2), N(3)–Ga(1)–N(5) 93.8(2), N(3)–Ga(1)–N(6) 171.9(2), N(4)–Ga(1)–N(5) 92.4(2), N(4)–Ga(1)–N(6) 95.4(2), N(5)–Ga(1)–N(6) 79.9(2).

For sake of comparison the 1:1 reaction of the tridentate 4′-phenyl-2,2′:6′,2″-terpyridine (Phterpy) ligand with "GaI" in toluene was carried out and this gave rise to a yellow, insoluble precipitate. On recrystallisation of this precipitate from acetonitrile the salt $[GaI_2(Phterpy)][I]$, **4**, could be isolated in a high yield (Scheme 1). Due to its poor solubility in common organic solvents, little meaningful spectroscopic data could be obtained on the complex and so crystals suitable for X-ray diffraction were grown from acetonitrile in order to determine its structure, the cationic component of which is depicted in Fig. 3 (see Table 1). The geometry around the gallium atom is distorted trigonal bipyramidal, with N(1) and N(3) taking up the axial positions [N(1)–Ga(1)–N(3) 154.6(2)°]. As would be expected, the two axial Ga–N bonds are longer [2.104 Å av.] than the equatorial bond, [Ga(1)–N(2) 2.007(5) Å], though the average length for all three [2.071 Å] is close to that observed for neutral $[GaCl_3(terpy)]$ [2.086 Å av.][16] and complexes **1**–**3**. The Ga–I bond distances are in the normal range[10] and the iodide anion has no close contacts with the cation.

It was thought of sufficient interest to examine the reactivity of the imino-substituted pyridines, RN=C(H)Py, Py = 2-pyridyl, R = Ar ($C_6H_3Pr^i{}_2$-2,6) or $Bu^t$, with "GaI" as such compounds often display similar coordination chemistry to both bipyridines and 1,4-diazabutadienes. In this case, however, significant differences were observed and the 1:2 reactions led to intermolecular reductive couplings of two imine carbon centres with concomitant gallium iodide disproportionation to give good yields of the diamido-digallium(III) complexes, **5** and **6** (Scheme 1). The spectroscopic data for both confirm that a ligand coupling has occurred. Specifically, no C=N stretching absorptions were observed in their IR spectra, and methine resonances at $\delta$ 4.20 ppm (**5**) and 5.29 ppm (**6**) could be seen in the $^1H$ NMR spectra of the complexes. Additionally, in the $^{13}C$ NMR spectrum of **5** the C=N resonance of the

**Table 1** Crystal data for compounds **1**–**9**

| | **1**·4CH$_3$CN | **2**·8CH$_3$CN | **3**·5CH$_3$CN | **4**·CH$_3$CN | **5** | **6** | **7** | **8** | **9**·0.5C$_6$H$_{14}$ |
|---|---|---|---|---|---|---|---|---|---|
| Chemical formula | C$_{38}$H$_{36}$GaI$_3$N$_{10}$ | C$_{96}$H$_{92}$Ga$_6$I$_{12}$N$_{24}$O$_4$ | C$_{50}$H$_{49}$Ga$_2$I$_4$N$_{13}$O$_2$ | C$_{23}$H$_{18}$GaI$_3$N$_4$ | C$_{36}$H$_{44}$Ga$_2$I$_4$N$_4$ | C$_{20}$H$_{28}$Ga$_2$I$_4$N$_4$ | C$_{22}$H$_{30}$Cl$_3$InN$_2$O | C$_{33}$H$_{43}$Ga$_2$I$_6$N$_3$ | C$_{39}$H$_{40}$GaN$_2$I$_2$ |
| $M_r$ | 1083.19 | 3587.06 | 1511.06 | 800.83 | 1179.79 | 971.50 | 559.65 | 1382.54 | 860.25 |
| Crystal system | Orthorhombic | Monoclinic | Triclinic | Triclinic | Monoclinic | Monoclinic | Orthorhombic | Triclinic | Triclinic |
| Space group | $Pna2_1$ | $C2/c$ | $P\bar{1}$ | $P\bar{1}$ | $C2/c$ | $P2_1/n$ | $Pbca$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$/Å | 21.246(4) | 28.873(6) | 11.000(2) | 7.3570(15) | 22.813(5) | 9.6170(19) | 17.008(3) | 10.285(2) | 12.480(3) |
| $b$/Å | 17.803(4) | 14.539(3) | 12.525(3) | 13.306(3) | 14.364(3) | 14.831(3) | 16.621(3) | 13.001(3) | 12.706(3) |
| $c$/Å | 11.048(2) | 29.261(6) | 21.899(4) | 13.759(3) | 17.672(4) | 10.140(2) | 17.465(4) | 16.458(3) | 13.148(3) |
| $\alpha$/° | 90 | 90 | 105.18(3) | 99.44(3) | 90 | 90 | 90 | 76.95(3) | 70.68(3) |
| $\beta$/° | 90 | 101.29(3) | 94.44(3) | 97.59(3) | 124.81(3) | 107.11(3) | 90 | 86.76(3) | 77.02(3) |
| $\gamma$° | 90 | 90 | 99.69(3) | 102.53(3) | 90 | 90 | 90 | 81.91(3) | 81.03(3) |
| $V$/Å$^3$ | 4178.8(14) | 12 046(4) | 2846.8(10) | 1277.2(5) | 4754.6(17) | 1382.3(5) | 4937.2(17) | 2121.8(7) | 1909.6(7) |
| $Z$ | 4 | 4 | 2 | 2 | 4 | 2 | 8 | 2 | 2 |
| $T$/K | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) |
| $\mu$(Mo-K$_\alpha$)/mm$^{-1}$ | 2.914 | 4.454 | 3.165 | 4.720 | 3.756 | 6.431 | 1.297 | 5.660 | 2.364 |
| Reflections collected | 34 157 | 62 937 | 49 843 | 22 859 | 21 124 | 8771 | 23 141 | 26 217 | 25 014 |
| Unique reflns. ($R_{int}$) | 8934 (0.0865) | 11 727 (0.0924) | 12 403 (0.1738) | 4945 (0.0980) | 5406 (0.0587) | 2811 (0.0589) | 4490 (0.1004) | 7606 (0.1385) | 6880 (0.0523) |
| $R1$ ($I > 2\sigma(I)$) | 0.0484 | 0.0569 | 0.0553 | 0.0450 | 0.0325 | 0.0290 | 0.0463 | 0.0655 | 0.0512 |
| $wR2$ (all data) | 0.1174 | 0.1319 | 0.1446 | 0.0970 | 0.0736 | 0.0683 | 0.0995 | 0.1757 | 0.1252 |

iminopyridine starting material has been replaced by one at $\delta$ 71.53 ppm that was assigned to the NC(H)C(H)N moiety of the coupled ligand. Unfortunately, the low solubility of compound **6** in normal deuterated solvents prevented the acquisition of meaningful $^{13}$C NMR data.

Crystals of both compounds were grown from DME solutions and their X-ray crystal structures obtained (Figs. 4 and 5, see Table 1). Both structures confirm that coupling reactions have occurred and both compounds exist in their *meso*-isomeric form. Each gallium centre is chelated by a covalent amido interaction and a dative interaction from the pyridyl substituents. In addition, each gallium centre has a heavily distorted tetrahedral geometry which arises from the small bite angle of the ligands [N(1)–Ga(1)–N(2) **5**: 85.90(10)°; **6**: 88.05(13)°], whilst the dative and covalent Ga–N bond lengths differ significantly in each complex [pyridyl N(1)–Ga(1) **5**: 1.974(3) Å, **6**: 2.020(3) Å; amido N(2)–Ga(1) **5**: 1.869(2) Å, **6**: 1.884(3) Å]. Finally, it is worth noting that the distances between the coupled carbon centres are longer than would normally be expected for C(sp$^3$)–C(sp$^3$) bonds [C(6)–C(6′) **5**: 1.603(5) Å, **6**: 1.581(7) Å] though there is precedent for this in NCCN moieties of reductively coupled diazabutadiene complexes in which each N-centre is covalently bonded to a metal.[17]

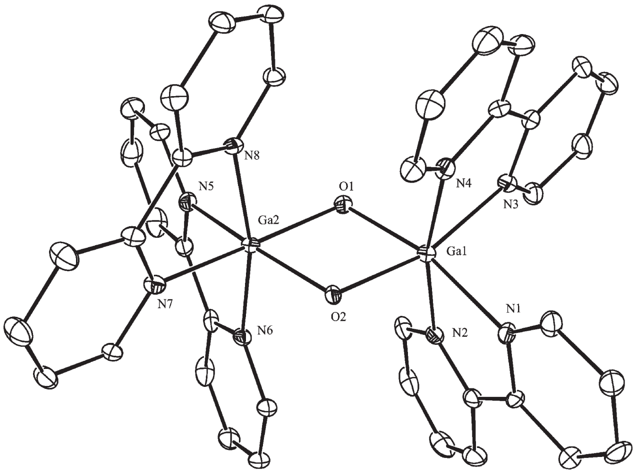


**Fig. 2** Structure of the cationic component of **2**. Selected bond lengths (Å) and angles (°): Ga(1)–O(1) 1.942(5), Ga(1)–O(2) 1.941(5), Ga(2)–O(1) 1.942(5), Ga(2)–O(2) 1.937(5), Ga(1)–N(1) 2.071(6), Ga(1)–N(2) 2.094(6), Ga(1)–N(3) 2.066(6), Ga(1)–N(4) 2.085(7), Ga(2)–N(5) 2.070(6), Ga(2)–N(6) 2.075(6), Ga(2)–N(7) 2.078(6), Ga(2)–N(8) 2.088(6); O(1)–Ga(1)–O(2) 77.0(2), O(1)–Ga(1)–N(1) 166.4(2), O(1)–Ga(1)–N(2) 91.5(2), O(1)–Ga(1)–N(3) 93.4(2), O(1)–Ga(1)–N(4) 99.5(2), O(1)–Ga(2)–N(5) 91.7(2), O(1)–Ga(2)–N(6) 92.7(2), O(1)–Ga(2)–N(7) 169.2(2), O(1)–Ga(2)–N(8) 93.8(2), O(2)–Ga(1)–N(1) 95.8(2), O(2)–Ga(1)–N(2) 98.4(2), O(2)–Ga(1)–N(3) 164.1(2), O(2)–Ga(1)–N(4) 90.3(2), O(2)–Ga(2)–N(5) 165.1(2), O(2)–Ga(2)–N(6) 92.7(2), O(2)–Ga(2)–N(7) 95.7(2), O(2)–Ga(2)–N(8) 95.8(2), Ga(1)–O(1)–Ga(2) 102.8(2), Ga(1)–O(2)–Ga(2) 103.0(2).

Transition metal mediated C–C couplings of diazabutadiene ligands have been observed on many occasions.[18] Similarly, the reductive coupling of iminopyridines have been reported. Most relevant to this study is that which arises from the reaction of Bu$^t$N=C(H)Py with ZnEt$_2$.[19] This leads to a diamagnetic, dimeric complex which closely resembles **6**, *viz.* [{EtZn[$\eta^2$-(Py)(NBu$^t$)C(H)]}$_2$]. The mechanism of formation

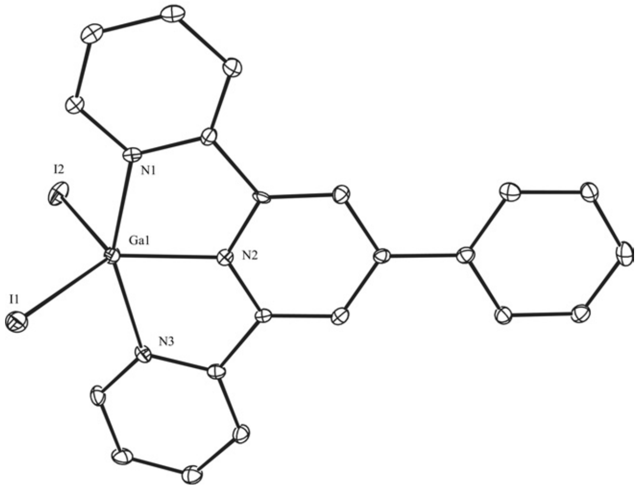


**Fig. 3** Structure of the cationic component of **4**. Selected bond lengths (Å) and angles (°): Ga(1)–I(1) 2.5389(11), Ga(1)–I(2) 2.5144(12), Ga(1)–N(1) 2.087(5), Ga(1)–N(2) 2.007(5), Ga(1)–N(3) 2.121(5); N(1)–Ga(1)–N(2) 77.4(2), N(1)–Ga(1)–N(3) 154.6(2), N(1)–Ga(1)–I(1) 97.08(15), N(1)–Ga(1)–I(2) 96.75(15), N(2)–Ga(1)–N(3) 77.3(2), N(2)–Ga(1)–I(1) 122.34(15), N(2)–Ga(1)–I(2) 120.29(15), N(3)–Ga(1)–I(1) 95.11(15), N(3)–Ga(1)–I(2) 97.32(15), I(1)–Ga(1)–I(2) 117.37(4).

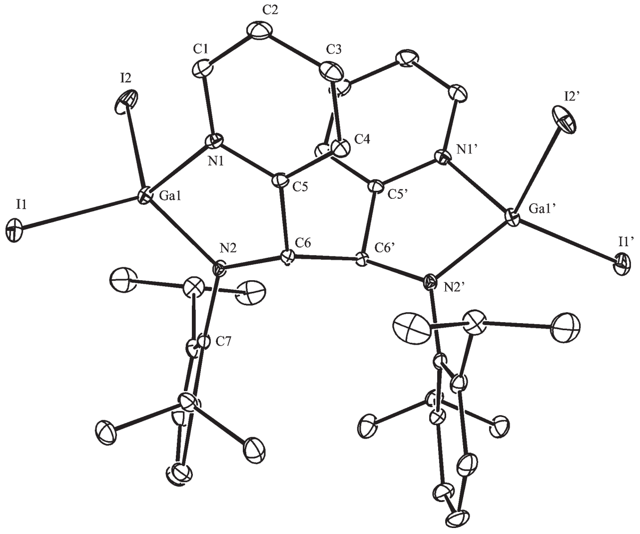


**Fig. 4** Molecular structure of **5**. Selected bond lengths (Å) and angles (°): Ga(1)–I(1) 2.5092(13), Ga(1)–I(2) 2.5485(5), Ga(1)–N(1) 1.974(3), Ga(1)–N(2) 1.869(2), N(2)–C(6) 1.462(3), C(6)–C(6′) 1.603(5), C(5)–C(6) 1.526(4); I(1)–Ga(1)–I(2) 106.94(2), I(1)–Ga(1)–N(1) 115.85(7), I(I)–Ga(1)–N(2) 118.99(8), I(2)–Ga(1)–N(1) 102.66(8), I(2)–Ga(1)–N(2) 123.56(8), N(1)–Ga(1)–N(2) 85.90(10), Ga(1)–N(2)–C(6) 115.52(18), C(6)–N(2)–C(7) 119.4(2), Ga(1)–N(2)–C(7) 121.75(18). Symmetry operation: $-x+1$, $y$, $-z+3/2$.

of this complex has been shown to involve a paramagnetic monomeric intermediate, [EtZn{Bu$^t$NC(H)Py}$^•$], *via* loss of an ethyl radical. It was confirmed that in solution this intermediate is in equilibrium with its diamagnetic dimer. Given this, and the fact that our previously reported reactions of diazabutadienes (DAB) with "GaI" lead to paramagnetic complexes of the type [{(DAB$^•$)GaI}$_2$],[4] it seems entirely feasible that the mechanism of formation of **5** and **6** involves a one-electron reduction of the ligand by "GaI", followed by radical coupling and disproportionation reactions to give the observed products. One difference between **5** and **6**, and [{EtZn[η$^2$-(Py)(NBu$^t$)C(H)]}$_2$] is the fact that the former exist as their *meso*-isomers whereas the latter crystallises as its *RR′*/*SS′*-enantiomeric pair. Interestingly, the report on the zinc complex suggested that the diamido ligand would have difficulty in coordinating two metal centres in its *meso*-form which is clearly not the case given the isolation of **6**.

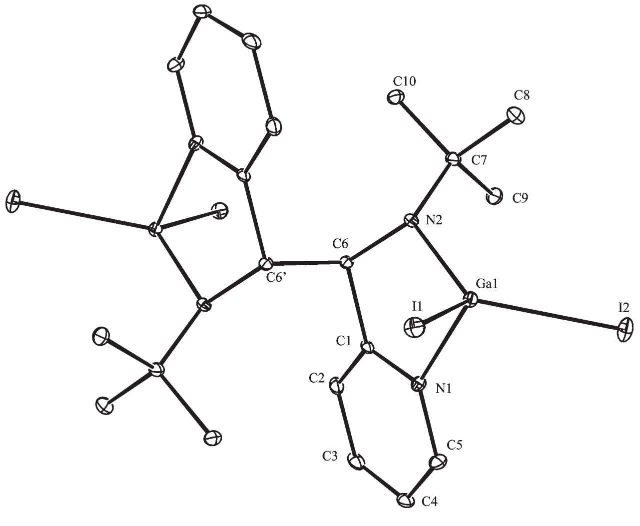


**Fig. 5** Molecular structure of **6**. Selected bond lengths (Å) and angles (°): Ga(1)–I(1) 2.5490(6), Ga(1)–I(2) 2.5232(6), Ga(1)–N(1) 2.020(3), Ga(1)–N(2) 1.884(3), N(2)–C(6) 1.459(5), C(6)–C(6′) 1.581(7), C(1)–C(6) 1.522(5); I(1)–Ga(1)–I(2) 110.38(2), I(1)–Ga(1)–N(1) 106.81(9), I(1)–Ga(1)–N(2) 114.58(9), I(2)–Ga(1)–N(1) 104.24(9), I(2)–Ga(1)–N(2) 127.22(9), N(1)–Ga(1)–N(2) 88.05(13), Ga(1)–N(2)–C(6) 107.5(2), C(6)–N(2)–C(7) 116.7(3), Ga(1)–N(2)–C(7) 121.6(2). Symmetry operation: $-x$, $-y$, $-z+1$.

The reductive coupling of the iminopyridines by "GaI" highlights the potential usefulness of this as a reagent in organic synthesis. This potential has only been demonstrated once before in the reaction of "GaI" with a 1,3-diyne, which led to a reductive C–C coupling of the diyne to give a novel ene-diyne-bis(*gem*-organodigallium(III)) complex.[19] In that report the greater reducing ability of "GaI" over indium(I) halides was highlighted by the fact that InI did not react with the diyne. Despite this, previous reports have shown that indium metal can be used to couple imines to form 1,2-diamines.[20] Therefore we wished to see if indium(I) halides would be sufficiently reducing to couple the imino-substituted pyridines used in this study. To this end, InCl was treated with 0.5 equivalents of ArN=C(H)Py which led to deposition of indium metal and the moderate yield formation of the adduct complex, [InCl$_3${η$^2$-ArN=C(H)Py}(THF)] **7**, by a disproportionation reaction. This result confirms the weaker reducing ability of InCl over "GaI". Complex **7** was subsequently prepared by the direct treatment of ArN=C(H)Py with InCl$_3$ in THF. The spectroscopic data for the complex support its proposed structure, especially the observed C=N stretching absorption at 1652 cm$^{-1}$ in its IR spectrum. In addition, a resonance at δ 127.5 ppm in the $^{13}$C NMR spectrum of the compound was assigned to the imine carbon.

Crystals of **7** were grown from a THF solution and its X-ray crystal structure obtained. (Fig. 6, see Table 1). The geometry around the indium atom is distorted octahedral with a *fac*-arrangement of the chloride ligands, whilst the bond lengths within the five-membered chelate ring are consistent with a localised C=N interaction [C(6)–N(2) 1.273(6) Å and C(5)–C(6) 1.458(6) Å]. These bond lengths are similar to those observed in the related complex [NiCl$_2${ArN=C(H)Py}]$_2$, *i.e.* 1.278(3) Å and 1.463(4) Å respectively.[21] Both the pyridyl N–In and imine N–In bond lengths are unremarkable.

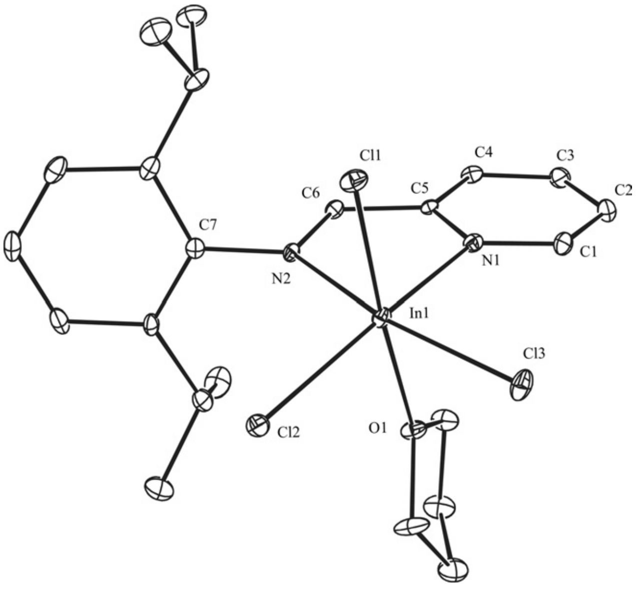


**Fig. 6** Molecular structure of **7**. Selected bond lengths (Å) and angles (°): In(1)–N(1) 2.306(4), In(1)–N(2) 2.348(4), In(1)–Cl(1) 2.4381(13), In(1)–Cl(2) 2.4103(13), In(1)–Cl(3) 2.4405(13), In(1)–O(1) 2.396(3), C(6)–N(2) 1.273(6), C(5)–C(6) 1.458(6); N(1)–In(1)–N(2) 71.72(13), N(1)–In(1)–Cl(1) 97.54(10), N(1)–In(1)–Cl(2) 156.94(10), N(1)–In(1)–Cl(3) 91.53(10), N(1)–In(1)–O(1) 77.16(12), N(2)–In(1)–Cl(1) 92.14(10), N(2)–In(1)–Cl(2) 93.21(10), N(2)–In(1)–Cl(3) 162.10(9), N(2)–In(1)–O(1) 85.69(12), Cl(1)–In(1)–Cl(2) 100.44(5), Cl(1)–In(1)–Cl(3) 96.41(5), Cl(2)–In(1)–Cl(3) 100.63(5), Cl(1)–In(1)–O(1) 174.67(8), Cl(2)–In(1)–O(1) 84.55(9), Cl(3)–In(1)–O(1) 84.39(9).

The potentially tridentate 2,6-bis(imino)pyridine ligand, 2,6-{ArN=C(Me)}$_2$(NC$_5$H$_3$), bimpy, has been recently used in non-metallocene based olefin polymerisation catalysts with great effect.[22] Its reactivity towards main group compounds has also been investigated and shown to give interesting results. For example, its reaction with AlMe$_3$ leads to carbometallation of one imine arm of the ligand to give a complex that is a precursor to an active ethylene polymerisation catalyst.[23] In light of this result and the similarity of the bimpy ligand to others utilised in this study we have investigated its reaction with "GaI" in toluene, which again leads to disproportionation of the gallium starting material and the low yield formation of the salt [GaI$_2$(bimpy)][GaI$_4$] **8** (Scheme 1). The IR spectrum of the compound displays a C=N stretching absorption at 1628 cm$^{-1}$, whilst its $^{13}$C NMR spectrum exhibits a C=N resonance at $\delta$ 169.0 ppm. Both data confirm that the imino functionalities were not reduced and no C–C coupling reactions had occurred, *cf.* the situation with **5** and **6**.

The structure of the cationic moiety of **8** is depicted in Fig. 7. Its gallium centre has a distorted square based pyramidal geometry, with the basal plane defined by the N(1), N(2), N(3) and I(2) centres, whilst the apical position is taken up by I(1). The metric parameters also confirm the spectroscopic observation of a simple adduct formation as the C=N bond lengths [1.284 Å av.] are close to those in the free ligand [1.273 Å av.].[24] Both imino N–Ga bond lengths [2.203 Å av.] are significantly longer than the pyridyl N–Ga interaction [Ga(1)–N(2) 2.014(7) Å] which itself is comparable with those of the other complexes in this study.

Because of its similarity to diazabutadienes, the final ligand investigated in this study was bis(2,6-diisopropylphenyl)acenaphthene (ArBIAN). It has, however, been reported that it is a better σ-donor and π-acceptor ligand than less rigid 1,4-diazabutadienes.[25] It was, therefore, thought that if it reacted similarly with "GaI" to form a paramagnetic complex, [GaI$_2$(ArBIAN)$^\bullet$], then this complex could be reduced to a gallium carbene analogue that would perhaps have greater stability than our aforementioned DAB based system.[4] The reaction of ArBIAN with "GaI" did, indeed, proceed as expected and complex **9** was isolated in moderate yield after recrystallisation from hexane (Scheme 1). The complex is paramagnetic and its EPR spectrum shows only a broad signal centred at $g = 2.0032$ (298 K) indicating that the unpaired electron is mainly ligand based. As no meaningful NMR data could be obtained for this compound an X-ray crystal structural analysis was carried out and its molecular structure is depicted in Fig. 8 (see Table 1). The gallium centre possesses a distorted tetrahedral geometry with an acute N–Ga–N angle [86.67(16)°]. This is, however, slightly more obtuse than those observed in the closely related complexes [GaCl$_2$(Ar-BIAN)]-[GaCl$_4$] [85.1(2)°][26] and [GaI$_2${[ArNC(H)]$^\bullet{}_2$}] [85.71(6)°].[27] In addition, the Ga–N [1.957 Å av.], C–N [1.334 Å av.] and backbone C–C [1.436(6) Å] bond lengths are close to those seen in [GaI$_2${[ArNC(H)]$^\bullet{}_2$}] [1.9449(10), 1.3386(15) and 1.406(2) Å, respectively]. As in that compound, these values indicate a degree of delocalisation over the ligand. The reduction of **8** to a gallium(I) carbene analogue will be reported in a future publication.

## Conclusion

In conclusion, the reactivity of "GaI" towards bipyridines, terpyridines, imino-substituted pyridines and imino-substituted acenaphthenes has been investigated with a variety of different outcomes depending on the ligand system employed. All reactions are, however, accompanied by disproportionation of the gallium starting material to give Ga(III) complexes. Reaction of "GaI" with bipy affords the homoleptic tricationic complex, [Ga(bipy)$_3$][I]$_3$, whilst reaction with Phterpy yields a monocationic complex, [GaI$_2$(Phterpy)][I]. Reaction

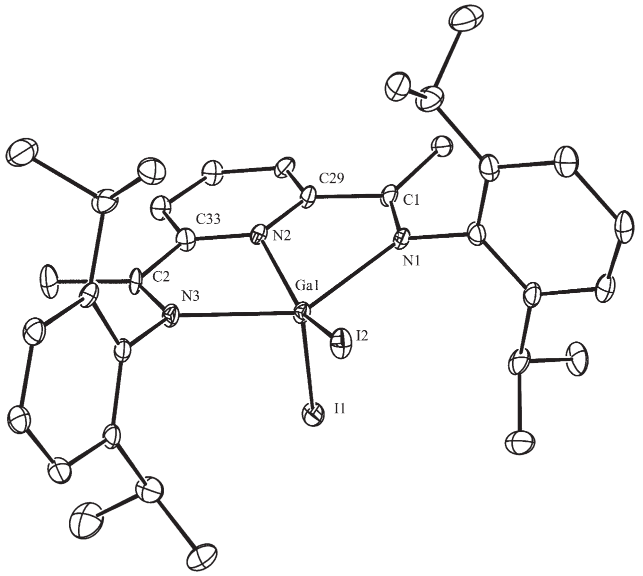


**Fig. 7** Structure of the cationic component of **8**. Selected bond lengths (Å) and angles (°): Ga(1)–I(1) 2.5442(13), Ga(1)–I(2) 2.4919(14), Ga(1)–N(1) 2.182(7), Ga(1)–N(2) 2.014(7), Ga(1)–N(3) 2.225(8), C(1)–N(1) 1.291(12), C(1)–C(29) 1.518(13), C(2)–N(3) 1.278(12), C(2)–C(33) 1.331(12); I(1)–Ga(1)–I(2) 120.74(5), I(1)–Ga(1)–N(1) 101.0(2), I(1)–Ga(1)–N(2) 93.7(2), I(1)–Ga(1)–N(3) 99.6(2), I(2)–Ga(1)–N(1) 97.4(2), I(2)–Ga(1)–N(2) 145.5(2), I(2)–Ga(1)–N(3) 95.9(2), N(1)–Ga(1)–N(2) 75.9(3), N(1)–Ga(1)–N(3) 145.0(3), N(2)–Ga(1)–N(3) 74.8(3).

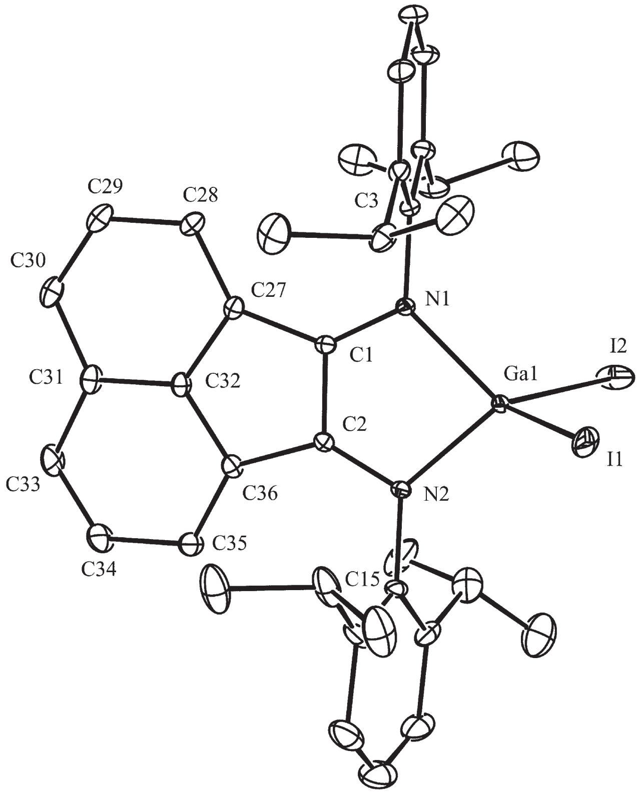


**Fig. 8** Molecular structure of **9**. Selected bond lengths (Å) and angles (°): Ga(1)–I(1) 2.5099(13), Ga(1)–I(2) 2.5015(12), Ga(1)–N(1) 1.961(4), Ga(1)–N(2) 1.954(4), N(1)–C(1) 1.335(6), N(2)–C(2) 1.332(6), C(1)–C(2) 1.436(6), C(1)–C(27) 1.464(7), C(2)–C(36) 1.464(7), N(2)–Ga(1)–N(1) 86.67(16); N(2)–Ga(1)–I(2) 117.30(12), N(1)–Ga(1)–I(2) 111.89(12), N(2)–Ga(1)–I(1) 112.81(12), N(1)–Ga(1)–I(1) 117.58(12), I(1)–Ga(1)–I(2) 109.34(4), C(1)–N(1)–Ga(1) 108.6(3), C(2)–N(2)–Ga(1) 108.6(3).

with mono(imino)pyridines leads to reductive coupling of the coordinated ligand to give neutral diamido-digallium complexes, $[\{I_2Ga[\eta^2\text{-}(Py)(NR)C(H)]\}_2]$ (R = Bu$^t$ or Ar), whereas the use of the bis(imino)pyridine, bimpy, affords the salt $[GaI_2(bimpy)][GaI_4]$. Finally, reaction of "GaI" with the bis(imino)acenaphthene, ArBIAN, yields the paramagnetic complex, $[GaI_2(ArBIAN)^{\bullet}]$. This work demonstrates the versatility of "GaI" as a reagent in inorganic and organic synthesis, which are areas we continue to explore.

## Experimental

### General remarks

All manipulations were carried out using standard Schlenk and glove-box techniques under an atmosphere of high purity argon. The solvents toluene, DME and THF were distilled over potassium whilst $Et_2O$ and hexane were distilled over Na/K alloy. $CH_2Cl_2$ and $CH_3CN$ were distilled over $CaH_2$ then freeze/thaw degassed prior to use. $^1H$ and $^{13}C$ NMR spectra were recorded on either a Bruker DXP400 spectrometer operating at 400.13 and 100 MHz respectively, or a JEOL Eclipse 300 spectrometer operating at 300.52 and 75.57 MHz, respectively. Spectra were referenced to either the $^{13}C$ or residual $^1H$ resonances of the solvent used. Mass spectra were recorded using a VG Fisons Platform II instrument under APCI conditions, or were obtained from the EPSRC National Mass Spectrometric Service at Swansea University (ESI). IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as a Nujol mulls between NaCl plates. Melting points were determined in sealed glass capillaries under argon and are uncorrected. "GaI" was synthesised by the literature method,[3] as were the ligands ArN=C(H)Py,[21] Bu$^t$N=C(H)Py,[28] bimpy[29] and ArBIAN.[30] Bipy and Phterpy were obtained commercially and recrystallised from MeCN prior to use, whilst InCl and $InCl_3$ were used as received.

**$[Ga(bipy)_3][I]_3$ 1.** To a suspension of "GaI" (5.80 mmol) in toluene (15 cm$^3$) was added a solution of 2,2′-bipyridine (0.90 g, 5.80 mmol) in toluene (15 cm$^3$) at −78 °C over 5 min. The resulting suspension was warmed to room temperature and stirred overnight to yield a yellow–orange precipitate. Volatiles were removed *in vacuo* and the residue extracted with $CH_3CN$ (30 cm$^3$) and filtered. Cooling of the filtrate to −30 °C overnight yielded orange crystals of **1** (1.28 g, 72%) mp 259–261 °C; $^1H$ NMR (400 MHz, $CD_3CN$, 298 K): $\delta$ 7.51 (m, 6H, C5H), 7.81 (m, 6H, C4H), 8.41 (m, 6H, C3H), 8.51 (m, 6H, C6H); $^{13}C$ NMR (100.6 MHz, $CD_3CN$, 298 K): $\delta$ 125.8 (C3), 128.7 (C5), 142.6 (C4), 146.7 (C6), 147.5 (C2); IR $\nu$/cm$^{-1}$ (Nujol): 1602(m), 1319(s), 1260(s), 1102(s), 801(s); MS/APCI $m/z$ (%): 157 [bipyH$^+$, 100].

**$[\{(bipy)_2Ga\}_2(\mu\text{-}OH)_2]_2[Ga_2I_6][I]_6$ 2 and $[\{(bipy)_2Ga\}_2(\mu\text{-}OH)_2][I]_4$ 3.** In an attempted preparation of **1** in which the reaction solvent was contaminated with water, the hydrolysis products, **2** (mp 140–142 °C decomp.) and **3** (mp 146–148 °C decomp.) were formed in low yield (*ca.* 20% as a mixture). Manual separation of **2** and **3** was achieved based on crystal morphology and the spectroscopic data for each were found to be indistinguishable. $^1H$ NMR (400 MHz, $CD_3CN$, 298 K): $\delta$ 2.05 (br, 2H, OH), 7.40 (m, 4H, C5H), 7.48 (m, 4H, C5′H), 8.26 (m, 4H, C4H), 8.42 (m, 4H, C4′H), 8.53 (m, 4H, C3H), 8.64 (m, 4H, C3′H), 8.76 (m, 4H, C6H), 8.83 (m, 4H, C6′H); $^{13}C$ NMR (100.6 MHz, $CD_3CN$, 298 K): $\delta$ 124.3 (C3), 124.8 (C3′), 128.9 (C5), 129.0 (C5′), 144.1 (C4), 145.0 (C4′), 145.8 (C6), 146.4 (C6′), 147.2 (C2), 147.6 (C2′); IR $\nu$/cm$^{-1}$ (Nujol): 3420(br), 1600(s), 1312(s), 1156(s), 1026(s), 774(s); MS/APCI $m/z$ (%): 469 [$(bipy)_2Ga_2OH^+$, 100].

**$[GaI_2(Phterpy)][I]$ 4.** To a suspension of "GaI" (1.30 mmol) in toluene (15 cm$^3$) was added a solution of Phterpy (0.40 g, 1.30 mmol) in toluene (15 cm$^3$) at −78 °C. The resulting suspension was warmed to room temperature and stirred overnight to yield a yellow precipitate. Volatiles were removed *in vacuo* and the residue extracted with $CH_3CN$ (30 cm$^3$) then filtered. Cooling the filtrate to −30 °C overnight yielded yellow crystals of **4** (0.28 g, 87%); mp 170–172 °C (decomp.); $^1H$ NMR (400 MHz, $CD_3CN$, 298 K): $\delta$ 7.67 (m, 3H, *o*-/*p*-PhH), 8.01 (m, 2H, C5H), 8.10 (m, 2 H, *m*-PhH), 8.46 (m, 2H, C4H), 8.72 (m, 2 H, C3H), 8.94 (s, 2 H, C3′H, C5′H), 8.97 (m, 2H, C6H); IR $\nu$/cm$^{-1}$ (Nujol): 1618(s), 1259(s), 1095(s), 1022(s), 800(s); MS/ESI $m/z$ (%): 310 [PhterpyH$^+$, 100].

**$[\{I_2Ga[\eta^2\text{-}(Py)(NAr)C(H)]\}_2]$ 5.** To a suspension of "GaI" (2.86 mmol) in toluene (10 cm$^3$) at −78 °C was added a solution of ArN=C(H)Py (0.38 g, 1.43 mmol) in toluene (10 cm$^3$) and the resulting suspension warmed to room temperature and stirred overnight to yield a green solution. This was filtered and volatiles removed *in vacuo*. The residue was extracted into $Et_2O$ (15 cm$^3$)–DME (7 cm$^3$) and the resulting solution filtered. The filtrate was concentrated to *ca* 10 cm$^3$ and cooled to −30 °C overnight to yield yellow–green crystals of **5** (0.22 g, 25%), mp 73–75 °C (decomp.); $^1H$ NMR (400 MHz, $C_6D_6$, 300 K): $\delta$ 1.25 (d, 12H, $^3J_{HH}$ = 6.7 Hz, $CH_3$), 1.29 (d, 12H, $^3J_{HH}$ = 6.7 Hz, $CH_3$), 3.23 (sept, 2H, $^3J_{HH}$ = 6.7 Hz, $CHMe_2$), 4.20 (s, 2H, CHN), 7.16 (t, 4H, $^3J_{HH}$ = 10.3 Hz, *p*-ArH), 7.27 (d, 4H, $^3J_{HH}$ = 10.3 Hz, *m*-ArH), 8.04 (m, 2H, Py-C5H), 8.39 (m, 2H, Py-C4H) 8.57 (m, 2H, Py-C3H), 8.71 (m, 2H, Py-C6H); $^{13}C$ NMR (75 MHz, $C_6D_6$, 300 K): $\delta$ 23.3 ($CH_3$), 24.9 ($CH_3$), 28.2 ($CHMe_2$), 71.5 (NC), 120.6 (*p*-Ar), 123.3 (*m*-Ar), 129.1 (*o*-Ar), 137.2 (Py-C5), 139.8 (*ipso*-Ar), 141.2 (Py-C4), 143.5 (Py-C3) 149.7 (Py-C6), 163.7 (Py-C2); IR (Nujol) $\nu$/cm$^{-1}$: 2895(s), 2353(w), 1609(w), 1564(w), 1459(s), 1377(m), 1261(w), 1105(m), 1053(m), 927(w), 800(m), 758(m), 719(m), 664(m); MS(APCI) $m/z$(%): 267 [ArN(H)C(H)Py$^+$, 100], 223 [ArN(H)C(H)Py$^+$ = Pr$^i$, 80].

**$[\{I_2Ga[\eta^2\text{-}(Py)(NBu^t)C(H)]\}_2]$ 6.** To a suspension of "GaI" (2.86 mmol) in toluene (10 cm$^3$) at −78 °C was added a solution of Bu$^t$N=C(H)Py (0.23 g, 1.43 mmol) in toluene (10 cm$^3$) and the resulting suspension warmed to room temperature and stirred overnight to yield a green solution. This was filtered and the volatiles removed *in vacuo*. The residue was extracted into DME (15 cm$^3$) and the resulting solution concentrated to *ca*. 10 cm$^3$. Cooling to −30 °C overnight yielded yellow crystals of **6** (0.20 g, 29%), mp 113–115 °C (decomp.); $^1H$ NMR (300 MHz, $CD_2Cl_2$, 300 K): $\delta$ 1.34 (s, 18H, $CH_3$), 5.29 (s, 2H, NCH), 8.17 (m, 2H, Py-C5H), 8.35 (m, 2H, Py-C3H), 8.61 (m, 2H, Py-C4H), 8.98 (m, 2H, Py-C6H); IR (Nujol) $\nu$/cm$^{-1}$: 2926(s), 2723(w), 1603(w), 1459(s), 1376(s), 1260(m), 1071(m), 1020(m), 944(w), 801(w), 722(w); MS(APCI) $m/z$(%): 972 [M$^+$, 10], 163 [Bu$^t$N(H)C(H)Py$^+$, 100].

**$[InCl_3(THF)\{\eta^2\text{-}ArN{=}C(H)Py\}]$ 7.** *Method 1.* To a suspension of InCl (0.25 g, 1.66 mmol) in THF (10 cm$^3$) at 25 °C was added ArN=C(H)Py (0.22 g, 0.83 mmol) in THF (10 cm$^3$). The resulting suspension was stirred for 5 h to yield a pale green solution. This was filtered, concentrated to *ca.* 10 ml and placed at −30 °C overnight to yield yellow crystals of **7** (0.15 g, 49%).

*Method 2.* To a suspension of $InCl_3$ (0.30 g, 1.35 mmol) in THF (10 cm$^3$) at 25 °C was added ArN=C(H)Py (0.36 g, 1.35 mmol) in THF (10 cm$^3$) over 5 min. The resulting suspension was stirred for 5 h to yield a pale green solution. This was filtered, concentrated to *ca.* 10 cm$^3$ and placed at −30 °C overnight to yield yellow crystals of **7** (0.50 g, 66%); mp 282–285 °C (decomp.); $^1$H NMR (400 MHz, $CD_3CN$, 300 K): $\delta$ 0.98 (d, 6 H, $^3J_{HH} = 6.6$ Hz, $CH_3$), 1.16 (d, 6H, $^3J_{HH} = 6.6$ Hz, $CH_3$), 1.73 (m, 4H, $CH_2$), 3.13 (sept, 2H, $^3J_{HH} = 6.6$ Hz, $CHMe_2$), 3.54 (m, 4H, $OCH_2$), 7.18 (d, 2H, $^3J_{HH} = 6.3$ Hz, *m*-ArH), 7.26 (t, 1H, $^3J_{HH} = 6.3$ Hz, *p*-ArH), 8.00 (m, 1H, Py-C5H), 8.10 (m, 1H, Py-C3H), 8.34 (m, 1H, Py-C4H), 8.60 (s, 1H, NCH), 9.09 (m, 1H, Py-C6H); $^{13}$C NMR (100.6 MHz, $CD_3CN$, 300 K): $\delta$ 22.1 ($CH_2$), 24.1 ($CH_3$), 24.9 ($CH_3$), 27.7 ($CHMe_2$), 66.9 ($OCH_2$), 118.0 (*p*-Ar), 123.5 (*m*-Ar), 127.5 (CN), 130.8 (*o*-Ar), 139.9 (Py-C4), 140.9 (*ipso*-Ar), 142.5 (Py-C5), 145.8 (Py-C3), 148.4 (Py-C6), 163.5 (Py-C2); IR (Nujol) $\nu/\mathrm{cm}^{-1}$: 2897(s), 1652(w), 1586(w), 1462(s), 1376(s), 1261(m), 1152(m), 1091(m), 1019(m), 803(m), 722(m); MS(APCI) $m/z$ (%): 487 [$M^+ -$ THF, 12], 267 [ArN(H)C(H)Py$^+$, 100].

**[$GaI_2$(bimpy)][$GaI_4$] 8.** To a suspension of "GaI" (2.58 mmol) in toluene (10 cm$^3$) at 25 °C was added a solution of bimpy (0.31 g, 0.65 mmol) in toluene (10 cm$^3$) over 5 min. The resulting suspension was stirred overnight to yield a yellow solution from which volatiles removed *in vacuo*. The residue was washed with hexane (5 cm$^3$) and extracted into $CH_2Cl_2$ (3 cm$^3$). Layering with hexane afforded yellow crystals of **8** (0.06 g, 10%); mp 212–215 °C; $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ 1.10 (d, $^3J_{HH} = 6.1$ Hz, 12H, $CH_3$), 1.24 (d, $^3J_{HH} = 6.1$ Hz, 12H, $CH_3$), 2.7 (sept, $^3J_{HH} = 6.1$ Hz, 4H, $CHMe_2$), 2.79 (s, 6H, $CH_3C{=}N$), 7.32 (d, $^3J_{HH} = 7.1$ Hz, 4H, *m*-ArH), 7.41 (t, $^3J_{HH} = 7.1$ Hz, 2H, *p*-ArH), 8.86 (d, $^3J_{HH} = 7.7$ Hz, 2H, Py-C3H), 9.24 (t, $^3J_{HH} = 7.7$ Hz, 1H, Py-C4H); $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ 20.8 ($CH_3$), 24.7 ($CH_3$), 24.8 (CH), 29.8 ($CH_3C{=}N$), 124.9 (*m*-Ar), 129.3 (Py-C3), 131.0 (Py-C4), 136.4 (*p*-Ar), 140.8 (*o*-Ar), 142.7 (*ipso*-Ar), 149.9 (Py-C2), 169.0 (C=N); IR (Nujol) $\nu/\mathrm{cm}^{-1}$: 2923(s), 1688(w), 1624(m), 1586(m), 1457(s), 1376(s), 1318(w), 1262(m), 1214(w), 1090(s), 1033(s), 935(w), 798(s), 775(m), 736(s); MS (APCI) $m/z$ (%): 480 [bimpyH$^+$, 100].

**[$GaI_2$(ArBIAN)$^\bullet$] 9.** To a suspension of "GaI" (4.00 mmol) in toluene (10 cm$^3$) at 25 °C was added a slurry of ArBIAN (1.00 g, 2.00 mmol) in toluene (40 ml) over 15 min and the resulting suspension stirred overnight to yield a red solution. Volatiles were removed *in vacuo* from this solution and the residue extracted into hexane (80 cm$^3$). Concentration to *ca.* 40 cm$^3$ and placement at −30 °C overnight gave large red blocks of **9** (0.60 g, 36%); mp 225–227 °C; IR (Nujol) $\nu/\mathrm{cm}^{-1}$: 1385(m), 1319(w), 1256(m), 1188(m), 820(m), 801(m), 770(s), 760(w); MS accurate mass (EI) calc. for $C_{36}H_{40}N_2I_2{}^{69}Ga$: $m/z$ 823.0531, measured: 823.0512.

### X-Ray crystallography

Crystals of **1**–**9** suitable for X-ray structural determination were mounted in silicone oil and crystallographic measurements 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)[31] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms included in calculated positions (riding model). Crystal data, details of data collections and refinement are given in Table 1.

CCDC reference numbers 223004–223012.

See http://www.rsc.org/suppdata/nj/b3/b310592j/ for crystallographic data in CIF or other electronic format.

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