Disproportionation and radical formation in the coordination of "GaI" with bis(imino)pyridines[†]

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Attempted coordination of "Ga^II" with two new sterically bulky, aryl substituted bis(imino)pyridine ligands lead to Ga^{III} species [2,6-{ArN=CPh}₂(NC₅H₃)]GaI₂+GaI₄⁻ (Ar = 2,5-¹Bu₂C₆H₃, 2,6-ⁱPr₂C₆H₃ = Dipp) arising from thermodynamically favorable disproportionation reactions. Examination of these reactions lead to isolation of a neutral radical species [2,6-{DippN=CPh}₂-(NC₅H₃)]GaI₂. Both EPR spectroscopy and DFT calculations on this compound indicate that the unpaired electron is localized in a di(imino)pyridine π^* orbital of an anionic ligand with nearly zero contribution from the Ga or I centers. Reaction of {2,5-¹Bu₂C₆H₃N=CPh}₂(NC₅H₃) with AlCl₃ yielded an analogous Al(III) product, [{2,5-¹Bu₂C₆H₃N=CPh}₂(NC₅H₃)]AlCl₂⁺AlCl₄⁻.

Introduction

The demonstration that iron and cobalt complexes bearing bis(imino)pyridine ligands, $2,6-\{R'N=C(R)\}_2NC_5H_3$ (1), afford exceptionally active polymerization catalysts amplified interest in these neutral, six-electron donor ligands. Furthermore, the modular steric and electronic features and the relative ease of synthesis of these species inspired their application to a range of transition metal ions.1 Some of these studies have revealed the potential for ligand centered reactivity.^{2,3} In particular, for the most commonly applied version of 1 in which R is a methyl group, single and double deprotonation of the imine methyl groups has been observed in the presence of strong bases. In some cases, this ligand system undergoes electron-transfer reactions leading to ligand reduction and, in many cases, further reaction. While the transition metal chemistry of this ligand class has received substantial attention, the main group chemistry of this species is less revealed.4



Our interest in reactive, low oxidation state p-block metal centers exhibiting nominal classical donor-acceptor coordination led us to the implementation of this ligand class for the isolation of the In(1) cation complex, $[2,6-\{2,5-$ 'Bu₂C₆H₃N=CPh}₂(NC₃H₃)]In^{+,5,6,7} These results prompted our

exploration of related chemistry with Ga(1). The development of a simple synthetic route to "GaI", *via* sonication of a stoichiometric ratio of elemental Ga and I₂, has afforded synthetic chemists entry to the fascinating realm of low oxidation state gallium chemistry.⁸ Although the formulation of this material has not been definitely established, its reactivity has indicated that it can be used as a source of Ga(I).⁹

We report the coordination of "GaI" with new bulky bis(imino)pyridine ligands and show that this reaction proceeds *via* a thermodynamically favored disproportionation pathway to yield products possessing pentacoordinate cationic and neutral paramagnetic [$\{Ar'N=CPh\}_2(NC_5H_3)$]GaI₂ architectures. Analogous Al(III) products were observed for reaction with AlCl₃ to yield [$\{2,5^{-t}Bu_2C_6H_3N=CPh\}_2(NC_5H_3)$]AlCl₂⁺AlCl₄⁻.

Discussion

In order to maximize the stability of the targeted Ga(1) species, we chose a 2,6-bis(imino)pyridine framework with bulky N-substituents, to provide steric load, and imino phenyl groups, to avoid the established deprotonation reactivity of the imino methyl groups.^{2a} To these ends we applied 2,5-¹Bu₂C₆H₃NH₂ and 2,6-¹Pr₂C₆H₃NH₂ (Dipp) in the synthesis of the two new ligand scaffolds **2** and **3** (Scheme 1).⁵ Using a modified literature synthesis,¹⁰ the two bis(imino)pyridine species were prepared in good yields as yellow powders. NMR spectroscopy and microanalyses confirmed the identities of these two species and, in the case of **2**, X-ray crystallography provided definitive structural elucidation.⁵

The steric demands of these ligand architectures were supported by the temperature dependent appearance of the ¹H and ¹³C NMR spectra of **2** and **3**. At ambient temperature both compounds displayed a complex set of signals in the aliphatic and aromatic regions of the spectrum that were attributed to hindered dynamics of solution conformers. While heating d_8 -toluene solutions of **2** and **3** to 80 °C did lead to coalescence of the spectra, the limiting spectra required higher temperatures (115 °C) using d_6 -dimethyl sulfoxide as the NMR solvent. Under these conditions, the ¹H NMR signals reduced to two resonances for the 'Bu groups of **2** and one set of signals for the 'Pr substituents of **3**.

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[†] Electronic supplementary information (ESI) available: A figure of the ESR spectrum of 7. Details for the computational studies. CIF files for 4–7. CCDC reference numbers 738765–738767 and 749531. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b920047a



Although the reaction of $2,6-\{2,5-^{t}Bu_{2}C_{6}H_{3}N=CPh\}_{2}(NC_{5}H_{3})$

(2) with "GaI" proceeded smoothly, this reaction consistently

yielded a mixed product of predominantly a red solid, a more

crystalline orange material, and some insoluble gray powder that

appeared to be Ga metal. Attempts to cleanly separate the two

soluble solids have, so far, been unsuccessful and the NMR analysis

of this mixture is complicated by broadness of the observed

resonances. Fortunately, we were able to isolate a small number

of orange single crystals 4 (Scheme 1). The molecular structure

of this Ga(III) species was confirmed through single crystal X-ray

analysis as summarized in Table 1 and Fig. 1. This Ga(III) complex

consisted of $[2,6-\{2,5-^{t}Bu_{2}C_{6}H_{3}N=CPh\}_{2}(NC_{5}H_{3})]GaI_{2}^{+}GaI_{4}^{-}$ as

a well-separated cation/anion pair with the cationic portion of

compound 4, shown in Fig. 1. Selected bond distances and angles for this species are presented in Tables 2 and 3 respectively. The

geometry of the gallium center within this cation is distorted trigonal bipyramidal with the three-fold plane (Σ angles = 360°)



Fig. 1 Structure of the $[2,6-\{2,5^{-t}BuC_6H_3N=CPh\}_2(NC_5H_3)]GaI_2^+$, cation of compound 4 with hydrogen atoms, the GaI_4^- counter-ion and co-crystallized CHCl₃ omitted for clarity.

defined by the pyridine center, N2, and the two I1 and I2 centers. The limitations of ligand geometry led to the pseudo-axial imine centers oriented with an N1-Ga-N3 angle of $148.8(2)^{\circ}$. The two five-membered rings resulting from the coordination of the pyridyl and imine moieties are planar. As anticipated the equatorial Ga-N2 distance of 2.017(5) Å is shorter than the axial Ga-Nimine distances of 2.151(5) Å and 2.181(5) Å.

distances of 2.151(5) Å and 2.181(5) Å. A more direct synthesis of **4** was provided by reaction of **2** with GaI₃ in a stoichiometric ratio of 1:2. The resulting redorange solution yielded bright orange **4** in 93% yield. The room temperature NMR spectra of **4** are simplified relative to that of the free ligand and indicate two conformers for **4**. The ratio between these species was dependent on temperature and solvent. These observations were attributed to atropisomerism arising from restricted rotation of the N-aryl groups in the coordinated 2,6-bis (imino)pyridine ligands of **4**.¹¹

Application of the related ligand 2,6-{DippN=C(Me)}₂-(NC₅H₃) (Dipp = 2,6-ⁱPr₂C₆H₃), in the isolation of cationic Ga(III) and Al(III) halide complexes ([LMX₂]⁺MX₄⁻, M = Ga, X = I; M = Al, X = Cl) has been reported.^{4c,g} The Ga complex was obtained

 Table 1
 Selected crystal data and data collection parameters for compounds 4–7

Compound	4	5	6	7	
Empirical formula	$C_{47}H_{55}I_6Ga_2N_3\cdots$ (CHCl ₃) ₃	$C_{47}H_{55}Cl_6Al_2N_3$	$C_{43}H_{47}I_6Ga_2N_3\cdots(OC_4H_8)$	C43H47GaI2N3	
Formula weight	1920.88	928.64	1578.78	929.36	
T/K	120(2)	120(2)	209	202(2)	
λ/Å	0.71073	0.71073	0.71073	0.71073	
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	
Space group	$P2_1/n$	Pnma	$P2_{1}2_{1}2_{1}$	P1	
a/Å	20.582(8)	15.124(4)	10.647(3)	8.411(2)	
b/Å	16.057(7)	18.054(5)	19.533(5)	9.720(2)	
c/Å	22.528(9)	22.939(6)	27.369(7)	13.536(3)	
α (°)	90	90	90	76.463(4)	
β (°)	113.432(6)	90	90	78.265(4)	
γ (°)	90	90	90	67.402(4)	
$V/Å^3$	6831(5)	6263(3)	5692(3)	985.3(4)	
Z	4	4	4	1	
ρ (calc)/Mg m ⁻³	1.868	1.080		1.566	
μ/mm^{-1}	3.885	0.428	4.234	2.298	
Absorption correction		Semi-empirical from equivalents			
Flack parameter		* *	0.36(7)	0.02(4)	
R _{int}	0.0483	0.0529	0.136	0.0495	
Final R indices $[I > 2\sigma(I)]$					
R_1^a	0.0638	0.0657	0.0897	0.0738	
wR2 ^b	0.1792	0.1869	0.2232	0.1589	
${}^{a}R_{1} = \sum F_{o} - F_{c} / \sum F_{o} $	$.^{b} WR_{2} = (\sum W(F_{o} - F_{c})^{2} / \sum$	$\sum F_{o} ^{2})^{1/2}$.			

Table 2Selected bond distances (Å) for compounds 4–7

4		5		6		7	
C(15)-C(22)	1.493(8)	C(4)-C(3)	1.494(4)	C(13)-C(20)	1.48(3)	C(13)-C(20)	1.462(15)
C(26)-C(27)	1.495(9)	_	_	C(24)-C(25)	1.50(3)	C(24)-C(25)	1.473(16)
C(25)-C(26)	1.384(10)	_	_	C(23)-C(24)	1.36(3)	C(20)-C(21)	1.3900
C(22)-C(23)	1.396(9)	C(3)-C(2)	1.389(4)	C(20)-C(21)	1.36(3)	C(23)-C(24)	1.3900
C(24)-C(25)	1.384(10)	C(1)-C(2A)	1.377(4)	C(22)-C(23)	1.28(3)	C(21)-C(22)	1.3900
C(23)-C(24)	1.391(9)	C(2)-C(1)	1.377(4)	C(21)-C(22)	1.46(3)	C(22)-C(23)	1.3900
Ga(1)-I(1)	2.5478(12)	Al(1)-Cl(1)	2.126(2)	Ga(1)-I(1)	2.512(3)	Ga-I(1)	2.5230(18)
Ga(1)-I(2)	2.5067(12)	Al(1)-Cl(2)	2.129(2)	Ga(1)-I(2)	2.538(2)	Ga-I(2)	2.562(2)
Ga(1)-N(1)	2.181(5)	Al(1)-N(2)	2.048(3)	Ga(1)-N(1)	2.214(17)	Ga-N(1)	2.171(13)
Ga(1)-N(2)	2.017(5)	Al(1)-N(1)	1.947(3)	Ga(1)-N(2)	2.022(16)	Ga-N(2)	1.952(6)
Ga(1)-N(3)	2.151(5)	Al(1)-N(2A)	2.048(3)	Ga(1)-N(3)	2.189(17)	Ga-N(3)	2.334(13)
N(1)-C(6)	1.448(7)	N(2)-C(16)	1.461(4)	N(1)-C(9)	1.52(3)	N(1)-C(6)	1.433(14)
N(3)-C(34)	1.449(8)		_	N(3)-C(32)	1.48(2)	N(3)-C(37)	1.426(14)
N(1)-C(15)	1.278(8)	N(2)-C(4)	1.285(4)	N(1)-C(13)	1.27(3)	N(1)-C(13)	1.318(17)
N(3)-C(27)	1.296(8)		_	N(3)-C(25)	1.36(3)	N(3)-C(25)	1.321(18)
N(2)-C(26)	1.344(8)	N(1)-C(3A)	1.333(3)	N(2)-C(24)	1.31(2)	N(2)-C(24)	1.3900
N(2)-C(22)	1.323(8)	N(1)-C(3)	1.333(3)	N(2)-C(20)	1.38(3)	N(2)-C(20)	1.3900

 Table 3
 Selected bond angles (°) for compounds 4–7

4		5		6		7	
N(2)-Ga(1)-N(3)	76.2(2)	N(1)-Al(1)-N(2A)	77.95(8)	N(2)-Ga(1)-N(3)	75.2(6)	N(2)-Ga-N(3)	75.9(4)
N(2)-Ga(1)-N(1)	75.3(2)	N(1)-Al(1)-N(2)	77.95(8)	N(2)-Ga(1)-N(1)	76.0(6)	N(2)-Ga-N(1)	77.6(4)
N(2)-Ga(1)-I(2)	143.80(15)	N(1)-Al(1)-Cl(2)	108.11(13)	N(2)-Ga(1)-I(2)	95.9(4)	N(2)-Ga-I(2)	103.2(3)
N(2)-Ga(1)-I(1)	100.25(15)	N(1)-Al(1)-Cl(1)	133.82(13)	N(2)-Ga(1)-I(1)	144.7(4)	N(2)-Ga-I(1)	143.8(3)
N(2)-C(22)-C(23)	121.7(6)	N(1)-C(3)-C(2)	120.2(3)	N(2)-C(20)-C(21)	118.3(19)	N(2)-C(20)-C(21)	120.0
N(2)-C(26)-C(25)	120.7(6)	_	_	N(2)-C(24)-C(23)	121.6(18)	N(2)-C(24)-C(23)	120.0
N(2)-C(22)-C(15)	113.3(5)	N(1)-C(3)-C(4)	112.5(3)	N(2)-C(20)-C(13)	114.2(18)	N(2)-C(20)-C(13)	112.4(7)
N(2)-C(26)-C(27)	113.7(6)	_	_	N(2)-C(24)-C(25)	112.8(18)	N(2)-C(24)-C(25)	115.1(7)
N(1)-C(15)-C(22)	115.3(5)	N(2)-C(4)-C(3)	113.1(3)	N(1)-C(13)-C(20)	115.1(19)	N(1)-C(13)-C(20)	116.7(12)
N(3)-C(27)-C(26)	114.2(5)	_	_	N(3)-C(25)-C(24)	113.5(16)	N(3)-C(25)-C(24)	116.1(12)
N(1)-C(15)-C(21)	126.4(6)	N(2)-C(4)-C(10)	127.3(3)	N(1)-C(13)-C(14)	128(2)	N(1)-C(13)-C(19)	126.1(12)
N(3)-C(27)-C(33)	126.9(6)	_	_	N(3)-C(25)-C(26)	122.5(18)	N(3)-C(25)-C(31)	125.3(13)
C(34)-N(3)-Ga(1)	123.2(4)	C(16)-N(2)-Al(1)	121.9(2)	C(32)-N(3)-Ga(1)	125.8(12)	C(37)-N(3)-Ga	129.7(9)
C(6)-N(1)-Ga(1)	123.3(4)	_	_	C(9)-N(1)-Ga(1)	123.7(13)	C(6)-N(1)-Ga	128.3(8)
C(15)-N(1)-Ga(1)	114.4(4)	C(4)-N(2)-Al(1)	116.7(2)	C(13)-N(1)-Ga(1)	114.2(14)	C(13)-N(1)-Ga	111.3(9)
C(27)-N(3)-Ga(1)	115.5(4)	_	_	C(25)-N(3)-Ga(1)	113.1(12)	C(25)-N(3)-Ga	110.0(10)
C(15)-N(1)-C(6)	122.0(5)	C(4)-N(2)-C(16)	121.3(3)	C(13)-N(1)-C(9)	120.3(18)	C(13)-N(1)-C(6)	119.6(12)
C(27)-N(3)-C(34)	121.2(5)	_	_	C(25)-N(3)-C(32)	121.0(16)	C(25)-N(3)-C(37)	119.8(12)
C(22)-C(15)-C(21)	118.3(5)	C(10)-C(4)-C(3)	119.5(3)	C(20)-C(13)-C(14)	117(2)	C(20)-C(13)-C(19)	117.2(10)
C(33)-C(27)-C(26)	118.9(6)		_	C(24)-C(25)-C(26)	124.0(17)	C(24)-C(25)-C(31)	118.4(11)
C(22)-N(2)-Ga(1)	118.5(4)	C(3)-N(1)-Al(1)	117.98(18)	C(20)-N(2)-Ga(1)	115.0(13)	C(20)-N(2)-Ga	117.3(4)
C(26)-N(2)-Ga(1)	117.5(5)	C(3A)-N(1)-Al(1)	117.98(17)	C(24)-N(2)-Ga(1)	118.5(13)	C(24)-N(2)-Ga	119.5(4)
C(22)-N(2)-C(26)	121.0(6)	C(3A)-N(1)-C(3)	122.1(4)	C(20)-N(2)-C(24)	121.3(17)	C(20)-N(2)-C(24)	120.0

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as a yellow solid in only 10% yield from the reaction of the ligand with "GaI". The Al complex was formed from the direct reaction of the ligand with AlCl₃. Similarly, ligand 2 combines readily with AlCl₃ in a 1:2 stoichiometric ratio that ultimately yielded a bright-yellow powder 5 in 96% yield (eqn (1)). Coordination of the ligand in a symmetrical fashion was clearly indicated by the appearance of a simplified ¹H NMR spectrum of the ^tBu substituents as two singlets of appropriate integration. Singlecrystal X-ray analysis for this Al complex (Table 1) revealed 5 to be $[\{2,5^{+}Bu_2C_6H_3N=CPh\}_2(NC_5H_3)]AlCl_2^+AlCl_4^-$ as a well separated cation/anion pair; the cationic portion of compound 5 is shown in Fig. 2 with relevant bond lengths and angles given in Tables 2 and 3. The geometry of the aluminium center within this constituent is distorted trigonal bipyramidal, with the threefold plane (Σ angles = 360°) defined by the N1, Cl1, and Cl2 centers. Like 4, limitations of the ligand geometry lead to a pseudoaxial N2-Al-N2A angle of only 153.9(2)°. The two fivemembered rings resulting from the coordination of the pyridyl and

imine moieties display a sum of internal angles of 538.3, values indicating planarity.

Clearly, the reaction between "GaI" and **2** involves more than simple ligand coordination. In an effort to unravel the details of this reaction, obtain simpler spectroscopic data and perhaps determine the identity of the major red product, we replaced the $N(2,5-Bu_2C_6H_3)$ groups of **2** with the more symmetrical Dipp substituent in ligand **3**. Similar to the reaction with **2**, the 1:1 reaction between "GaI" and **3** produced a rapid color change from the yellow color of the initial solution to red. Along with some gray powder of elemental Ga, two soluble species, one red



Fig. 2 Structure of the $[{2,5^{-t}BuC_6H_3N=C(Me)}_2(NC_5H_3)]AlCl_2^+$, cation of compound 5 with hydrogen atoms and the $AlCl_4^-$ counter-ion omitted for clarity.

and the other yellow-orange, were obtained. As we observed from the reaction of ligand 2, the major product appears to be the red material. From the reaction, a mixture of crystals of a yelloworange compound 6 and a red compound 7 could be isolated and it was fortunate that both of these were suitable for single crystal analysis (Table 1).

The structure obtained for the yellow-orange species, **6**, is a Ga(III) complex analogous to that of **4** and is depicted in Fig. 3 with selected bond distances and angles presented in Tables 2 and 3. The cationic component of **6** presents the Ga center in a distorted trigonal bipyramidal geometry with an equatorial pyridyl nitrogen (N2) and two coordinated iodide (I1, I2) centers. The pseudo-axially coordinated imine centers (N1-Ga-N3 = 146.0(6)°) exhibit slightly longer bond distances (2.189(17) Å and 2.214(17) Å) than the Ga-N_{py} distance of 2.022(16) Å.



Fig. 3 Structure of the $[2,6-{DippN=CPh}_2(NC_5H_3)]GaI_2^+$, cation of compound 6 with hydrogen atoms, the GaI_4^- counter-ion and co-crystallized THF omitted for clarity.

The energetic features for the disproportionation reaction of DippN=C(Me) $_2(NC_5H_3)$ and "GaI" to compound **6** and Ga(0) were examined computationally. These DFT computations using the B3LYP functional and DGDZVP basis set supported the thermodynamic favorability of the disproportionation process with an enthalpy for this reaction of -28.50 kJ mol⁻¹.¹²

Consideration of the route to obtain **6** lead to an investigation of an *in situ* method to access **6** from the elements that is provided by direct sonication of Ga and I_2 with addition of ligand **3**. The yield of this reaction was directly linked to the stoichiometry of the ratio Ga : I_2 used in the sonication step. A lower yield was provided by a 2:1 ratio of "GaI" while the 2:3 ratio, corresponding to GaI₃, provided a 98% yield of **6**. These observations are consistent with the observed disproportionation from the "GaI" reagent. Excellent yields (>90%) of **6** were also obtained from reaction of **3** with GaI_3 .

Red crystals of 7, the second and a major product from the reaction of "GaI" and 3, were also analyzed by single crystal X-ray analysis and the results as well as a direct comparison with the structure of 6 are presented in Fig. 4. Selected bond distances and angles for this compound are presented in Tables 2 and 3. The first notable feature of these results is the observation that 7 is the neutral analogue of the cation of compound 6. Secondly, the similarity of the coordination of ligand 3 to the GaI₂ unit in these two species and the apparent undistorted nature of the ligand is significant and accentuated by the overlay of the structures of 6 and 7 shown in Fig. 4. These features indicate that 7 is a radical species.



Fig. 4 An overlay of the structures of the cation of compound 6, $[2,6-{DippN=CPh}_2(NC_5H_3)]GaI_2^+$ (red), and the radical 7, $[2,6-{DippN=CPh}_2(NC_3H_3)]GaI_2$ (blue). Hydrogen atoms have been omitted for clarity.

Although it may be initially tempting to interpret these data as compound 7 consisting of a $Ga^{II}I_2$ radical species coordinated by a neutral ligand 3, the alternative view that 7 is composed of a GaI_2^+ cation coordinated to an anion radical of the ligand is certainly precedented for the non-innocent di(imino)pyridine ligand system.^{2a,3a} We examined 7 by EPR spectroscopy and DFT computations in an effort to more decisively assign the unpaired electron density.

The observation of an EPR signal with a g value of 2.0029 confirms the fact that 7 possesses radical character and indicates that the free electron is ligand localized. A slightly asymmetric triplet pattern further suggests that the electron predominantly samples one N center in the ligand.

A DFT computational study was undertaken to obtain a more thorough understanding of the electronic nature of radical 7. Calculations were carried out with the B3LYP functional and the DGDZVP basis set. The results of these computations place the unpaired electron on the ligand. The SOMO is depicted in Fig. 5 and consists mainly of a delocalized di(imino)pyridine π^* orbital of an anionic ligand with nearly zero contribution from the Ga or I centers.

Conclusions

While in some cases "GaI" may provide synthetic access to Ga¹ species, the coordination of this species with two new aryl substituted bis(imino)pyridine ligands leads to a thermodynamically



Fig. 5 The SOMO for the radical $[2,6-{DippN=CPh}_2(NC_3H_3)]GaI_2$ 7. Hydrogen atoms are omitted for clarity. Isovalue = 0.0300.

favorable disproportionation reaction with ultimate isolation of the Ga^{III} species $[2,6-{Ar'N=CPh}_2(NC_5H_3)]GaI_2^+GaI_4^- (Ar' = 2,5-IBu_2C_6H_3$ **4**, 2,6-IPr_2C_6H_3 **6**). These observations allowed for the development of a direct, "one-pot" synthesis from elemental Ga and I₂. Apparent intermediates of this reaction were isolated and characterized as neutral radical species. Employing similar strategies, our continuing efforts are aimed at revealing the features that will promote isolation of new low-valent main group metal complexes.

Experimental

General methods

Unless otherwise stated, reactions were performed in a glovebox with a nitrogen atmosphere. All solvents were sparged with nitrogen and then dried by passage through a column of activated alumina using an apparatus purchased from Anhydrous Engineering. Deuterated chloroform was dried using activated molecular sieves. Metal halides were purchased from Strem Chemicals and used as received. All other reagents were purchased from Aldrich and used without further purification. NMR spectra were run on a Bruker Avance 300 MHz spectrometer with deuterated chloroform as a solvent and internal standard. Elemental analyses were performed by Midwest Microlab LLC, Indianapolis IN. EPR measurements were performed using a JEOL FA-100 X-Band EPR spectrometer equipped with a JEOL ES-UCX2 cylindrical cavity. Samples were held in clear-fused silica tubes (5 mm diameter) purchased from Wilmad. All spectra were recorded over 2 min at 5 mW power, modulation width of 0.025 mT, time constant of 0.03 s, and a sweep width of 30 mT. "GaI" was prepared according to the literature.8

Both the thermochemical analysis of the disproportionation reaction of 2,6-{DippN=CPh}₂(NC₅H₃)]GaI in the presence of GaI and the optimization of compound **6** were performed with DFT calculations and the B3LYP functional using the Gaussian 03 (revision D.01) suite of programs.¹³ The DGDZVP basis set was employed. Further details are provided in the supplementary information (ESI⁺.

2,6-Bis{1-[(2,5-ditertbutylphenyl)imino]-benzyl}pyridine (2)⁵

The synthetic procedure was adapted from a literature preparation described by Kleigrewe *et al.*¹⁰ Under lab atmosphere, a 250 mL round bottom flask was charged with 2,6-dibenzoylpyridine (5.4 g 18.8 mmol), 2,5-di-*tert*-butylaniline (7.4 g, 41.4 mmol), and *p*-toluenesulfonic acid (0.1 g) in toluene (150 mL). A Dean–Stark trap was attached to the flask and the reaction mixture was placed under nitrogen atmosphere and heated to reflux (140 °C) for

48 h. Over this time, the reaction mixture became brown and a brown precipitate formed. The mixture was concentrated in vacuo, resulting in a thick brown paste, which was subsequently dissolved in cold methanol to give a yellow precipitate. The yellow solid was collected by filtration and washed with a minimal amount of cold hexanes: ether (9:1) to remove aniline impurities. The filtrate was reduced again to a thick paste and this procedure was repeated several times. Compound 2 was isolated as a bright yellow powder in 67% yield (8.377 g). Analysis calcd for C₄₇H₅₅N₃: C, 85.28; H, 8.37; N, 6.35. Found: C, 84.68; H, 8.73; N, 6.12. MS (EI) m/z 605 (M⁺). Room temperature NMR spectra, ¹H NMR (CDCl₃, 300 MHz) and ¹³C NMR (CDCl₃, 75 MHz), displayed a complex array of resonances which could not be completely assigned due to rotational confomers. NMR spectra obtained at 115 °C resulted in simplification of the spectra. ¹H NMR (d_6 -dimethyl sulfoxide, 500 MHz, $T = 115 \,^{\circ}\text{C}$) δ 8.20–6.90 (br m, 17 H, Ar–H), 6.21 (br s, 2H, Ar-H), 1.39 (br s, 18H, 'Bu), 0.99(br s, 18H, 'Bu). ¹³C NMR (d₆-dimethyl sulfoxide, 125 MHz, T = 115 °C) δ 148.5 (Ar-CH), 147.9 (Ar-CH), 138.7 (Ar-CH), 129.1 (Ar-CH), 128.4 (Ar-CH), 128.3 (Ar-CH), 126.1 (Ar-CH), 120.8 (Ar-CH), 118.8 (Ar-CH), 131.6 (Ar-CH), 99.9 (Ar-CH), 35.0 (Ar-'Bu, C-(CH₃)₃), 33.8 (Ar-^{*i*}Bu, C-(CH₃)₃), 31.1 (Ar-^{*i*}Bu, CH₃), 30.5 (Ar-^{*i*}Bu, CH₃).

2,6-Bis{[2,6-di(isopropyl)phenyl)imino]benzyl}pyridine (3)

Following a procedure similar to that described for 2, a mixture of 2,6-dibenzoylpyridine (5.0 g, 17.4 mmol), 2,6-diisopropylaniline (7.5 g, 38.3 mmol), and p-toluenesulfonic acid (0.2 mg) in toluene (50 mL) were placed in a round bottom flask equipped with a Dean-Stark trap. Under a nitrogen atmosphere, the reaction mixture was heated to reflux in an oil bath at 140 °C for 48 h then cooled to room temperature and the solvent was removed under vacuum to give a dark yellow oil. Hexanes were added and a small quantity of a white solid was removed by filtration. The filtrate was removed under vacuum yielding a dark yellow oil. Methanol (~400 mL) was added to this oil and the mixture was stirred for several minutes, causing the product to precipitate as a yellow solid which was filtered off and rinsed with methanol. The filtrate was reduced to about half the initial volume under vacuum, and then placed in a refrigerator, causing additional product to precipitate, which was filtered off and rinsed with methanol. The product was obtained as a yellow powder. Yield: 7.2 g (68%). Elemental analysis for C₄₃H₄₇N₃ Calculated: C, 85.25; H, 7.82; N, 6.94 Found: C, 85.08; H, 7.69; N, 6.86. MS (EI) m/z 605 (M⁺). ¹H NMR (T =115 °C, d_6 -dimethyl sulfoxide, 300 MHz) δ 7.82 (br t, 1 H, py, p-CH), 7.55-7.20 (br m, 12 H, Ar-H), 6.94 (br s, 6H, Ar-H), 2.90 (m, 4H, ^{*i*}Pr), 1.00 (d, 24H, ^{*i*}Pr). ¹³C NMR (T = 115 °C, d_{6} -dimethyl sulfoxide, 75 MHz) δ 164.6 (C=N imine), 155.2 (py, o-C=N), 146.2 (Ar-CH), 136.8 (Ar-i-C), 135.5 (Ar-CH), 130.1 (Ar-CH), 128.9 (Ar-CH), 128.1 (Ar-CH), 123.7 (Ar-CH), 123.2 (Ar-CH), 122.7 (Ar-CH), 28.2 (Ar-ⁱPr, CH-(CH₃)₂), 22.9 (Ar-ⁱPr, CH₃), 22.3 (Ar-^{*i*}Pr, CH₃).

Reaction of [2,6-bis{2,5- ${}^{t}Bu_{2}C_{6}H_{3}N=CPh$ }₂(NC₅H₃)] (2) with "GaI"

"GaI" powder (59 mg, 0.300 mmol) was added to a clear yellow solution of 2(200 mg, 0.300 mmol) in 8 mL of toluene. The reaction mixture changed color immediately from translucent yellow to a

dark opaque red/purple. The reaction was sealed and allowed to stir for 4.5 h and then cooled to -20 °C overnight, over which time a dark red precipitate formed. The solution was filtered and a red solid was washed with 10×2 mL hexanes, and allowed to dry under vacuum. Dark red powder (80 mg) was isolated, dissolved in toluene and cooled to -20 °C to give a mixture of dark red powder and a small amount of orange powder. Despite multiple attempts, these two compounds could not be completely isolated from each other. The red powder is poorly soluble and shows only very broad ¹H signals by NMR. Small dark red crystals that were not suitable for X-ray crystallography could be grown.

Synthesis of $[2,6-bis{2,5-'Bu_2C_6H_3N=CPh}_2(NC_5H_3)]GaI_2(GaI_4)$ (4)

GaI₃ powder (135 mg, 0.300 mmol) was added to a clear yellow solution of 2 (100 mg, 0.151 mmol) in 8 mL of toluene. Colour change was immediate as the solution went from translucent yellow to a bright translucent red, gradually becoming opaque. The reaction mixture was sealed and allowed to stir for 6 h and then cooled to -20 °C overnight, over which time a bright orange precipitate formed. The solution was filtered, washed with $10 \times$ 2 mL hexanes, and the solid was allowed to dry under vacuum. A bright orange powder of 4 was isolated in 93% yield. Yelloworange needle like crystals suitable for X-ray analysis were grown by diffusion of hexanes into a saturated CDCl₃ solution held at -20 °C for several days. ¹H and ¹³C NMR point to the existence of two conformers in solution. Conformer A: ¹H NMR (CDCl₃, 300 MHz): δ 9.02 (br t, 1 H, py, p-CH), 8.53 (br d, 2 H, py, m-CH), 8.13 (br m, 2 H, aromatic), 7.80-7.05 (br m, 13H, aromatic), 6.48 (br s, 1 H, aromatic), 1.39 (br s, 18H, 'Bu), 0.95 (br s, 18H, 'Bu). ¹³C NMR (CDCl₃, 75 MHz). δ 164.8 (C=N imine), 150.1 (py, o-C=N), 149.8 (Ar-CH), 145.2 (Ar-CH), 140.8 (Ar, i-C), 138.4 (Ar-CH), 134.6 (Ar-CH), 132.2 (Ar, i-C), 131.4 (Ar-CH), 130.1 (Ar-CH), 129.4 (Ar-CH), 128.6 (Ar-CH), 125.6 (Ar-'Bu, C-'Bu), 124.1 (Ar-'Bu, C-'Bu), 36.7 (Ar-'Bu, C-(CH₃)₃), 34.9 (Ar-'Bu, C-(CH₃)₃), 31.6 (Ar-^{*i*}Bu, CH₃), 31.2 (Ar-^{*i*}Bu, CH₃). Conformer B: ¹H NMR (CDCl₃, 300 MHz): δ 8.63 (br t, 1 H, py, *p*-CH), 8.46 (br d, 2 H, py, m-CH), 7.80-7.05 (br m, 16H, aromatic), 1.36 (br s, 18H, 'Bu), 1.01 (br s, 18H, 'Bu).¹³C NMR (CDCl₃, 75 MHz). δ 162.1(C=N imine), 149.6 (Ar-CH), 145.3 (py, o-C=N), 142.7 (Ar, i-C), 138.3 (Ar-CH), 133.6 (Ar-CH), 131.7 (Ar-CH), 130.6 (Ar, i-C), 129.9 (Ar-CH), 129.2 (Ar-'Bu, C-'Bu), 128.9 (Ar-'Bu, C-'Bu), 126.9 (Ar-CH), 124.8 (Ar-CH), 121.1 (Ar-CH), 35.3 (Ar-^tBu, C-(CH₃)₃), 34.5 (Ar-^tBu, C-(CH₃)₃), 35.3 (Ar-^tBu, CH₃), 30.9 (Ar-'Bu, CH₃). A sample for elemental analysis was obtained by recrystallization in toluene, resulting in a 4:3 toluene adduct of 4. Calculated for [C47H55I6Ga2N3]3[C7H8]4: C 40.14, H 3.93, N 2.49, Found C 40.03, H 4.14, N 2.80.

$$\label{eq:synthesis of constraint} \begin{split} &Synthesis of [2,6-bis\{2,5-'Bu_2C_6H_3N=CPh\}_2-(NC_5H_3)] AlCl_2[AlCl_4] (5) \end{split}$$

AlCl₃ powder (40 mg, 0.300 mmol) was added to a clear yellow solution of 2(100 mg, 0.151 mmol) in 8 mL of toluene. The reaction mixture was sealed and allowed to stir for 6 h. Colour change was immediate as the solution went from translucent yellow to opaque orange. The solution was then held at -20 °C overnight, over which time a bright yellow precipitate formed. The reaction

mixture was filtered, washed with 10 × 2 mL hexanes, and allowed to dry under vacuum. Compound **5** was isolated as a bright yellow powder in 96% (132 mg yield). Yellow/orange needle-like crystals were obtained by diffusion of saturated THF solution in hexanes, and storing at -20 °C for several days. Analysis calcd for C₄₇H₅₅Cl₆Al₂N₃: C 60.79, H 5.97, N 4.52. Found C 59.94, H 5.97, N 4.65. ¹H NMR (CDCl₃, 300 MHz): δ 8.90 (t, 1H, py, *p*-CH), 8.39 (d, 2H, py, *m*-CH), 8.20–6.90 (br m, 16H, aromatic), 1.39 (br s, 18H, 'Bu), 1.06 (br s, 18H, 'Bu).¹³C NMR (CDCl₃, 75 MHz). δ 168.9 (C=N imine), 149.3 (py, *m*-CH), 148.2 (py, *o*-C=N), 138.7 (py, *p*-CH), 138.1 (Ph, *o*-CH), 133.8 (Ph, *i*-C), 132.9 (Ar-'Bu, *i*-C), 131.7 (Ar-'Bu, C-'Bu), 129.4 (Ph, *m*-CH), 128.6 (Ph, *p*-CH), 128.2 (Ar-'Bu, CH), 125.7 (Ar-'Bu, C-'CH₃)₃), 34.8 (Ar-'Bu, C-(CH₃)₃), 32.9 (Ar-'Bu, CH₃), 31.1 (Ar-'Bu, CH₃).

Reaction of [2,6-bis{2,6- ${}^{i}Pr_{2}C_{6}H_{3}N=CPh\}_{2}(NC_{5}H_{3})]$ (3) and "Gal"

"GaI" powder (65 mg, 0.331 mmol) was added to a clear yellow solution of 3 (200 mg, 0.331 mmol) in 8 mL of toluene. The reaction mixture changed color immediately from translucent yellow to a dark opaque red and was allowed to stir for 6 h at room temperature. The reaction mixture was cooled to -20 °C and stored overnight. During this period a combination of bright yellow and red precipitate formed. The reaction mixture was filtered and the solid was washed with 10×2 mL hexanes then dried under vacuum to yield 160 mg of bright red powder mixed with yellow powder. Despite multiple attempts, these two compounds could not be completely isolated from each other. The red powder is poorly soluble and showed only very broad ¹H NMR signals. A combination of orange needle like crystals, and small red rectangular plate-like crystals suitable for X-ray diffraction were grown by diffusion of saturated solution of toluene in hexanes. The orange needle like crystals were identified as compound 6, $[2,6-{DippN=CPh}_{2}(NC_{5}H_{3})]GaI_{2}^{+}GaI_{4}^{-}$, and the red platelets as complex 7, $[2,6-{DippN=CPh}_2(NC_5H_3)]GaI_2$.

Solution state EPR of compound 7 provided an asymmetric triplet centered at 336.000 mT. The spectrum is shown in Figure S1 (ESI[†]).

Synthesis of [2,6-bis{2,6- $^{i}Pr_{2}C_{6}H_{3}N=CPh$ }₂(NC₅H₃)]GaI₂GaI₄ (6)

Method 1. Ga metal (80 mg, 1.15 mmol) and I_2 (437 mg, 1.72 mmol) were added to a clear yellow solution of 3 (347 mg, 0.659 mmol) in 15 mL of toluene. The reaction mixture immediately changed color resulting in a deep red solution. The reaction mixture was sealed and sonicated for 3 h. During this period the solution became an intense opaque yellow/orange colored mixture. The solution was allowed to stir overnight, then filtered, washed with 5×2 mL hexanes, and allowed to dry under vacuum. A deep yellow-orange powder of 6 was isolated in 98% yield.

Method 2. GaI₃ powder (149 mg, 0.331 mmol) was added to a clear yellow solution of **3** (100 mg, 0.166 mmol) in 8 mL of toluene. The reaction mixture immediately changed color from translucent yellow to bright translucent red, which gradually become opaque and was sealed and allowed to stir for 6 h. The reaction mixture was then cooled to -20 °C overnight, over which time a

yellow-orange precipitate formed. The reaction mixture was filtered and the solid washed with 10×2 mL hexanes, and allowed to dry under vacuum. A pale yellow-orange powder of **6** was isolated in 92% yield. Yellow-orange needle like crystals of **6**, suitable for X-ray analysis, were grown by diffusion of saturated THF solution in hexanes.

¹H NMR (CDCl₃, 23 °C): δ 8.99 (t, 1H, py, *p*-CH), 8.49 (d, 2H, py, *m*-CH), 7.90–7.05 (br m, 16H, aromatic), 3.00 (v br s, 4H, ⁱPr-CH), 1.24 (br d, 12H, CH₃), 0.89 (v br d, 12H, CH₃).¹³C NMR (CDCl₃). δ 167.7(C=N imine), 148.9 (py, *o*-C=N), 146.3 (py, *m*-CH), 139.5 (py, *p*-CH), 134.9 (Ph, *o*-CH), 134.1 (Ph, *m*-CH), 129.4 (Ar-ⁱPr, C-ⁱPr), 129.2 (Ar-ⁱPr, CH), 128.9 (Ph, *i*-C), 128.6 (Ph, *p*-CH), 125.7 (Ar-ⁱPr, C-ⁱPr), 125.2 (Ar-ⁱPr, CH₃). 29.7 (Ar-ⁱPr,CH₃), 26.7 (Ar-ⁱPr, CH-(CH₃)₂), 24.3 (Ar-ⁱPr,CH₃).

The sample for elemental analysis was obtained from recrystallization in toluene. Elemental analysis calculated for $[C_{43}H_{47}I_6Ga_2N_3]_3[C_7H_8]$ C 35.42, H 3.26, N 2.73, Found C 35.00, H 3.22, N 2.65.

Crystallography

Crystals of compounds 4 to 7 were grown from slow evaporation of saturated solutions of $CDCl_3$ (4), THF (5,6), or toluene (7). Single crystals were mounted on a glass fibre or plastic mesh with viscous oil and flash cooled to the data collection temperature. Unit cell measurements and intensity data collections were performed on a Bruker-AXS SMART 1k or APEX CCD diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Unit cell parameters were obtained from 60 data frames, 0.3° ω , from three different sections of the Ewald sphere. The unit cell parameters, equivalent reflections, and systematic absences in the diffraction data are consistent with space groups $Pna2_1$ $(Pn2_1a)$ and Pnma for 5, $P2_1/n$ for 4, $P2_12_12_1$ 6, and P1 for 7. The data-sets were treated with SADABS absorption corrections based on redundant multiscan data.¹⁴ The crystal data and refinement parameters for compounds 4-7 are listed in Table 1. The structures were solved using direct methods and refined with full-matrix, least-squares procedures on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. For compound 6, the GaI4- moiety was disordered over two positions and modeled as an 80:20 mixture with the thermals restrained with SIMU. The C-C and C-O bond distances of the THF solvent molecule were restrained with the commands DFIX and SADI and the thermals were restrained with the command SIMU. The data obtained for 7 represent the best from several trials and nonhydrogen, covalently bonded atoms were restrained to have the same equivalent isotropic parameter and equal components of the anisotropic displacement parameters in the direction of the bond. Three disordered chloroform molecules per unit cell in 5 were treated as diffused contributions.¹⁵ Atomic scattering factors and anomalous dispersion coefficients are contained in various versions of the SHELXTL program library.14

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