The Reactivity of Primary and Secondary Amines, Secondary Phosphanes and N-Heterocyclic Carbenes towards Group-13 Metal(I) Halides

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The reactions of a variety of primary and secondary amines and secondary phosphanes with "GaI" have been examined. In all cases disproportionation reactions occurred which led to the gallium(II) iodide complexes $[Ga_2I_4(L)_2]$ [L = $NCyH_2$, $NtBuH_2$, NCy_2H, PCy_2H or $PtBu_2H$ (Cy = cyclohexyl)]. All complexes have been crystallographically characterised and have been shown to be dimers possessing Ga–Ga bonds. The reaction of the sterically hindered N-heterocyclic carbene IPr [**:**$CN(Ar)C_2H_2N(Ar)$ (Ar = $C_6H_3iPr_2$-2,6)] with "GaI" was also carried out and the novel salt $[Ga_2I_5(IPr)][IPrH]$ was formed in good yield and crystallographically characterised. Finally, the related reaction of the less hindered cyclic carbene IMe [**:**$CN(Me)C_2Me_2N(Me)$] with InCl gave a low yield of the crystallographically characterised salt $[\{InCl(IMe)\}_2(\mu\text{-}Cl)(\mu\text{-}O)][Cl]$ which presumably forms due to the presence of adventitious oxygen in the reaction mixture.

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Introduction

Over the past five years there has been a rapidly increasing interest in the chemistry of metastable aluminium(I) and gallium(I) halide complexes $[\{MX(L)\}_n]$ (**1**: M = Al or Ga; X = halide; L = ether, amine or phosphane). These have been invariably prepared by the co-condensation of the metal(I) halide with the donor solvent using a specially designed reactor, and several have been crystallographically characterised, for example $[Al_4Br_4(NEt_3)_4]$.[1] Studies of the reactivity of group-13 metal(I) halide complexes have provided an array of remarkable results, not least of which come from their use in the formation of polyhedral halide, such as $[Al_{22}Br_{20}(THF)_{12}]$, amide, such as $[Ga_{84}\{N(SiMe_3)_2\}_{20}]^{4-}$, alkyl, such as $[Ga_{19}\{C(SiMe_3)_3\}_6]^{-}$, and silyl, such as $[Ga_{26}\{Si(SiMe_3)_3\}_8]^{2-}$, metalloid clusters.[2] Attempts have been made to prepare **1**, with M = Ga and L = PEt_3 or PPh_3, from the reaction of PEt_3 or PPh_3 with "GaI".[3] These reactions, however, led to partial disproportionation and the facile formation of the gallium(II) iodide complexes $[Ga_2I_4(PR_3)_2]$ (R = Et or Ph), and the mixed oxidation state complex $[Ga_3I_5(PEt_3)_3]$, all of which were crystallographically characterised. It is noteworthy that only two other neutral gallium(II) iodide adducts $[Ga_2I_4(L)_2]$ (L = NEt_3 [4] or $AsEt_3$ [5]), which were prepared by alternative routes, have been structurally authenticated.

Surprisingly there are no known structurally characterised indium analogues of **1**. Recently, we attempted the preparation of such a compound using an N-heterocyclic carbene (NHC) as the donor ligand in a reaction with InBr. As in the aforementioned reactions of phosphanes with "GaI" this led to partial disproportionation and the formation of the indium(II) bromide complex $[In_2Br_4(IMes)_2]$ with IMes being the cyclic carbene **:**CN(Mes)C(H)C(H)N(Mes) (Mes = mesityl).[6] In the present study we have extended this work by examining the reactivity of several NHCs towards indium(I) and gallium(I) halides. In addition, the reactions of a variety of primary and secondary amines and secondary phosphanes with "GaI" have been carried out and these have led to the formation of the first crystallographically characterised complexes of the type $[Ga_2I_4(L)_2]$ (L = NR_2H, NRH_2, PR_2H).

Results and Discussion

Amine and Phosphane Reactions

In all reactions depicted in Scheme 1 "GaI" was prepared by sonicating gallium metal with 0.5 equiv. of I_2 in toluene at 50 °C according to the method of Green et al.[7] A toluene suspension of this material was treated with a variety of amines and phosphanes at −78 °C. Upon warming the reaction mixtures to room temperature gallium metal deposition was observed. The resulting suspensions were filtered and cooled to −30 °C affording moderate to high yields of the gallium(II) iodide adducts **2**−**6**. The mechanism of formation of these compounds presumably involves partial disproportionation of the "GaI" reagent upon treatment with the Lewis bases. All compounds are, however, quite stable at room temperature in both solution and the solid state and no further disproportionation to gallium(III) iodide complexes was observed.

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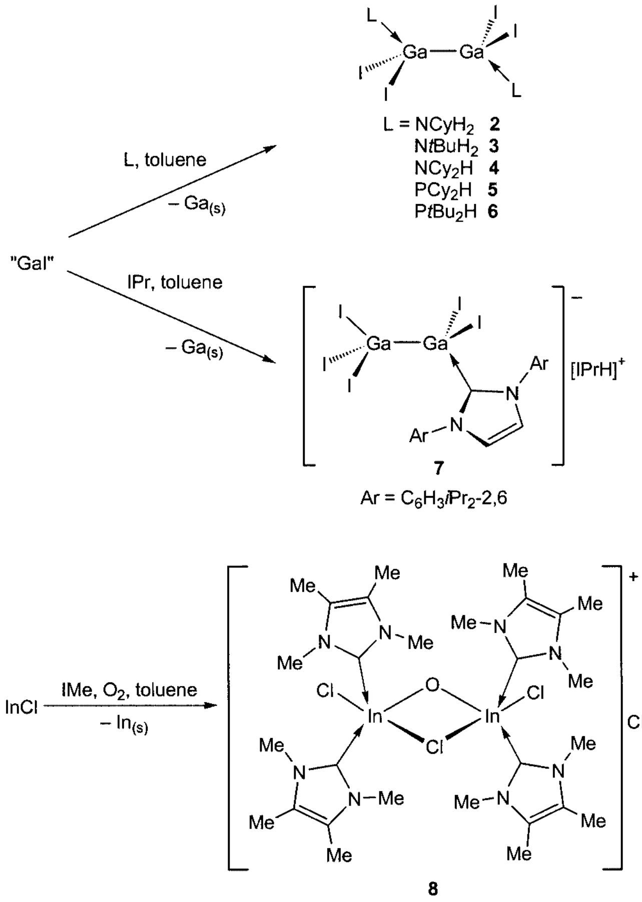

Scheme 1. Preparation of complexes **2**−**8**

The infrared spectra of all the amine complexes **2**−**4** display strong, broad N−H stretching absorptions in the expected region but the amine proton resonance was only observed in the ^{1}H NMR spectrum of **3**. The infrared spectra of **2**−**4** exhibit bands at 450, 453 and 409 cm^{-1} which have been assigned to Ga−N stretches from comparisons with related alkylgallium−amine adducts.[8] The infrared spectra of the secondary phosphane complexes **5** and **6** show P−H stretching bands at 2258 and 2353 cm^{-1}, respectively. In addition, their ^{31}P NMR spectra reveal doublet resonances with $^{1}J_{PH}$ coupling constants (**5**: 359 Hz; **6**: 351 Hz) of a significantly greater magnitude than those recorded for the free phosphanes (PCy_2H: 193 Hz; $PtBu_2H$: 198 Hz). A similar trend has been reported for secondary phosphane adducts of trialkylgallium compounds.[9] It should be noted that the reactions of several primary phosphanes, thiols and bulky alcohols with "GaI" were carried out but no tractable products could be obtained.

N-Heterocyclic Carbene Reactions

Due to the now well-known analogy between phosphanes and NHCs,[10] and given our previous preparation of $[In_2Br_4(IMes)_2]$, it was thought worthwhile to examine the reactivity of a series of NHC ligands with "GaI". Unfortunately, success was only achieved with the reaction of the very hindered cyclic carbene IPr and "GaI" in toluene. Considerable gallium metal deposition was observed in this reaction and upon workup a good yield of the novel salt **7** resulted (Scheme 1). It is interesting that the nature of this product is different to that of the neutral complex $[In_2Br_4(IMes)_2]$, but it seems likely that the imidazolium proton of the cation was abstracted from the solvent as this reaction is entirely reproducible in good yield, even when it is carried out under strictly anhydrous conditions. The fact that the anion of **7** contains only one coordinated carbene ligand, as opposed to the two cyclic carbene ligands in $[In_2Br_4(IMes)_2]$, could be due to the greater bulk of the cylic carbene IPr and a lesser covalent radius of the metal atom in the former complex. It is also worth noting here that the formulation of "GaI" has been proposed to be $[Ga]_2[Ga_2I_6]$ based on Raman spectroscopic studies.[11] It is not inconceivable that the anion of **7** could be formed by displacement of one iodide ligand from the $[Ga_2I_6]^{2-}$ dianion of such a compound. The ^{1}H and ^{13}C NMR spectra of **7** show two sets of resonances which integrate in a 1:1 ratio and were assigned to the imidazolium cation and the cyclic carbene IPr coordinated to a gallium centre. The distinction between the two sets of resonances can be confidently made as the imidazolium cation has recently been structurally and spectroscopically characterised in the salt $[IPrH][InBr_4]$.[12] The fact that sharp resonances were observed for both the imidazolium and carbene moieties over a range of temperatures suggests that the carbene ligand is strongly coordinated to the gallium centre and there is no carbene/imidazolium exchange occurring in this complex.

Reaction of the sterically less hindered cyclic carbene :CN(Me)C(Me)C(Me)N(Me) (IMe) with "GaI" also resulted in considerable gallium metal deposition, but only an inseparable mixture of unknown products formed. In contrast, the reaction of the same cyclic carbene with InCl afforded the unusual oxo-bridged dimer $[\{InCl(IMe)_2\}_2(\mu\text{-}Cl)(\mu\text{-}O)][Cl]$ (**8**) in low yield (Scheme 1). This probably forms due to the presence of adventitious oxygen in the reaction mixture. Neither compound **8** nor any other product could be isolated or identified when the reaction was repeated under strictly anaerobic conditions. The spectroscopic data for **8** fully support its proposed structure; most notably an In−O stretch was observed at 335 cm^{-1} in its infrared spectrum. This is in good agreement with other examples in the literature.[13] No O−H stretching absorption could be seen in the same spectrum, which provides good evidence that there is no proton attached to the bridging oxygen centre.

Structural Studies

Crystals of **2**−**8** were grown from toluene solutions and the molecular structures of these compounds are depicted in Figures 1−7 (see also Tables 1 and 2). The five amine and phosphane complexes of Ga_2I_4, viz. **2**−**6**, display similar structural features in that their gallium centres all possess distorted tetrahedral environments and each

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$[Ga_2I_4(L)_2]$ molecule exhibits a staggered conformation with respect to the Ga−Ga bond. A previous report has suggested that some geometrical parameters of complexes of the type $[Ga_2I_4(L)_2]$ can be used to gauge the relative Lewis basicity of the donor ligands L with respect to the Ga^{II} centres in these complexes.[3] Specifically, differences in gallium−gallium bond lengths and trends towards more sp^2-like geometries at the gallium centres, as evidenced by an increase in the I−Ga−I angle, were employed for this task. The complexes in the present study do not, however, appear to follow any trends (see Table 1). For example, the Ga−Ga bond lengths in **2**−**6** are all very similar [2.4243(9)−2.459 Å (av.)] despite incorporating a range of amine and phosphane ligands of variable basicity. In addition, the I−Ga−I angles in all complexes do not vary to any great degree. We believe, however, that a better indication of the degree of sp^2 character at each gallium centre can be gained from the sum of the I−Ga−I and Ga−Ga−I angles around them. In the five complexes studied here, these values range from 332.1 to 336.4°. Again, this range is too narrow to draw any firm conclusions on the basicity of the ligands involved. The Ga−P bond lengths in complexes **5** and **6** are similar to those in $[Ga_2I_4(PEt_3)_2]$ (2.413 Å) and $[Ga_2I_4(PPh_3)_2]$ (2.445 Å),[3] whilst the Ga−N distances in compounds **2**−**4** are close to those in the only known tertiary amine complex of gallium(II) iodide, namely $[Ga_2I_4(NEt_3)_2]$ (2.094 Å av.).[4]

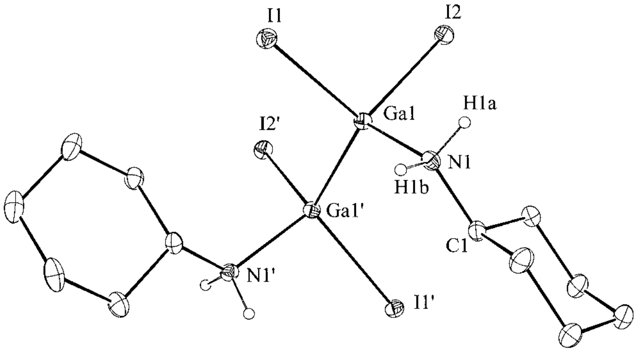

Figure 1. Molecular structure of **2**; symmetry operation: ′ −x + 3/2, −y − 1/2, z

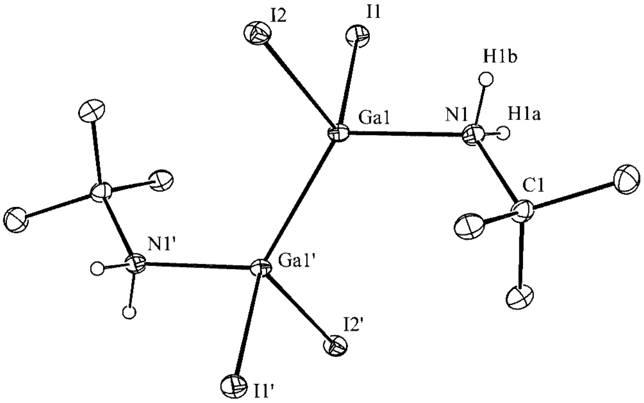

Figure 2. Molecular structure of **3**; symmetry operation: ′ −x + 1, −y + 1, z

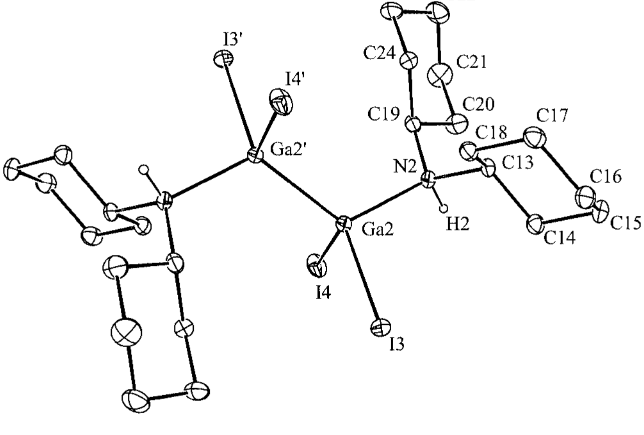

Figure 3. Molecular structure of **4**; symmetry operation: ′ −x, −y + 1, −z

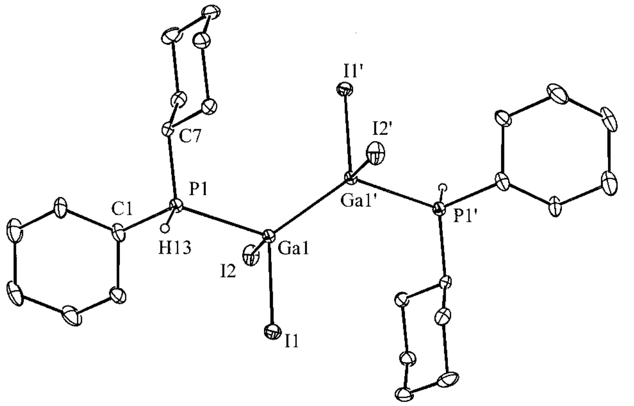

Figure 4. Molecular structure of **5**; symmetry operation: ′ −x + 2, −y, −z + 2

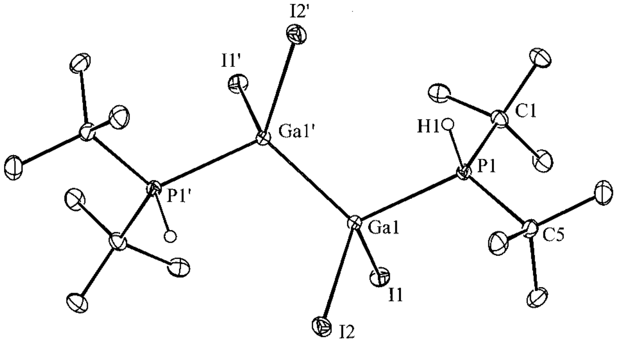

Figure 5. Molecular structure of **6**; symmetry operation: ′ −x + 1, y, −z + 3/2

The molecular structure of the anion of **7** is depicted in Figure 6. Both gallium centres have distorted tetrahedral coordination environments and the Ga−Ga distance [2.4739(12) Å] is slightly longer than any in **2**−**6**, and significantly longer than previously seen in the $[Ga_2I_6]^{2-}$ dianion, for example 2.413 Å in $[PPh_3H][Ga_2I_6]$.[14] All the Ga−I distances are similar to those in related systems, for example $[PPh_3H][Ga_2I_6]$, although the Ga−I bond lengths of the

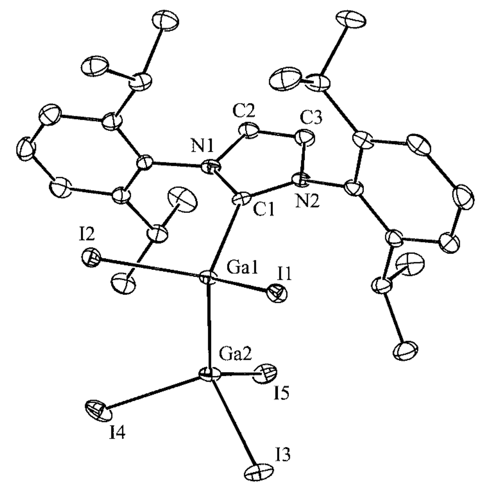

Figure 6. Structure of the anionic component of **7**; selected bond lengths [Å] and angles [°]: Ga(1)−Ga(2) 2.4739(12), Ga(1)−I(1) 2.5977(11), Ga(1)−I(2) 2.5819(10), Ga(2)−I(3) 2.6178(11), Ga(2)−I(4) 2.6153(12), Ga(2)−I(5) 2.6068(12), Ga(1)−C(1) 2.070(7), N(1)−C(1) 1.361(9), N(1)−C(2) 1.372(9), C(2)−C(3) 1.345(11), N(2)−C(3) 1.384(9), N(2)−C(1) 1.358(9); C(1)−Ga(1)−Ga(2) 117.54(18), C(1)−Ga(1)−I(2) 109.81(19), Ga(2)−Ga(1)−I(2) 108.64(4), C(1)−Ga(1)−I(1) 107.09(19), Ga(2)−Ga(1)−I(1) 109.57(4), I(2)−Ga(1)−I(1) 103.24(4), Ga(1)−Ga(2)−I(5) 120.13(4), Ga(1)−Ga(2)−I(4) 111.00(5), I(5)−Ga(2)−I(4) 105.40(4), Ga(1)−Ga(2)−I(3) 112.29(4), I(5)−Ga(2)−I(3) 103.80(4), I(4)−Ga(2)−I(3) 102.53(4), C(1)−N(1)−C(2) 111.1(6), C(1)−N(1)−C(4) 127.0(6), C(2)−N(1)−C(4) 121.0(6), C(1)−N(2)−C(3) 110.1(6), N(2)−C(1)−N(1) 104.7(6), C(3)−C(2)−N(1) 106.7(7), C(2)−C(3)−N(2) 107.4(7)

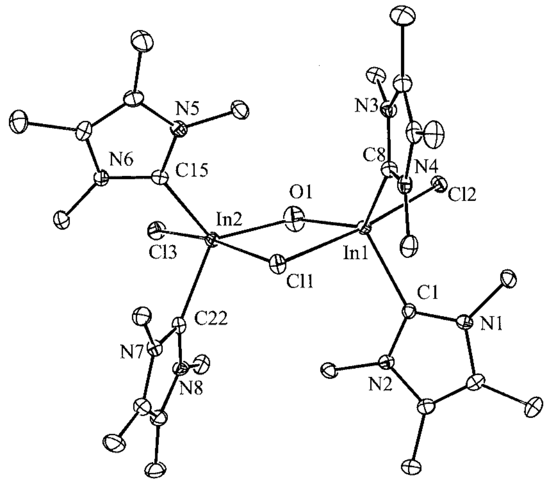

Figure 7. Structure of the cationic component of **8**; selected bond lengths [Å] and angles [°]: In(1)−Cl(1) 2.823(2), In(1)−Cl(2) 2.592(2), In(1)−O(1) 2.174(7), In(1)−C(1) 2.233(7), In(1)−C(8) 2.235(7), In(2)−Cl(1) 2.921(2), In(2)−Cl(3) 2.542(2), In(2)−O(1) 2.172(7), In(2)−C(15) 2.221(7), In(2)−C(22) 2.218(8); In(1)−O(1)−In(2) 113.6(3), In(1)−Cl(1)−In(2) 78.54(5), Cl(2)−In(1)−C(1) 94.64(18), Cl(2)−In(1)−C(8) 91.51(19), C(1)−In(1)−C(8) 109.2(3), Cl(1)−In(1)−Cl(2) 172.16(6), O(1)−In(1)−C(1) 120.0(3), O(1)−In(1)−C(8) 128.7(3), C(15)−In(2)−C(22) 107.9(3), C(15)−In(2)−Cl(3) 95.46(19), C(22)−In(2)−Cl(3) 92.6(2), C(15)−In(2)−O(1) 121.3(3), C(15)−In(2)−Cl(1) 87.00(19), C(22)−In(2)−O(1) 126.9(3), C(22)−In(2)−Cl(1) 81.1(2), Cl(1)−In(2)−Cl(3) 173.72(7), N(1)−C(1)−N(2) 105.5(6), N(3)−C(8)−N(4) 105.6(6), N(5)−C(15)−N(6) 103.9(6), N(7)−C(22)−N(8) 104.9(6)

Table 1. Selected bond lengths [Å] and angles [°] for compounds **2**−**6**

Compound	**2**	**3**	**4**	**5**	**6**
Ga−N/P	2.020(4)	2.036(3)	2.083 av.	2.424(2)	2.4459(10)
Ga−Ga	2.4287(10)	2.4243(9)	2.459 av.	2.4370(15)	2.4448(9)
Ga−I	2.5951(7)	2.5769(7)	2.586 av.	2.5924(10)	2.5935(6)
	2.5727(7)	2.5731(8)		2.5755(11)	2.5745(6)
I−Ga−I	108.17(2)	107.965(1)	104.8 av.	110.07(3)	104.91(2)
ΣI−Ga−I and Ga−Ga−I	335.8	334.8	334.8 av.	336.4	332.1

GaI_3 fragment are slightly longer than those associated with the carbene-coordinated gallium centre. The metric parameters of the coordinated NHC ligand are similar to those seen in other group-13 complexes, such as $[InBr_3(IPr)]$,[12] and the Ga−C interaction is similar to those in NHC−Ga(III) complexes, cf. 2.077 Å (av.) in $[GaH_3\{CN(i\text{Pr})C_2Me_2N(i\text{Pr})\}]$.[15]

The crystal structure of the cationic component of **8** is shown in Figure 7. The indium atoms both have distorted trigonal-bipyramidal coordination environments whilst the four-membered In_2ClO ring is essentially flat (In−Cl−In−O torsion angle 0.7°). The average In−C bond of 2.227 Å is similar to that found in the complex $[InH_3(IMes)]$ [2.250(10) Å].[16] Interestingly, both the terminal and bridging In−Cl bonds (2.567 Å av. and 2.872 Å av., respectively) are considerably longer than the norms for such bonds (2.45 and 2.59 Å)[17] and indeed, the bridging Cl^- ligand can be thought of as only having an interaction with the indium centres. The acuteness of the In−Cl−In angle [78.54(5)°] adds weight to this proposal. This situation most likely arises from the fact that each indium centre is coordinated by two highly nucleophilic NHC ligands, which weaken the bonds from the other ligands to these metal centres.

Conclusions

In conclusion, we have shown that "GaI" reacts with a range of primary and secondary amine and secondary phosphane ligands to give adducts of the type $[Ga_2I_4(L)_2]$ (L = Lewis base), which are formed by disproportionation reactions. A range of these complexes have been crystallographically characterised, as have the products from the related reactions of N-heterocyclic carbenes with either "GaI" or InCl. We believe that complexes of the type **2**−**6**

Table 2. Crystallographic data for compounds **2**−**8**

	2	**3**	**4**	**5**	**6**·C_7H_8	**7**·$(C_7H_8)_4$	**8**·CH_2Cl_2
Empirical formula	$C_{12}H_{26}Ga_2I_4N_2$	$C_8H_{22}Ga_2I_4N_2$	$C_{24}H_{46}Ga_2I_4N_2$	$C_{24}H_{46}Ga_2I_4P_2$	$C_{23}H_{46}Ga_2I_4P_2$	$C_{82}H_{105}Ga_2I_5N_4$	$C_{29}H_{50}Cl_6In_2N_8O$
Formula mass	845.39	793.32	1009.67	1043.59	1031.58	1920.64	969.11
Temp. [K]	293(2)	150(2)	298(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	*Pccn*	$P2_1/c$	$P2_1/c$	$P2_1/n$	*Pbcn*	$P2_1/c$	$P2_1/n$
a [Å]	20.992(4)	9.2720(19	19.688(4)	9.6600(19)	18.548(4)	17.216(3)	12.774(3)
b [Å]	8.0880(16)	10.325(2)	9.858(2)	14.478(3)	14.559(3)	27.028(5)	25.620(5)
c [Å]	13.222(3)	10.928(2)	17.111(3)	13.154(3)	13.125(3)	17.801(4)	13.118(3)
β [°]	90	94.22(3)	90.11(3)	107.98(3)	90	92.48(3)	92.49(3)
V [Å^3]	2244.9(8)	1043.3(4)	3321.0(11)	1749.8(6)	3544.3(12)	8275(3)	4289.1(15)
Z	4	2	4	2	4	4	4
$D_{calcd.}$ [g/cm^3]	2.501	2.525	2.019	1.981	1.933	1.542	1.501
μ [mm^{-1}]	7.896	8.484	5.356	5.171	5.105	2.559	1.481
Unique reflections	2567	2381	5837	3193	4061	14469	7503
Observed reflections [$I > 2\sigma(I)$]	2111	2093	4067	2784	3533	11598	6168
R (obsd. data)	0.0303	0.0300	0.0411	0.0452	0.0306	0.0598	0.0679
R_w (wR^2) (all data)	0.0636	0.0693	0.0906	0.1003	0.0720	0.1364	0.1522

have significant potential for use as precursors in the formation of heterocyclic and cage compounds containing low oxidation state Ga centres. To this end we are currently examining their reactivity towards a number of strong bases in the expectation that HI abstraction will occur. Our efforts in this area will be reported in a forthcoming publication.

Experimental Details

General Remarks: All manipulations were carried out using standard Schlenk and glove-box techniques under high-purity argon. Toluene was distilled from potassium whilst CH_2Cl_2 was distilled from CaH_2 then freeze/thaw-degassed prior to use. ^1H and ^{13}C NMR spectra were recorded with a Bruker DXP400 spectrometer and are referenced to the residual ^1H or ^{13}C resonances of the solvent used. ^{31}P NMR spectra were recorded with a Jeol Eclipse 300 spectrometer and are referenced to 85% H_3PO_4. APCI mass spectra were recorded using a VG Fisons Platform II instrument. FAB mass spectra were recorded by the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between CsI plates. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Reproducible microanalyses were not obtained on any of the crystallographically characterised complexes because of the presence of solvent of crystallisation and/or the air-sensitive nature of these complexes. In all cases, however, the spectroscopic data pointed to the bulk materials having a purity of greater than 98%. "GaI" was synthesised by a variation of the literature method[7] as were the cyclic carbenes IPr[18] and IMe.[19] All other chemicals were obtained commercially and used as received. Compounds **2**−**6** were prepared by the general procedure outlined below.

$[Ga_2I_4(NCyH_2)_2]$ (2): GaI was synthesised by sonicating Ga (0.343 g, 4.92 mmol) and I_2 (0.62 g, 2.45 mmol) in toluene (10 mL) at 50 °C for approx. 2 h. The resulting green suspension was cooled to −78 °C and a solution of $NCyH_2$ (1.12 mL, 9.8 mmol) in toluene (5 mL) added to it over 5 min. The reaction mixture was warmed to room temperature and stirred for 12 h to give a brown solution and a precipitate of Ga metal. Filtration, concentration in vacuo and placement at −30 °C overnight yielded colourless crystals of **2** (0.38 g, 36%). M.p. 255−258 °C (dec). ^1H NMR (400 MHz, C_6D_6, 300 K): δ = 1.16 (m, 8 H, CH_2), 1.69 (m, 8 H, CH_2), 2.03 (m, 4 H, CH_2), 2.94 (m, 2 H, CH) ppm; NH_2 resonance not observed. ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ = 35.6, 25.4, 24.9 (CH_2), 51.4 (CH) ppm. IR (Nujol): $\tilde{\nu}$ = 3427 (br.), 1940 (br.), 1463 (sh), 1377 (sh), 1260 (sh), 1087 (br.), 1017 (br.), 956 (m), 888 (w), 799 (s), 723 (m), 584 (w), 534 (w), 467 (m), 450 (m), 377 (br.), 331 (m). MS APCI: *m*/*z* (%) = 83 (100) [Cy^+], 100 (40) [$CyNH_3^+$], 268 (10) [Ga_2I^+].

$[Ga_2I_4(NtBuH_2)_2]$ (3): Yield 48%. M.p. 161−164 °C (dec). ^1H NMR (400 MHz, C_6D_6, 300 K): δ = 1.17 (s, 18 H, *t*Bu), 8.52 (br., 4 H, NH_2) ppm. ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ = 27.8 [$C(CH_3)_3$], 53.1 [$C(CH_3)_3$] ppm. IR (Nujol): $\tilde{\nu}$ = 3236 (sh), 3176 (sh), 1554 (sh), 1463 (s), 1374 (s), 1277 (m), 1257 (m), 1197 (w), 1163 (m), 1101 (br.), 1016 (w), 820 (m), 801 (m), 733 (m), 681 (m), 596 (br.), 453 (br.), 371 (w) cm^{-1}. MS FAB: *m*/*z* (%) = 57 (100) [*t*Bu$^+$], 74 (24) [*t*BuNH$_3^+$].

$[Ga_2I_4(NCy_2H)_2]$ (4): Yield 95%. M.p. 215−217 °C (dec). ^1H NMR (400 MHz, C_6D_6, 300 K): δ = 1.05 (m, 16 H, CH_2), 1.70 (m, 16 H, CH_2), 1.95 (m, 8 H, CH_2), 3.30 (m, 4 H, CH) ppm; NH resonance not observed. ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ = 23.8, 23.9, 32.2 (CH_2), 57.7 (CH) ppm. IR (Nujol): $\tilde{\nu}$ = 3427 (w), 1453 (s), 1376 (s), 1260 (m), 1162 (w), 1122 (m), 1081 (s), 1028 (m), 960 (m), 916 (w), 895 (w), 800 (m), 715 (m), 409 (br.) cm^{-1} . MS FAB: *m*/*z* (%) = 182 (100) [Cy_2NH^+], 648 (8) [Ga_2I_2].

$[Ga_2I_4(PCy_2H)_2]$ (5): Yield 41%. M.p. 78−81 °C (dec). ^1H NMR (400 MHz, C_6D_6, 300 K): δ = 1.10 (m, 16 H, CH_2), 1.62 (m, 16 H, CH_2), 2.09 (m, 8 H, CH_2), 2.59 (m, 4 H, CH), 4.45 (d, $^1J_{P-H}$ = 359 Hz, 2 H, PH) ppm. ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ = 25.2 (d, $J_{P,C}$ = 13 Hz, CH_2), 27.1 (d, $^3J_{P,C}$ = 12 Hz, CH_2), 29.8 (d, $^4J_{P,C}$ = 8 Hz, CH_2), 32.2 (d, $^1J_{P,C}$ = 18 Hz, CH) ppm. $^{31}P\{^1H\}$ NMR (101.6 MHz, C_6D_6, 300 K): δ = −27.5 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 2258 (m), 1448 (s), 1377 (s), 1349 (w), 1327 (w), 1295 (m), 1264 (m), 1202 (w), 1180 (w), 1117 (br.), 1002 (br.), 888 (m), 854 (w), 791 (m), 727 (w), 502 (br.), 381 (br.) cm^{-1} . MS FAB: *m*/*z* (%) = 197 (45) [$PCy_2H_2^+$]

$[Ga_2I_4(PtBu_2H)_2]$ (6): Yield 54%. M.p. 137−140 °C (dec). ^1H NMR (400 MHz, C_6D_6, 300 K): δ = 1.26 (d, $^3J_{P-H}$ = 15 Hz, 36 H, *t*Bu);

4.92 (d, $^1J_{P-H}$ = 351 Hz, 2 H, PH) ppm. ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ = 21.2 [C(CH_3)$_3$], 53.1 (d, $^1J_{P,C}$ = 10 Hz C(CH_3)$_3$] ppm. ^{31}P{^{1}H} NMR (101.6 MHz, C_6D_6, 300 K): δ = −9.04 (s) ppm. IR (Nujol): $\tilde{\nu}$ = 2353 (w), 1459 (s), 1376 (s), 1260 (m), 1162 (w), 1086 (m), 1021 (m), 936 (w), 870 (w), 803 (m), 727 (s), 694 (m), 555 (w), 462 (br.), 383 (br.), 323 (m) cm^{-1}. MS FAB: *m*/*z* (%) = 57 (100) [*t*Bu], 793 (4) [M$^+$ − PH*t*Bu$_2$].

[Ga$_2$I$_5$(IPr)][IPrH] (7): GaI was synthesised by sonicating Ga (0.125 g, 1.79 mmol) and I_2 (0.22 g, 0.88 mmol) in toluene (10 mL) at 50 °C for approx. 2 h. The resulting green suspension was cooled to −78 °C and a solution of the cyclic carbene IPr (0.69 g, 1.79 mmol) in toluene (20 mL) added to it over 5 min. The reaction mixture was warmed to room temperature and stirred for 12 h to give a brown solution and a precipitate of Ga metal. Filtration, concentration in vacuo and placement at −30 °C overnight yielded colourless crystals of **7** (0.36 g, 42%). M.p. 238−242 °C (dec). ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ = 1.10 (d, $^3J_{HH}$ = 7 Hz, 12 H, CH_3, cation), 1.21 (d, $^3J_{H,H}$ = 7 Hz, 12 H, CH_3, cation), 2.33 [sept, $^3J_{H,H}$ = 7 Hz, 4 H, C*H*(CH_3)$_2$, cation], 7.31 (d, $^3J_{H,H}$ = 8 Hz, 4 H, *m*-CH, cation), 7.54 (t, $^3J_{H,H}$ = 8 Hz, 2 H, *p*-CH, cation), 7.99 (s, 2 H, NC_2H_2N, cation), 8.42 (s, 1 H, NCHN, cation), 1.00 (d, $^3J_{H,H}$ = 7 Hz, 12 H, CH_3, anion), 1.36 (d, $^3J_{H,H}$ = 7 Hz, 12 H, CH_3, anion), 2.68 [sept, $^3J_{H,H}$ = 7 Hz, 4 H, C*H*(CH_3)$_2$, anion], 7.26 (d, $^3J_{H,H}$ = 8 Hz, 4 H, *m*-CH, anion), 7.40 (t, $^3J_{H,H}$ = 8 Hz, 2 H, *p*-CH, anion), 7.99 (s, 2 H, NC_2H_2N, anion) ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2, 300 K): δ = 23.7, 25.7 (CH_3, cation), 29.1 [*C*(CH_3)$_2$, cation], 124.9 (*p*-Ar, cation), 125.2 (*m*-Ar, cation), 132.4 (*o*-Ar, cation), 134.7 (*ipso*-Ar, cation), 145.1 (NCHN, cation), 145.7 (NC_2H_2N, cation), 23.9, 24.5 (CH_3, anion), 28.8 [*C*H(CH_3)$_2$, anion], 125.0 (*p*-Ar, anion), 127.0 (*m*-Ar, anion), 131.1 (*o*-Ar, anion), 136.1 (*ipso*-Ar, anion), 146.1 (NC_2H_2N, anion) ppm. IR (Nujol): $\tilde{\nu}$ = 2853 (br.), 1526 (m), 1455 (s), 1372 (s), 1260 (m), 1096 (s), 1055 (s), 1014 (s), 799 (s), 748 (m), 722 (m), 686 (w), 625 (w), 507 (w), 461 (w), 392 (br.), 305 (w), 289 (w), 245 (w) cm^{-1}. MS FAB: *m*/*z* (%) = 389 (100) [IPrH$^+$], 909 (61) [Ga$_2$I$_3$(IPr)$^+$]

[{InCl(IMe)$_2$}$_2$(μ-Cl)(μ-O)][Cl] (8): A solution of the cyclic carbene IMe (0.66 g, 5.31 mmol) in toluene (10 mL) was added to a suspension of InCl (0.40 g, 2.66 mmol) in toluene (10 mL) held at −78 °C. The reaction mixture was stirred for 4 h during which time indium metal deposition was observed. The resulting suspension was filtered and volatiles removed from the filtrate in vacuo. The yellow residue was extracted with CH_2Cl_2 (2 × 5 mL). Concentration to ca. 5 mL and the addition of toluene (2 mL) followed by placement at −30 °C overnight yielded colourless crystals of **8** (0.37 g, 16%). M.p. 155−158 °C (dec). ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K): δ = 2.11 (s, 24 H, CMe), 3.64 (s, 24 H, NMe) ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2, 300 K): δ = 8.14 (s, CMe), 34.62 (s, NMe) ppm. IR (Nujol): $\tilde{\nu}$ = 2919 (s), 2852 (s), 1634 (m), 1598 (m), 1588 (m), 1470 (sh), 1372 (s), 1250 (sh), 1081 (s), 1034 (s), 891 (w), 850 (w), 799 (m), 727 (sh), 688 (sh), 563 (m), 533 (m), 461 (sh), 392 (br.), 335 (s), 289 (w) cm^{-1}. MS FAB: *m*/*z* (%) = 125 (100) [IMeH$^+$].

Structure Determinations: Crystals of **2**−**8** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full-matrix least squares (SHELX97)[20] using all unique data. All non-hydrogen atoms are anisotropic with H atoms included in calculated positions (riding model). The structure of **4** contains two crystallographically independent monomeric moieties in the asymmetric unit. The geometries of the dimeric units generated from these are not significantly different and thus the ORTEP diagram of only one is shown in Figure 3. The geometrical parameters for **4** in Table 1 are, however, an average of those in the two molecules. Crystal data, details of data collections and refinement are given in Table 2. The molecular structures of the complexes are depicted in Figures 1−7 and show thermal ellipsoids set at the 30% probability level. CCDC-203134 (**2**), -203135 (**3**), -203136 (**4**), -203137 (**5**), -203138 (**6**), -203139 (**7**) and -203140 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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