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Structural and spectroscopic studies of carbene and N-donor ligand complexes of Group 13 hydrides and halides

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Abstract

The syntheses of two Group 13 complexes of the sterically demanding carbene, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, (IPr), are reported, vis. $[MX_3(IPr)]$ M = Al, X = H; M = In, X = Br; both of which have been structurally characterised. Also reported is the crystal structure of the imidazolium salt $[IPrH][InBr_4]$, formed by the presence of adventitious water in the preparation of the $[InBr_3(IPr)]$ adduct. The preparation of the complex $[InBr_3(IMes)]$, IMes = 1,3-bis(2,4,6-trimethylpheny)imidazol-2-ylidene, is described as are details of its crystal structure analysis. In addition, two indium tribromide adducts of nitrogen donor ligands, namely a bulky diazabutadiene and quinuclidine have been investigated. The crystal structures of *N*,*N*′-1,4-bis(2,6-diisopropylphenyl)diazabutadiene indium tribromide and bis(quinuclidine)indium tribromide are reported. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carbene; Indium halide; Aluminium hydride; N-donor; Crystal structures

1. Introduction

Neutral ligands containing N, P, O or S donor atoms show a rich variety of co-ordination complexes with indium(III) halides [1]. Depending on the stoichiometry employed, many geometries have been observed in the solid state, e.g. $[InI_3(PHBu^t_2)]$ is distorted tetrahedral [2], $[InCl_3(PMe_3)_2]$ is trigonal bipyramidal [3], whilst both fac and mer isomers of $[InCl_3(OPMe_3)_3]$ have been isolated [4]. There is also the possibility of ionic complexes being formed as in $[InI_2(dmso)_4][InI_4]$ (dmso = dimethyl sulfoxide) [5].

The coordination chemistry of indium halides and other Group 13 halides and hydrides has recently been extended to complexes employing *N*-heterocyclic carbene ligands. In this area we have utilised such carbenes as stabilising ligands in the formation of a variety of complexes, e.g. $[MH_3(IMes)]$, M = Ga or In [6]; $[MCl_3(IMes)]$, M = In or Tl [7]; $[MH_3\{(CN(Pr^i)C_2H_2N(Pr^i)\}]$, M = Al, Ga or In [8] and $[InX_3\{(CN(Pr^i)C_2H_2N(Pr^i)\}_n]$, X = Cl or Br, $n = 1$ or 2 [9]. The stabilising properties of these carbene ligands are perhaps best exemplified by $[InH_3(IMes)]$ (dec. 115 °C) which is by far the most thermally robust InH_3 complex yet reported, a fact which has led to its application in both organic [10] and inorganic synthesis [11].

Herein, we report the preparation of a number of related *N*-heterocyclic carbene and N-donor ligand complexes of several Group 13 trihydride and trihalide fragments, several of which have been crystallographically characterised.

2. Results and discussion

2.1. Carbene complexes

Previous results from our laboratory have shown that steric bulk is an important factor in the kinetic stabilisation of carbene–InH_3 complexes, e.g. $[InH_3(IMes)]$. As such, it would be expected that the bulky 2,6-diisopropylphenyl substituted carbene (IPr) should stabilise the InH_3 fragment to an even greater extent than IMes. However, following our published metho-

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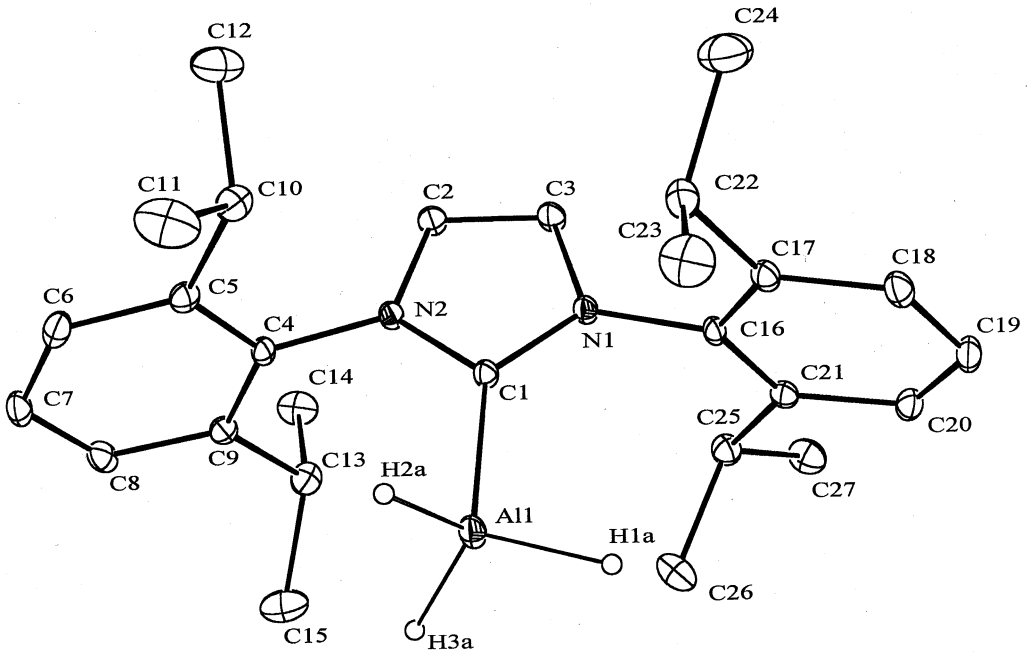
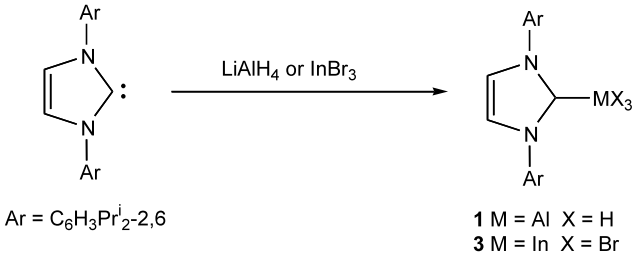


Fig. 1. Molecular structure of compound **1**. Selected bond lengths (Å) and angles (°): Al(1)–H(1a) 1.527(15), Al(1)–H(2a) 1.546(17), Al(1)–H(3a) 1.510(17), Al(1)–C(1) 2.0556(13), C(1)–N(1) 1.3562(15), C(1)–N(2) 1.3567(15), N(1)–C(3) 1.3824(15), N(1)–C(16) 1.4488(14), N(2)–C(2) 1.3826(15), N(2)–C(4) 1.4474(15), C(2)–C(3) 1.3417(18), N(1)–C(1)–N(2) 103.86(10), C(1)–Al(1)–H(1a) 106.1(6), C(1)–Al(1)–H(2a) 106.0(6), H(1a)–Al(1)–H(2a) 111.1(9), C(1)–Al(1)–H(3a) 104.6(6), H(1a)–Al(1)–H(3a) 113.9(9), H(2a)–Al(1)–H(3a) 114.3(9).

dology [6] the product from the reaction of $LiInH_4$ and this carbene, $[InH_3(IPr)]$, proved to be of disappointing thermal stability and slowly decomposed below −30 °C in solution and thus was impossible to characterise. This is possibly due to the close proximity of the isopropyl groups to the hydride ligands in the complex which could lead to decomposition via. metallation of the isopropyl substituents by the InH_3 unit. This has been previously postulated for the complex $[InH_3\{CN(Pr^i)C_2H_2N(Pr^i)\}]$ [8]. In contrast, the 1:1 reaction of IPr with either $LiAlH_4$ or $[AlH_3(NMe_3)]$ in diethyl ether did afford the thermally stable alane complex, $[AlH_3(IPr)]$ (**1**) in good yield (Scheme 1).

The infrared spectrum of **1** shows a broad, strong stretch at 1729 cm^{-1} confirming the presence of an AlH_3 unit. This is in the same region as other carbene adducts of alane, e.g. $[AlH_3\{CN(Pr^i)C_2H_2N(Pr^i)\}]$ ν(Al–H) 1730 cm^{-1} [8]. Its proton NMR spectrum does not show a resonance for the hydride ligands, probably due to the quadrupolar nature of the alumi-



Ar = $C_6H_3Pr^i_2$-2,6

1 M = Al X = H
3 M = In X = Br

Scheme 1.

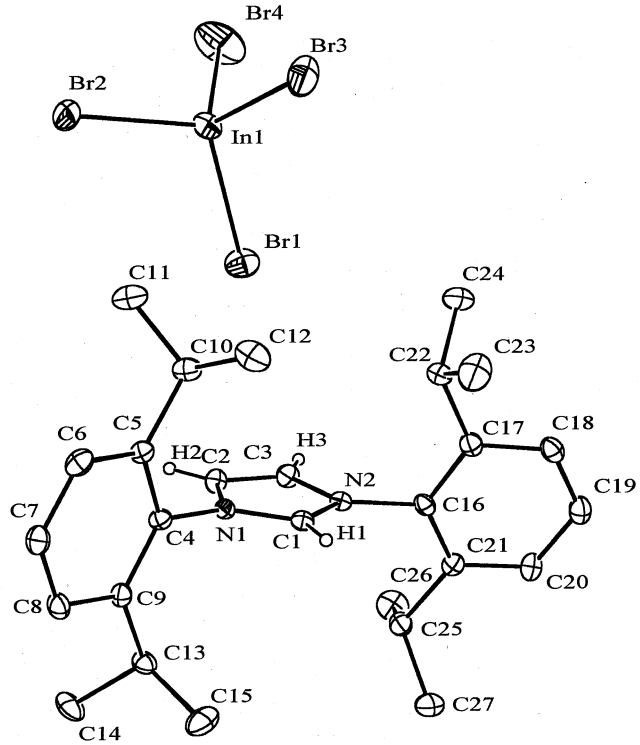


Fig. 2. Molecular structure of compound **2**. Selected bond lengths (Å) and angles (°): C(1)–N(1) 1.329(11), N(1)–C(2) 1.367(11), N(1)–C(4) 1.467(11), C(2)–C(3) 1.361(13), N(2)–C(1) 1.339(10), N(2)–C(3) 1.374(11), N(2)–C(16) 1.457(11), In(1)–Br(1) 2.4995(16), In(1)–Br(2) 2.4862(16), In(1)–Br(3) 2.4699(17), In(1)–Br(4) 2.4814(19), N(1)–C(1)–N(2) 108.0(7), C(1)–N(2)–C(3) 108.9(7), C(1)–N(2)–C(16) 125.3(7), C(1)–N(1)–C(2) 109.3(7), C(1)–N(1)–C(4) 123.7(7), Br(1)–In(1)–Br(2) 111.16(6), Br(2)–In(1)–Br(4) 107.27(9), Br(4)–In(1)–Br(3) 108.55(9), Br(3)–In(1)–Br(1) 107.97(6).

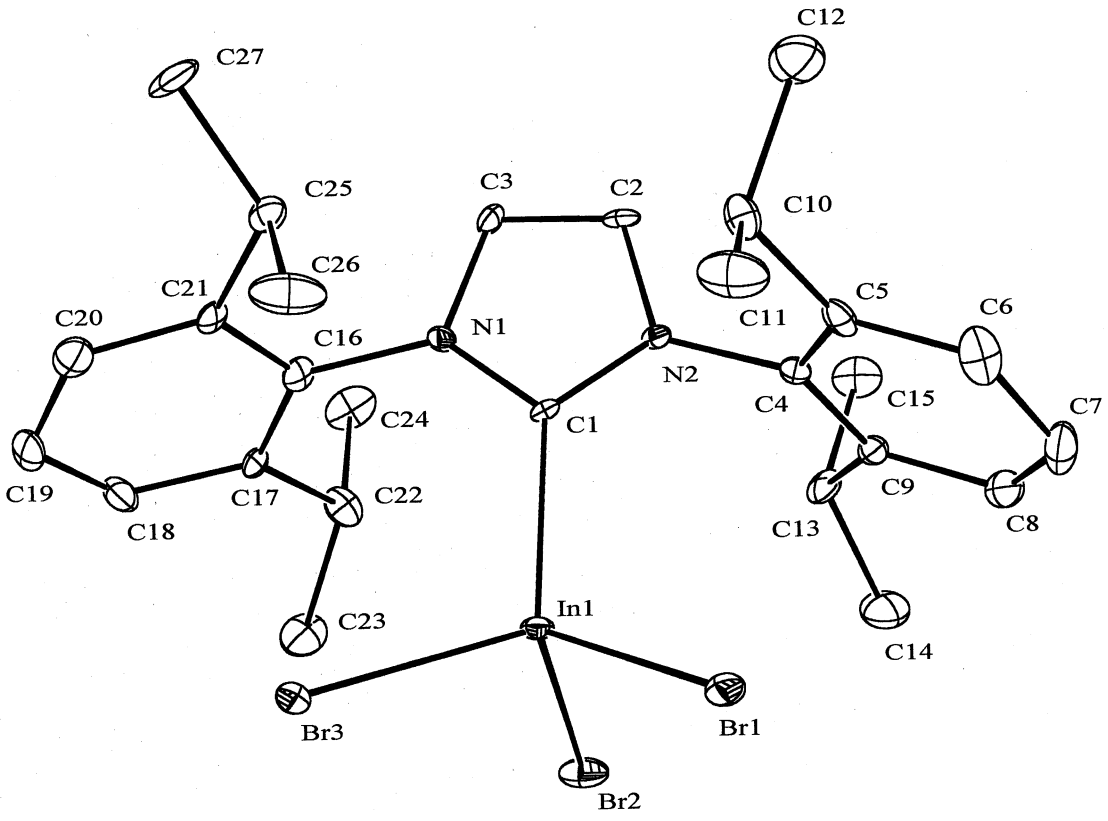


Fig. 3. Molecular structure of compound **3**. Selected bond lengths (Å) and angles (°): C(1)–In(1) 2.212(8), C(1)–N(1) 1.331(12), N(1)–C(3) 1.407(12), N(1)–C(16) 1.449(13), C(2)–C(3) 1.320(13), N(2)–C(2) 1.397(11), N(2)–C(1) 1.322(12), N(2)–C(4) 1.462(13), In(1)–Br(1) 2.4935(14), In(1)–Br(2) 2.5000(12), In(1)–Br(3) 2.4999(13), N(1)–C(1)–N(2) 106.5(7), C(1)–N(2)–C(2) 109.8(8), C(1)–N(2)–C(4) 124.6(7), C(1)–N(1)–C(3) 110.3(8), C(1)–N(1)–C(16) 126.4(8), Br(1)–In(1)–Br(2) 107.43(5), Br(2)–In(1)–Br(3) 107.92(5), Br(3)–In(1)–Br(1) 107.34(4), C(1)–In(1)–Br(1) 113.6(3), C(1)–In(1)–Br(2) 108.1(2), C(1)–In(1)–Br(3) 112.2(3).

nium, but there are two doublets arising from the isopropyl methyl protons, indicating restricted rotation of both the aryl and isopropyl substituents. The compound is thermally robust but decomposes at 229 °C, a value which can be compared to the melting point of the most stable carbene–AlH_3 complex, [AlH_3(IMes)] (246 °C) [12]. The molecular structure of **1** is shown in Fig. 1 and is consistent with its spectroscopic data. The steric protection afforded by the bulky carbene is obvious from the crystal structure; the two diisopropylphenyl substituents are close to perpendicular to the imidazole ring and the isopropyl methyl substituents are folded back from the metal centre. The hydride ligands were located from difference maps and refined isotropically. The average Al–H bond length of 1.527 Å is similar to the mean value (1.54 Å) for all crystallographically determined terminal Al–H bonds [13], whilst the angles about Al(1) indicate that it is in a distorted tetrahedral environment. The Al–C bond length of 2.0556(13) Å is close to those in both [AlH_3(IMes)] [2.034(3) Å] [12] and [AlH_3{$CN(Pr^i)C_2H_2N(Pr^i)$}] [2.046(5) Å] [8]. The metric parameters for the carbene ligand indicate some delocalisation over the NCN fragment whilst the N–C–Al angles are very similar to those seen in [AlH_3{$CN(Pr^i)C_2H_2N(Pr^i)$}] and [AlH_3(IMes)].

The carbene, IPr, has also been used to prepare a complex of indium tribromide. An initial reaction of IPr with $InBr_3$ in Et_2O did not gave the expected 1:1 adduct, [$InBr_3$(IPr)], but instead the imidizolium salt [IPr-H][$InBr_4$] (**2**) which has been structurally characterised (Fig. 2). From our previous work on carbene–InX_3 (X = Cl, Br) compounds in which the formation of similar imidazolium compounds has been observed [9,14], it is thought that **2** probably arises from a trace of water in the $InBr_3$ starting material which reacts with the carbene to give **2** and '$InBr_2OH$' as the reaction by-product. The structure of **2** contains two crystallographically independent molecules in the asymmetric unit which display very similar geometries so data for only one will be discussed here. The tetrahedral $InBr_4^-$ anion has no interaction with the cation and the metric parameters of the imidazole ring indicate a more delocalised system than the heterocycle of the alane complex, **1** [N–C–N angles **2** 108.0(7); **1** 103.86(10)°].

The reaction was repeated with carefully resublimed $InBr_3$ and the 1:1 adduct, [$InBr_3$(IPr)] (**3**) was isolated in low yield. The spectroscopic data for **3** are only slightly

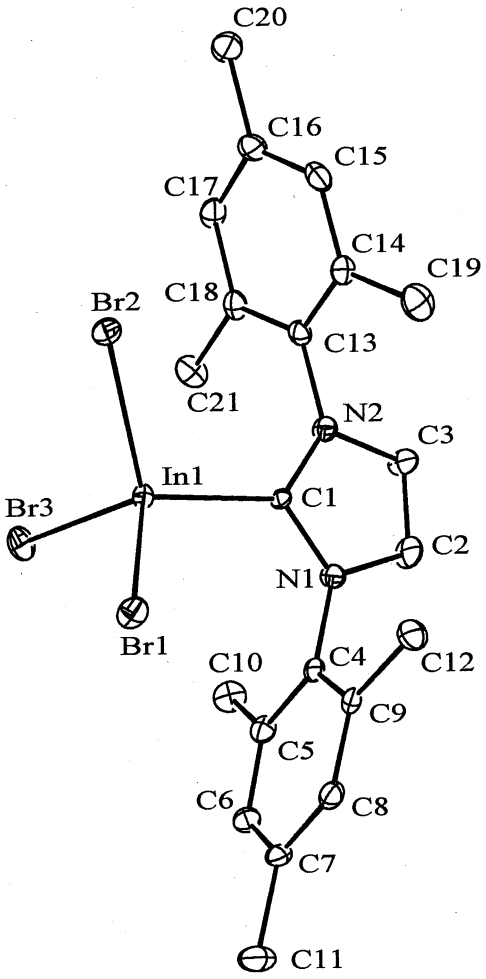


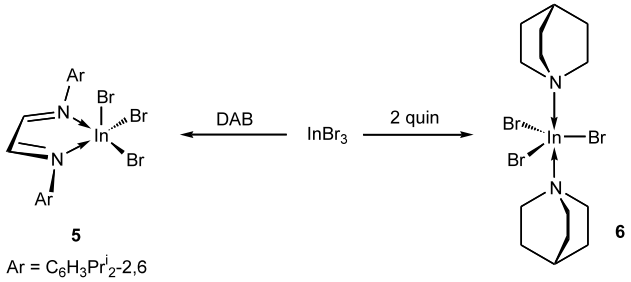
Fig. 4. Molecular structure of compound **4**. Selected bond lengths (Å) and angles (°): C(1)–In(1) 2.195(5), C(1)–N(1) 1.355(7), N(1)–C(2) 1.385(7), N(1)–C(4) 1.427(7), C(2)–C(3) 1.344(9), N(2)–C(3) 1.392(8), N(2)–C(1) 1.346(7), N(2)–C(13) 1.442(7), In(1)–Br(1) 2.4994(8), In(1)–Br(2) 2.4935(8), In(1)–Br(3) 2.4947(9), N(1)–C(1)–N(2) 106.3(5), C(1)–N(2)–C(3) 109.5(5), C(1)–N(2)–C(13) 127.5(5), C(1)–N(1)–C(2) 110.0(5), C(1)–N(1)–C(4) 126.4(5), Br(1)–In(1)–Br(2) 107.38(3), Br(2)–In(1)–Br(3) 109.33(3), Br(3)–In(1)–Br(1) 107.95(3), C(1)–In(1)–Br(1) 112.54(14), C(1)–In(1)–Br(2) 110.52(13), C(1)–In(1)–Br(3) 109.03(14).

shifted from those for the free carbene with the exception of the carbene carbon resonance which cannot be observed in its ^{13}C-NMR spectrum, presumably due to the quadrupolar nature of indium. As in **1**, the ^{1}H-NMR spectrum displays two doublets for the isopropyl methyl protons suggesting restricted rotation of the aryl and isopropyl substituents. An X-ray crystal structure determination was carried out and it was found that the asymmetric unit contains two crystallographically independent molecules with no significant geometrical differences between them. The ORTEP diagram for one of these is shown in Fig. 3. The compound is monomeric and the indium atom sits in a slightly distorted tetrahedral environment with the In–Br bond lengths almost equivalent (2.497 Å average). The In–C bond length is very similar to that seen in [$InBr_3${$CN(Pr^i)C_2H_2N(Pr^i)$}] [2.212(8) and 2.199(5) Å, respectively] but longer than In–C bonds in many indium alkyl complexes [e.g. 2.174 Å in (trimethyl)quinuclidine indium) [15]]. The N–C–N angle [106.5(7)°] is again indicative of a degree of delocalisation over that fragment. As was the case for the alane complex, **1**, the aryl groups are almost perpendicular to the imidazole ring and the isopropyl methyl groups are directed away from the metal centre.

For the purposes of comparison the complex, [$InBr_3$(IMes)] (**4**) was prepared using similar conditions. The spectroscopic data are consistent with its proposed structure which was confirmed by X-ray crystallography. Again, it was found that there are two crystallographically independent molecules in the asymmetric unit, one of which is shown in Fig. 4. As expected, the complex is monomeric and the bond lengths and angles about the indium centre are similar to those in **3**. It is noteworthy that compound **4** is isomorphous and isostructural with its known [$InCl_3$(IMes)] analogue [6].

2.2. Nitrogen donor ligand complexes

An intermediate in the synthesis of the IPr carbene is *N*,*N*′-bis(2,6-diisopropylphenyl)diazabutadiene (DAB) and thus it was deemed of interest to synthesise the $InBr_3$ complex of this ligand. The reaction of DAB with one equivalent of $InBr_3$ in Et_2O gave the 1:1 adduct, **5**, in good yield (Scheme 2). It is noteworthy that the same product was obtained when the reaction was carried out in a 1:2 stoichiometry. Both the ^{1}H- and ^{13}C-NMR spectra suggest that the four isopropyl methyl groups are chemically equivalent in solution. The molecular structure of **5** is shown in Fig. 5. This represents the first structural characterisation of a diazabutadiene–MX_3 complex (M = Group 13 metal, X = halide) reported in the literature. The compound crystallises in the chiral space group *P*1 with four crystallographically independent molecules in the asymmetric unit. The geometries of these are significantly different, ranging from distorted square based pyramidal to distorted trigonal pyramidal. Despite these differences, comment will only be made on one of the molecules here. It is



5

Ar = $C_6H_3Pr^i_2$-2,6

6

Scheme 2.

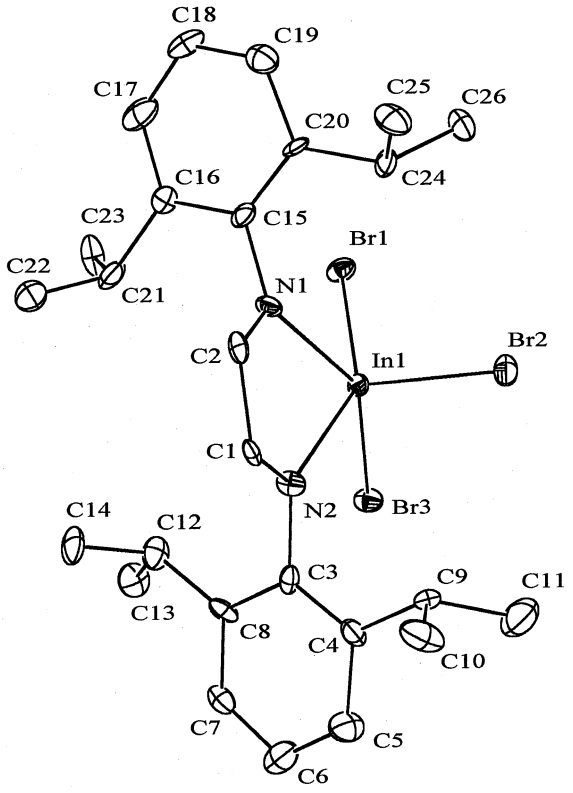


Fig. 5. Molecular structure of compound **5**. Selected bond lengths (Å) and angles (°): In(1)–N(1) 2.332(14), N(1)–C(2) 1.27(2), N(1)–C(15) 1.45(2), C(1)–C(2) 1.57(2), N(2)–C(1) 1.24(2), N(2)–C(3) 1.46(2), In(1)–N(2) 2.314(12), In(1)–Br(1) 2.532(2), In(1)–Br(2) 2.505(2), In(1)–Br(3) 2.539(2), N(1)–In(1)–N(2) 71.1(4), N(1)–In(1)–Br(1) 88.8(3), Br(1)–In(1)–Br(3) 95.37(7), Br(3)–In(1)–N(2) 89.4(3), Br(1)–In(1)–Br(2) 108.98(8), Br(3)–In(1)–Br(2) 107.34(8), N(1)–In(1)–Br(2) 101.5(3), N(2)–In(1)–Br(2) 100.0(3).

interesting, in light of these solid state geometrical differences, that in solution all the methyl groups of **5** are chemically equivalent which strongly suggests that there is a fluxional process occurring in solution involving the decomplexation/complexation of the DAB molecule from the $InBr_3$ unit. Cooling solutions of **5** to −50 °C did not lead to a resolution of the spectrum and all resonances broadened only slightly, presumably because the fluxional process is rapid even at this temperature.

The chirality of the crystal structure arises from an 'end to end' packing of the molecules of **5** which gives rise to an infinite helical chain. The geometry around In(1) is distorted square based pyramidal with the two Br ligands trans to the nitrogen centres and at similar distances from the indium atom [In(1)–Br(1) 2.532(2) and In(1)–Br(3) 2.539(2) Å] with one closer apical Br ligand [In(1)–Br(2) 2.505(2) Å]. The In–N bond lengths are comparable but slightly longer than the mean for all crystallographically characterised In–N bond lengths, 2.294 Å [13]. There is an acute N–In–N angle at 71.1(4)° and the C–N and C–C bond lengths within the DAB ligand suggest that there is little delocalisation over this ligand.

Quinuclidine (quin) has been used as a ligand in the formation of aluminium and gallium halide complexes but structurally characterised examples of indium trihalide adducts are unknown. In order to prepare such a complex two equivalents of quinuclidine were reacted with one equivalent of $InBr_3$ in Et_2O which yielded the complex, $[InBr_3(quin)_2]$ (**6**) in good yield. Interestingly, the analogous 1:1 adduct could not be prepared as only

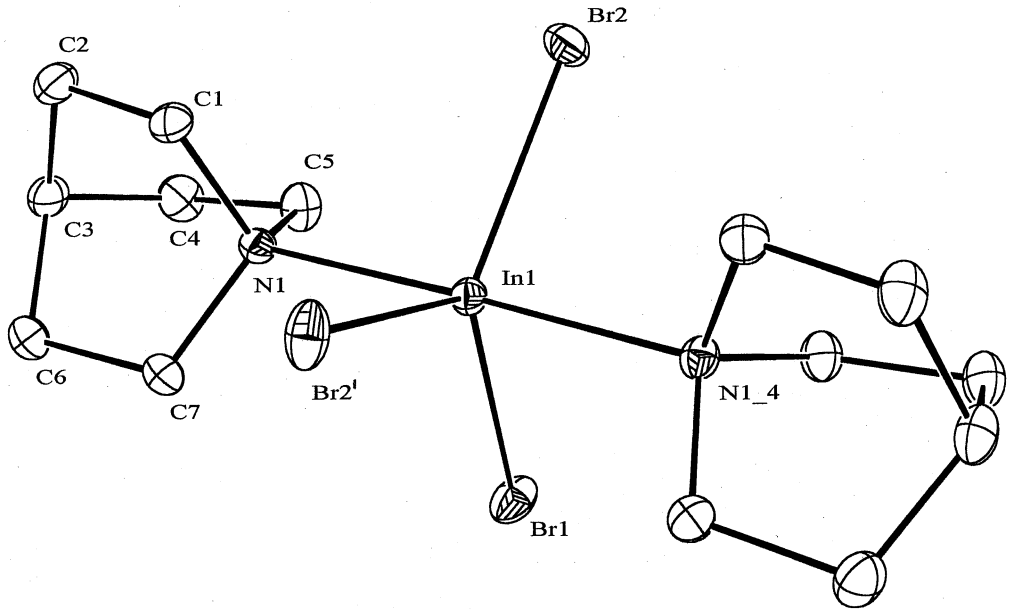


Fig. 6. Molecular structure of compound **6**. Selected bond lengths (Å) and angles (°): In(1)–Br(1) 2.5271(8), In(1)–Br(2) 2.5254(5), In(1)–N(1) 2.364(3), N(1)–In(1)–N(1′) 178.40(14), Br(2)–In(1)–Br(2′) 117.86(3), Br(1)–In(1)–Br(2) 121.07(2).

the 2:1 complex crystallised when the reaction was carried out in a 1:1 stoichiometry. This observation is consistent with the preference of indium to attain coordination numbers of 5 or 6 as opposed to 4 [1]. The spectroscopic data for **6** were of limited value in determining its structure as they closely resemble those for the free quin ligand. As a result an X-ray structural analysis was carried out and the molecular structure of **6** is shown in Fig. 6. The complex is trigonal bipyramidal with the bromide ligands in the equatorial sites and the amine ligands in the axial positions. A similar arrangement has been seen in $[GaHCl_2(quin)_2]$ [16] and $[AlClH_2(quin)_2]$ [17]. Both the In–Br (2.5959 Å average) and In–N bond lengths [2.364(3) Å] are unexceptional being close to those in related complexes, e.g $[InBr_3$(trimethyltriazacyclononane)] [18].

3. Conclusion

The very bulky carbene, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, has been used to prepare the Group 13 hydride and halide complexes, $[AlH_3(IPr)]$ and $[InBr_3(IPr)]$, which have been structurally characterised. Also structurally characterised is the related $[InBr_3(IMes)]$ adduct. In addition, two nitrogen donor ligand complexes of $InBr_3$ have been prepared and structurally characterised, viz. $[InBr_3(DAB)]$ and $[InBr_3(quin)_2]$. We are currently investigating the reduction of the $InBr_3$ adducts in order to prepare subvalent indium halide complexes. The results of these investigations will be reported in forthcoming publications.

4. Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. The solvents Et_2O, $C_6H_5CH_3$ and THF were distilled over either potassium or Na–K alloy then freeze/thaw degassed prior to use. CH_2Cl_2 was purified by distillation from CaH_2 under a dinitrogen atmosphere. ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker DXP400 or JEOL Eclipse 300 spectrometers in deuterated solvents and were referenced to the residual ^{1}H resonances of the solvent used. Mass spectra were recorded using a VG Fisons Platform II instrument under APCI conditions. Microanalyses were carried out by the Warwick Microanalytical Service. M.p.s were determined in sealed glass capillaries under argon and are uncorrected. $InBr_3$ was purchased from Aldrich and resublimed before use. The compounds IMes [19], IPr [20] and DAB [20] were prepared by literature methods and all other materials were used as received.

4.1. $[AlH_3(IPr)]$ (**1**)

To a cold (−78 °C) solution of $LiAlH_4$ (0.05 g, 1.32 mmol) in Et_2O (20 cm^3) was added a cold solution of IPr (0.51 g, 1.31 mmol) in Et_2O (40 cm^3) over 5 mins. This was allowed to warm to room temperature (r.t.) and stirred overnight. The solvent was removed in vacuo and the white residue extracted with $C_6H_5CH_3$ (2 × 40 cm^3). Concentration and cooling to −35 °C yielded colourless crystals of **1** (0.41 g, 74%). M.p. 229–234 °C (dec); ^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ 1.17 (d $^3J_{HH} = 6$ Hz, 12H, CH_3), 1.54 (d, $^3J_{HH} = 6$ Hz, 12H, CH_3), 2.80 (sept $^3J_{HH} = 6$Hz, 4H, CH), 6.55 (s, 2H, NC_2H_2N), 7.22 (d, $^3J_{HH} = 7$ Hz, 4H, *m*-Ph), 7.36 (t, $^3J_{HH} = 7$ Hz, 2H, *p*-Ph); ^{13}C-NMR (100.6 MHz, C_6D_6, 300 K): δ 23.4 (CH_3), 24.5 (CH_3), 28.75 (CH), 123.26 (*p*-Ph), 123.86 (*m*-Ph), 126.56 (*o*-Ph), 130.15 (*ipso*-Ph), 145.5 (NC_2H_2N); MS APCI: *m*/*z* (%) 417.2 [M−H$^+$, 5], 389.2 [IprH$^+$, 100]; IR (Nujol, cm^{-1}): *v* 1061 (sh), 1112 (s), 1212 (s), 1257 (s), 1322 (s), 1729 (br s, Al–H).

4.2. $[IPrH][InBr_4]\cdot(Et_2O)_{0.5}$ (**2**)

To a solution of IPr (0.54 g, 1.4 mmol) in Et_2O (10 cm^3) was added a solution of $InBr_3$ (0.50 g, 1.4 mmol) in Et_2O (10 cm^3). After stirring for 2 h the solution was concentrated and cooled to −35 °C to yield colourless crystals of **2** (0.11 g, 9%). M.p. 187–189 °C (dec); ^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ 1.15 (d, $^3J_{HH} = 7$ Hz, 12H, CH_3), 1.26 (d, $^3J_{HH} = 7$ Hz, 12H, CH_3), 2.38 (sept $^3J_{HH} = 7$ Hz, 4H, CH), 7.86 (s, 2H, NC_2H_2N), 7.30 (d, $^3J_{HH} = 8$ Hz, 4H, *m*-Ph), 7.51 (t, $^3J_{HH} = 8$ Hz, 2H, *p*-Ph), 8.42 (s, 1H NCHN); ^{13}C-NMR (100.6 MHz, C_6D_6, 300 K): δ 23.1 (CH_3), 26.1 (CH_3), 29.1 (CH), 124.8 (*p*-Ph), 126.6 (*m*-Ph), 131.9 (*o*-Ph), 136.5 (*ipso*-Ph), 145.0 (NCN), 145.3 (NC_2H_2N); IR (Nujol, cm^{-1}): *v* 1594 (m), 1328 (m), 1212 (m), 1117 (m), 1062 (m) 800 (w); $C_{29}H_{42}Br_4InN_2O_{0.5}$ requires: C, 40.45; H, 4.92; N, 3.25. Found: C, 41.69; C, 4.77; N, 3.45%.

4.3. $[InBr_3(IPr)]$ (**3**)

To a solution of IPr (0.54 g, 1.4 mmol) in Et_2O (10 cm^3) was added a solution of $InBr_3$ (0.50 g, 1.4 mmol) in Et_2O (10 cm^3). After stirring for 2 h the solution was concentrated and cooled to −35 °C to yield colourless crystals of **3** (0.11 g, 11%). M.p. 187 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ 1.10 (d, $^3J_{HH} = 7$ Hz, 12H, CH_3), 1.35 (d, $^3J_{HH} = 7$ Hz, 12H, CH_3), 2.48 (sept $^3J_{HH} = 7$ Hz, 4H, CH), 7.86 (s, 2H, NC_2H_2N), 7.31 (d, $^3J_{HH} = 8$ Hz, 4H, *m*-Ph), 7.57 (t, $^3J_{HH} = 8$ Hz, 2H, *p*-Ph); ^{13}C-NMR (100.6 MHz, C_6D_6, 300 K) δ 24.1 (CH_3), 24.8 (CH_3), 29.3 (CH), 125.1 (*p*-Ph), 126.7 (*m*-Ph), 129.4 (*o*-Ph), 132.7 (*ipso*-Ph), 145.0 (NC_2H_2N); MS APCI: *m*/*z* (%) 663 [M−Br$^+$, 41], 388 (IPr$^+$, 100); IR (Nujol,

cm^{-1}): ν 1568 (m), 1328 (m), 1257 (m), 1117 (m), 1062 (m).

4.4. $[InBr_3(IMes)]$ (**4**)

To a solution of $InBr_3$ (0.50 g, 1.44 mmol) in Et_2O (10 cm^3) was added a solution of IMes (0.43 g, 1.44 mmol) in Et_2O (10 cm^3). This was stirred for 2 h and the solvent removed in vacuo. The white residue was extracted with CH_2Cl_2 (2×20 cm^3) and concentrated. Placement at -30 °C overnight yielded large blocks of **4** (0.818 g, 88%). M.p. 208–210 °C (dec); ^{1}H-NMR (400 MHz, $CDCl_3$, 300 K) δ 2.04 (s, 12H, *o*-CH_3), 2.15 (s, 6H, *p*-CH_3), 6.75 (s, 4H, *m*-CH), 7.32 (s, 2H, NC*HCH*N); ^{13}C-NMR (100.6 MHz, $CDCl_3$, 300 K): δ 17.96 (*o*-CH_3), 21.35 (*p*-CH_3), 125.69 (NC_2H_2N), 132.31 (*p*-Ar), 133.91 (*o*-Ar), 135.24 (*m*-Ar), 141.21 (*ipso*-Ar); MS APCI: *m*/*z* (%) 579.1 [$M-Br^+$, 100], 277 [$IMes^+$, 15]; IR (Nujol, cm^{-1}): ν 1593 (sh), 1465 (s), 1378 (s), 1234 (s), 1122 (s), 1029 (s), 927 (m), 860 (sh), 753 (sh), 727 (m), 691 (m); $C_{21}H_{24}Br_3N_2In$ requires: C, 38.20%; H, 3.67; N, 4.25. Found: C, 38.12; H, 3.62; N, 4.05%.

4.5. $[InBr_3(DAB)]\cdot(OEt_2)_{0.5}$ (**5**)

To a solution of DAB (0.53 g, 1.4 mmol) in Et_2O (10 cm^3) was added a solution of $InBr_3$ (0.50 g, 1.4 mmol) in Et_2O (10 cm^3). This was stirred for 2 h to give a deep red solution, which was filtered, concentrated and cooled to -35 °C yielding red crystals of **5** (0.16 g, 31% on ether free sample). M.p. 178–180 °C; ^{1}H-NMR (400 MHz, C_6D_6, 300 K) δ 1.28 (d, 12H, $^3J_{HH} = 7$ Hz, CH_3), 3.25 (sept, $^3J_{HH} = 7$ Hz, 2H, CH), 7.16 (d, 4H, $^3J_{HH} = 7$ Hz, *m*-ArH), 7.18 (t, 2H, $^3J_{HH} = 7$ Hz, *p*-ArH), 8.45 (s, 2H, NCH); ^{13}C-NMR (100.1 MHz, C_6D_6, 300 K): δ 23.5 (CH_3), 28.9 (CH), 124.0 (*m*-Ar), 124.5 (*p*-Ar), 138.8 (*o*-Ar), 146.4 (*ipso*-Ar), 163.6 (CN); MS APCI: *m*/*z* (%): 649 [$M-Br^+$, 2], 376 (DAB^+, 5), 333 (DAB-Pr^{i+}, 100); IR (Nujol, cm^{-1}): ν 1654 (m), 1594 (m), 1172 (s), 1107 (m), 1042(m), 936 (m); $C_{26}H_{36}Br_3N_2In$ requires: C, 42.71; H, 4.96; N, 3.83%. Found: C, 41.51; H, 4.98; N, 3.55%.

4.6. $[InBr_3(quin)_2]$ (**6**)

To a solution of quinuclidine (0.31 g, 2.8 mmol) in Et_2O (10 cm^3) was added a solution of $InBr_3$ (0.50 g, 1.4 mmol) in Et_2O (10 cm^3). The reaction was stirred for 2 h to give a white precipitate, which was isolated by filtration and extracted into $C_6H_5O_3$ (2×20 cm^3). Concentration and cooling to -35 °C gave colourless crystals of **6** (0.67 g, 83%). M.p. 178–180 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ 1.88 (br m, 12H, CH_2), 2.17 (br m, 2H, CH), 3.24 (br m, 12H, CH_2N); ^{13}C-NMR (100.1 MHz, $CDCl_3$, 300 K): δ 19.6 (CH), 23.1 (CH_2), 46.8 (NCH_2); MS APCI: *m*/*z* (%) 385 [$M-Br^+$, 13], 274 [$InBr_2^+$, 21], 112 [$quin^+$, 100]; IR (Nujol, cm^{-1}): ν 1323 (m), 1281 (w), 1258 (w), 1044 (m), 979 (m), 771(m).

4.7. Crystallographic studies

Crystals of **1**–**6** suitable for X-ray structure 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 (SHELX-97) [21] using all unique data. All non-hydrogen

Table 1
Crystal data for compounds **1**, **2**·$(Et_2O)_{0.5}$, **3**, **4**, **5**·$(Et_2O)_{0.5}$ and **6**

	1	**2**·$(Et_2O)_{0.5}$	**3**	**4**	**5**·$(Et_2O)_{0.5}$	**6**
Chemical formula	$C_{27}H_{39}AlN_2$	$C_{29}H_{42}Br_4N_2InO_{0.5}$	$C_{27}H_{36}Br_3N_2In$	$C_{21}H_{24}Br_3N_2In$	$C_{28}H_{41}Br_3N_2InO_{0.5}$	$C_{14}H_{26}Br_3N_2In$
Formula weight	418.58	861.11	743.13	658.97	768.18	576.92
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Triclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$Pbca$	$Pca2_1$	$P1$	$Pbcn$
a (Å)	10.287(2)	19.322(4)	16.759(3)	16.502(3)	10.456(2)	8.9280(18)
b (Å)	18.396(4)	20.090(4)	20.352(4)	16.541(3)	15.351(3)	12.017(2)
c (Å)	14.707(3)	19.322(4)	35.424(7)	17.896(4)	21.508(4)	17.058(3)
α (°)	90	90	90	90	95.81(3)	90
β (°)	104.06(3)	90.99(3)	90	90	101.71(3)	90
γ (°)	90	90	90	90	105.11(3)	90
V (Å^3)	2699.8(9)	7500(3)	12082(4)	4884.9(17)	3219.9(11)	1830.2(6)
Z	4	8	16	8	4	4
μ (Mo–K_α) (mm^{-1})	0.089	4.912	4.768	5.884	4.476	7.835
Reflections collected	39 261	105 988	110 551	73 059	49 392	22 032
Unique reflections (R_{int})	5290 (0.0328)	13 646 (0.1046)	11 885 (0.1438)	11 164 (0.0753)	23 638 (0.0785)	2024 (0.0607)
R_1 ($I > 2\sigma(I)$)	0.0387	0.0767	0.0852	0.0399	0.0833	0.0360
wR_2' (all data)	0.0987	0.2352	0.1716	0.0808	0.2217	0.0779

atoms are anisotropic with H-atoms included in calculated positions (riding model) except for the hydride ligands of **1** which were located from difference maps and refined isotropically. Although the data for **2**, **3** and **5** were of poor quality the crystal structures of these compounds unambiguously confirm their gross molecular frameworks. Crystal data, details of data collections and refinement are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures of **1**–**6** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 183314–183319 for compounds **1**–**6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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