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Synthesis and characterisation of stable carbene–indium(III) halide complexes

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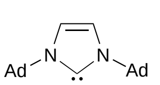
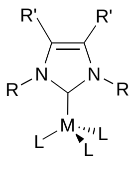
The reaction of the stable carbene, $:\overline{\mathrm{CN(Pr^i)C_2Me_2N}}\mathrm{Pr^i}$, with InX_3, X = Cl or Br, yielded either the 1 : 1 or 1 : 2 complexes, $[\mathrm{InX_3\{\overline{CN(Pr^i)C_2Me_2N}Pr^i\}}]$ and $[\mathrm{InX_3\{\overline{CN(Pr^i)C_2Me_2N}Pr^i\}_2}]$, depending upon the stoichiometry employed. X-Ray crystallography showed one of the 1 : 1 adducts, X = Br, to be monomeric and tetrahedral. The 2 : 1 adducts have a trigonal-bipyramidal geometry with two halides axial and one equatorial. Conductivity and NMR studies suggested all these complexes retain their neutrality in solution. Treatment of InX_3 with 1 equivalent of $\overline{\mathrm{CN(Pr^i)C_2Me_2N}}\mathrm{Pr^i}$ and half an equivalent of water afforded the ionic compounds $[\mathrm{H\overline{CN(Pr^i)C_2Me_2N}Pr^i}]\ [\mathrm{InX_4\{\overline{CN(Pr^i)C_2Me_2N}Pr^i\}}]$ which are fluxional in solution at room temperature. The crystal structures of both compounds show the anion to be trigonal bipyramidal with two axial and two equatorial halides.

The formation of co-ordination complexes between indium(III) halides and neutral ligands (L) containing either N, P, O or S donor centres is now a well established area of chemistry.[1] X-Ray crystallographic studies have shown that such complexes can exist in a variety of stoichiometries in the solid state, $[InX_3L_n]$, X = halide, $n = 1$, 2 or 3, which have either a distorted tetrahedral geometry $\{n = 1$, *e.g.* $[\mathrm{InI_3(PHBu^t_2)}]^2\}$, a trigonal-bipyramidal geometry with halides equatorial $\{n = 2$, *e.g.* $[\mathrm{InCl_3(PMe_3)_2}]^3\}$ or both *fac*- and *mer*-octahedral geometries $\{n = 3$, *e.g.* $[\mathrm{InCl_3(OPMe_3)_3}]^4\}$. When the 2 : 1 stoichiometry is employed there is also the possibility of ionic complexes forming in the solid state *e.g.* $[\mathrm{InI_2(dmso)_4}][\mathrm{InI_4}]$[5] (dmso = dimethyl sulfoxide).

In 1991 the preparation of the first of a series of stable imidazolylidenes, **I**, by Arduengo *et al.*[6] offered the ready availability of thermally robust, nucleophilic carbenes to the co-ordination chemist. In the following years this offer was taken up and many reports on carbene–transition metal complexes followed.[7] By contrast, the interaction of carbenes with main group metals has not been well investigated, and in the case of Group 13 can be confined to a handful of 1 : 1 complexes, **1**–**4**.[8–10] One interesting feature of compound **3** is its remarkable thermal stability (m.p. 246 °C, decomposition temperature not stated[9]) compared to that of other AlH_3 adducts which usually decompose at much lower temperatures, *e.g.* $[\mathrm{AlH_3(NMe_3)}]$, m.p. 78 °C, decomposition at *ca.* 100 °C.[11]

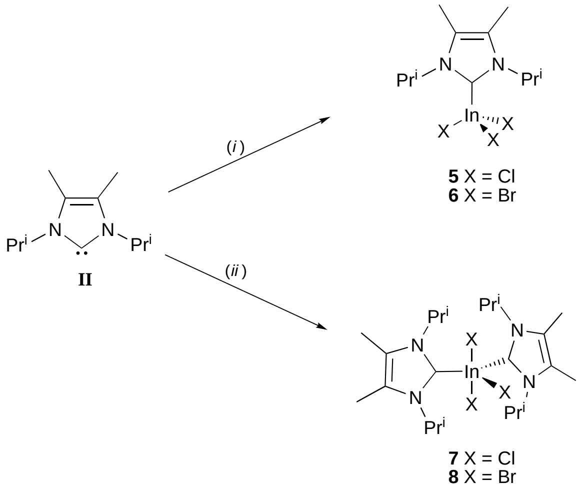


I Ad = adamantyl



1 M = B, L = H, R = Me, Et, Pr^i, R' = Me
2 M = B, L = F, R = Pr^i, R' = Me
3 M = Al, L = H, R = mesityl, R' = H
4 M = Al, Ga, L = Me, R = Pr^i, R' = Me

Here we report the results of a study aimed at the interaction of nucleophilic carbenes with indium(III) halides, which we have begun for a number of reasons. First, there are no known examples of indium–carbene complexes. Secondly, the propensity of indium to attain higher co-ordination numbers than its lighter congeners offered the possibility of carbene–indium halide adducts with a higher than 1 : 1 stoichiometry. Finally, and as part of a related study, we see carbene–indium halide adducts as potentially excellent precursors to carbene–InH_3 complexes. Although adducts of InH_3 are unknown due to their extreme thermal instability, we believe their eventual stabilisation by carbene complexation may be achieved considering the thermal robustness of **3**.



Scheme 1 (*i*) InX_3, 20 °C, 3 h; (*ii*) $\frac{1}{2}$ InX_3, 20 °C, 3 h

Results and Discussion

Treatment of a tetrahydrofuran solution of InX_3, X = Cl or Br, with either 1 or 2 equivalents of the carbene, II, at 20 °C led to moderate yields of the complexes **5**–**8** after recrystallisation from CH_2Cl_2–Et_2O (Scheme 1). The reaction of InX_3 with 5 equivalents of II afforded only the 2 : 1 adducts and unchanged carbene, which suggests that 3 : 1 complexes of InX_3 and II are

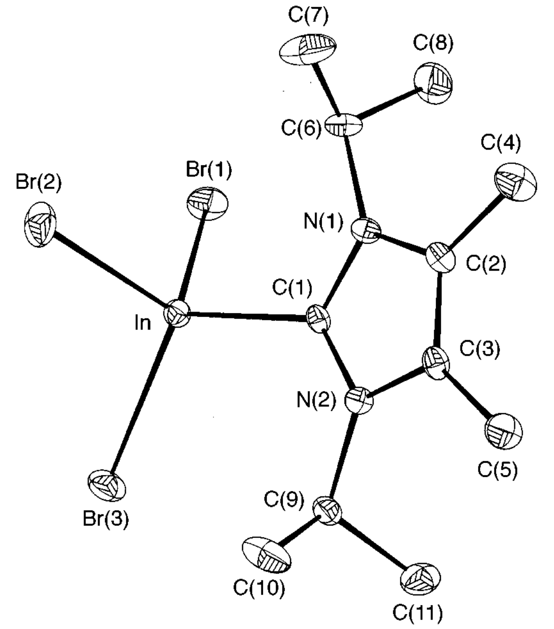


Fig. 1 Molecular structure of compound **6** (displacement ellipsoids are drawn at the 50% probability level)

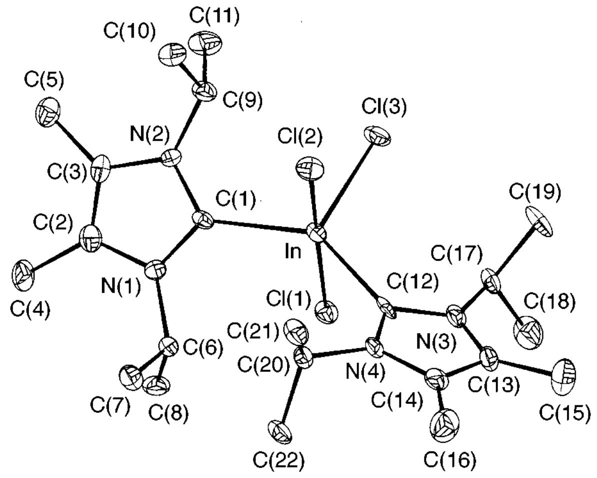


Fig. 2 Molecular structure of compound **7**. Details as in Fig. 1

not sterically viable. Compounds **5**–**8** are thermally stable and all are only mildly air sensitive in the solid state.

The ^{1}H and ^{13}C NMR spectra of complexes **5** and **6** showed the expected resonances with the exception of those due to the carbene carbons which could not be seen in the ^{13}C NMR spectrum of either compound. By comparison with the related compounds **1**–**3** these carbons would be expected to resonate at *ca.* δ 170 but in this case the high quadruple moment of the coordinated indium centre (^{115}In, 95%, $I = \frac{9}{2}$; ^{113}In, 5%, $I = \frac{9}{2}$) broadens them sufficiently to make them unobservable. The fact that their resonances were not observed suggests that the solid-state structures are retained in solution and they are not in equilibrium with ionic dimers of the type $[InX_2L_2][InX_4]$, the possibility of which has been put forward for other 1 : 1 adducts of indium(III) halides.[2] This hypothesis was confirmed first by studying the ^{115}In NMR spectra of **5** and **6** which showed no distinguishable resonances in CD_2Cl_2 solutions. If $[InX_4]^-$ anions were present relatively narrow resonances would be visible at δ 430 and 176 for the $[InCl_4]^-$ and $[InBr_4]^-$ ions respectively.[12] Final confirmation of the neutrality of **5** and **6** in solution was obtained by measuring their molar conductivities in 10^{-3} mol dm^{-3} CH_2Cl_2 solutions which proved to be very low (<1 S cm^2 mol^{-1}). The FAB mass spectrum of **6** showed a molecular ion cluster with the correct isotopic distribution pattern.

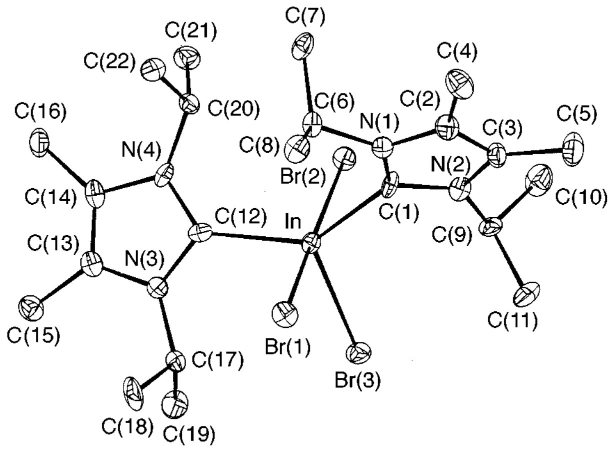


Fig. 3 Molecular structure of compound **8**. Details as in Fig. 1

Table 1 Selected intramolecular distances (Å) and angles (°) for compound **6** with estimated standard deviations (e.s.d.s) in parentheses

In–C(1)	2.199(5)	In–Br(3)	2.4915(6)
In–Br(1)	2.5030(6)	In–Br(2)	2.5063(7)
N(1)–C(1)	1.358(6)	N(1)–C(2)	1.391(6)
N(1)–C(6)	1.472(6)	N(2)–C(1)	1.347(5)
N(2)–C(3)	1.393(6)	N(2)–C(9)	1.478(6)
C(2)–C(3)	1.345(6)	C(2)–C(4)	1.497(7)
C(3)–C(5)	1.509(6)		
C(1)–In–Br(3)	116.33(12)	C(1)–In–Br(1)	111.43(11)
Br(3)–In–Br(1)	107.07(2)	C(1)–In–Br(2)	105.21(13)
Br(3)–In–Br(2)	108.52(2)	Br(1)–In–Br(2)	108.00(2)
C(1)–N(1)–C(2)	109.7(4)	C(1)–N(1)–C(6)	122.9(4)
C(2)–N(1)–C(6)	127.4(4)	C(1)–N(2)–C(3)	109.0(4)
C(1)–N(2)–C(9)	122.8(4)	C(3)–N(2)–C(9)	128.2(4)
N(2)–C(1)–N(1)	106.8(4)	N(2)–C(1)–In	129.4(3)
N(1)–C(1)–In	122.5(3)	C(3)–C(2)–N(1)	106.5(4)
C(3)–C(2)–C(4)	128.3(4)	N(1)–C(2)–C(4)	125.1(4)
C(2)–C(3)–N(2)	108.0(4)	C(2)–C(3)–C(5)	127.4(4)
N(2)–C(3)–C(5)	124.6(4)		

Solution-state NMR studies on the 2 : 1 adducts, **7** and **8**, were similar to those of their 1 : 1 counterparts and highlight the chemical equivalence of both carbene ligands in each complex. Again, no carbene carbon resonances were observed in the ^{13}C NMR spectrum of each compound which again suggests that no fluxional processes are taking place. This was confirmed by the fact that no distinguishable resonances were observed in their ^{115}In NMR spectra and both compounds had negligible molar conductivities (<1 S cm^2 mol^{-1}) in 10^{-3} mol dm^{-3} CH_2Cl_2 solutions.

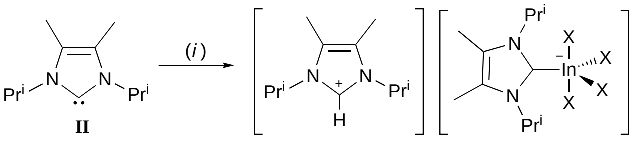
The molecular structures of compounds **6**–**8** are depicted in Figs. 1–3 respectively (see also Tables 1–3). The structure of complex **6** is the first of any 1 : 1 adduct of $InBr_3$ and shows it to be monomeric in the solid state without any intermolecular contacts, which contrasts to contacts seen in other 1 : 1 adducts of indium(III) halides.[2] The indium centre has a distorted tetrahedral geometry with all In–Br lengths being almost equivalent (average 2.500 Å) and slightly shorter than is normal for 2 : 1 adducts of $InBr_3$, *e.g.* $[InBr_3(SAsMe_3)_2]$ average 2.548 Å.[13] Compared to normal In–C (terminal) distances, *e.g.* trimethyl(quinuclidine)indium average 2.174 Å,[14] the In–C (carbene) distance in **6** is relatively long at 2.199(5) Å. Similar trends in M–C (carbene) bond lengths have been observed in other Group 13–carbene complexes.[8–10] In addition, the bond lengths and angles within the carbene heterocycle are similar to those in related Group 13–carbene complexes and suggest a degree of delocalisation within the ring. Of particular note is the N–C (carbene)–N angle of 106.8(4)° which lies between the normal value for free imidazolylidene carbenes (*ca.* 102°) and imidazolium cations (*ca.* 108°).[9]

Table 2 Selected intramolecular distances (Å) and angles (°) for compound **7** with e.s.d.s in parentheses

In–C(12)	2.220(10)	In–C(1)	2.236(9)
In–Cl(3)	2.431(2)	In–Cl(1)	2.578(2)
In–Cl(2)	2.586(2)	N(1)–C(1)	1.353(11)
N(1)–C(2)	1.400(12)	N(1)–C(6)	1.495(11)
N(2)–C(1)	1.351(11)	N(2)–C(3)	1.397(11)
N(2)–C(9)	1.464(11)	N(3)–C(12)	1.360(11)
N(3)–C(13)	1.385(12)	N(3)–C(17)	1.504(11)
N(4)–C(12)	1.362(11)	N(4)–C(14)	1.404(11)
N(4)–C(20)	1.498(10)	C(2)–C(3)	1.350(13)
C(2)–C(4)	1.497(13)	C(3)–C(5)	1.529(13)
C(13)–C(14)	1.376(13)	C(13)–C(15)	1.472(13)
C(14)–C(16)	1.498(14)		
C(12)–In–C(1)	137.2(3)	C(12)–In–Cl(3)	113.3(2)
C(1)–In–Cl(3)	109.5(2)	C(12)–In–Cl(1)	87.0(2)
C(1)–In–Cl(1)	91.7(2)	Cl(3)–In–Cl(1)	93.84(8)
C(12)–In–Cl(1)	85.9(2)	C(1)–In–Cl(2)	91.0(2)
Cl(3)–In–Cl(2)	92.31(8)	Cl(1)–In–Cl(2)	172.05(8)
C(1)–N(1)–C(2)	109.7(8)	C(1)–N(1)–C(6)	124.4(8)
C(2)–N(1)–C(6)	125.9(8)	C(1)–N(2)–C(3)	109.4(8)
C(1)–N(2)–C(9)	123.3(8)	C(3)–N(2)–C(9)	127.1(8)
C(12)–N(3)–C(13)	112.2(8)	C(12)–N(3)–C(17)	121.7(8)
C(13)–N(3)–C(17)	126.2(7)	C(12)–N(4)–C(14)	110.5(7)
C(12)–N(4)–C(20)	122.1(7)	C(14)–N(4)–C(20)	127.3(8)
N(2)–C(1)–N(1)	106.8(8)	N(2)–C(1)–In	124.5(6)
N(1)–C(1)–In	128.2(6)	C(3)–C(2)–N(1)	106.7(8)
C(3)–C(2)–C(4)	126.8(9)	N(1)–C(2)–C(4)	126.5(9)
C(2)–C(3)–N(2)	107.5(8)	C(2)–C(3)–C(5)	127.2(9)
N(2)–C(3)–C(5)	125.0(9)	N(3)–C(12)–N(4)	104.8(8)
N(3)–C(12)–In	125.5(6)	N(4)–C(12)–In	129.2(6)
C(14)–C(13)–N(3)	105.8(6)	C(14)–C(13)–C(15)	127.0(10)
N(3)–C(13)–C(15)	127.2(9)	C(13)–C(14)–N(4)	106.7(8)
C(13)–C(14)–C(16)	127.0(10)	N(4)–C(14)–C(16)	126.2(9)
Cl(5)–C(23)–Cl(4)	107.3(8)		

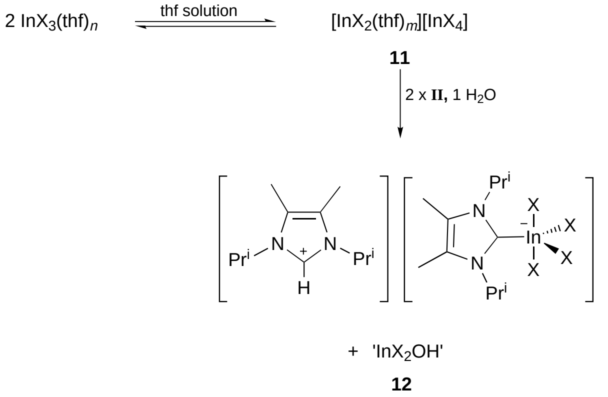
Table 3 Selected intramolecular distances (Å) and angles (°) for compound **8** with e.s.d.s in parentheses

In–C(1)	2.230(10)	In–C(12)	2.231(10)
In–Br(3)	2.586(6)	In–Br(2)	2.737(12)
In–Br(1)	2.744(13)	N(1)–C(1)	1.357(12)
N(1)–C(2)	1.395(11)	N(1)–C(6)	1.516(11)
N(2)–C(1)	1.351(11)	N(2)–C(3)	1.363(12)
N(2)–C(9)	1.501(13)	N(3)–C(12)	1.369(12)
N(3)–C(13)	1.397(11)	N(3)–C(17)	1.483(12)
N(4)–C(12)	1.348(11)	N(4)–C(14)	1.436(12)
N(4)–C(20)	1.477(12)	C(2)–C(3)	1.380(13)
C(2)–C(4)	1.522(14)	C(3)–C(5)	1.489(12)
C(13)–C(14)	1.353(14)	C(13)–C(15)	1.499(13)
C(14)–C(16)	1.518(13)		
C(1)–In–C(12)	136.8(4)	C(1)–In–Br(3)	113.9(2)
C(12)–In–Br(3)	109.3(3)	C(1)–In–Br(2)	86.5(3)
C(12)–In–Br(2)	91.4(2)	Br(3)–In–Br(2)	93.6(4)
C(1)–In–Br(1)	86.4(3)	C(12)–In–Br(1)	91.7(2)
Br(3)–In–Br(1)	92.0(4)	Br(2)–In–Br(1)	172.39(5)
C(1)–N(1)–C(2)	110.8(8)	C(1)–N(1)–C(6)	122.1(8)
C(2)–N(1)–C(6)	126.7(8)	C(1)–N(2)–C(3)	112.6(8)
C(1)–N(2)–C(9)	121.2(8)	C(3)–N(2)–C(9)	126.3(8)
C(12)–N(3)–C(13)	110.8(8)	C(12)–N(3)–C(17)	125.0(8)
C(13)–N(3)–C(17)	124.2(9)	C(12)–N(4)–C(14)	108.8(10)
C(12)–N(4)–C(20)	124.8(9)	C(14)–N(4)–C(20)	126.3(9)
N(2)–C(1)–N(1)	104.5(8)	N(2)–C(1)–In	125.4(7)
N(1)–C(1)–In	129.4(7)	C(3)–C(2)–N(1)	106.0(9)
C(3)–C(2)–C(4)	127.9(10)	N(1)–C(2)–C(4)	126.1(9)
N(2)–C(3)–C(2)	106.1(8)	N(2)–C(3)–C(5)	129.1(9)
C(2)–C(3)–C(5)	124.8(10)	N(4)–C(12)–N(3)	106.6(9)
N(4)–C(12)–In	128.6(8)	N(3)–C(12)–In	124.2(7)
C(14)–C(13)–N(3)	106.3(9)	C(14)–C(13)–C(15)	127.0(10)
N(3)–C(13)–C(15)	126.6(10)	C(13)–C(14)–N(4)	107.5(10)
C(13)–C(14)–C(16)	128.9(10)	N(4)–C(14)–C(16)	123.6(11)



9 X = Br
10 X = Cl

Scheme 2 (*i*) InX$_3$, 0.5 H$_2$O, 20 °C, 3 h



Scheme 3 Proposed mechanism for the formation of compounds **9** and **10**

Compounds **7** and **8** are isostructural and both crystallise with a molecule of dichloromethane per molecule of complex, though these are not included in the figures. Both compounds are monomeric and do not display any intermolecular contacts. The co-ordination environment about the metal centres has been calculated[15] to be distorted trigonal bipyramidal with X(1) and X(2), X = Cl or Br, in the apical positions and X(3), C(1) and C(12) in the equatorial sites. This is surprising considering that in all other neutral 2:1 adducts of InX$_3$, with the exception of $[\mathrm{InCl_3\{SC(NMe_2)_2\}_2}]$,[16] the three halides occupy the equatorial sites. It is not known why this supposedly sterically unfavourable arrangement of ligands is adopted in **7** and **8**. The In–X$_{eq}$ bond lengths in **7** [2.431(2) Å] and **8** [2.586(6) Å] are in the normal region for 2:1 adducts, and in the case of **8** are longer than in the 1:1 adduct, **6**. As would be expected, the In–X$_{ax}$ distances (**7** 2.582, **8** 2.740 Å averages) are considerably longer than the corresponding In–X$_{eq}$ distances. Not surprisingly, the In–C (carbene) distances in **7** (2.228 Å average) and **8** (2.230 Å average) are slightly longer than in **6** [2.199(5) Å]. Finally, the geometries within the planar heterocyclic rings in both compounds are close to that in **6**.

In the early stages of this study the reaction of 1 equivalent of compound **II** with InBr$_3$ in thf was carried out and a small amount of crystalline material obtained. X-Ray crystallography confirmed this to be the ionic product **9**. It was believed that this arose from adventitious water in the reaction mixture which probably originated from a trace of water in the sublimed InBr$_3$. Careful purification of starting materials avoided this problem in further reactions but an intentional synthetic route to **9** and its chloride analogue, **10**, was desirable considering the novelty of these compounds. This was achieved by adding half an equivalent of water to a thf solution of the indium halide before the addition of 1 equivalent of **II** (Scheme 2). This did indeed afford compounds **9** and **10** after recrystallisation from CH$_2$Cl$_2$–Et$_2$O, albeit in low to moderate yields.

It is difficult to know the exact mechanism for the formation of the ionic compounds but we believe it involves the indium halide being in equilibrium with its ionic isomer **11** in thf solutions (Scheme 3). This is not unfeasible if a comparison is drawn with AlCl$_3$ and its interaction with thf. This has afforded both the neutral etherate, [AlCl$_3$(thf)$_2$],[17] and its ionic isomer [AlCl$_2$(thf)$_4$][AlCl$_4$],[18] both of which have been crystallographically characterised. Therefore, after successive additions of half an equivalent of water and 1 equivalent of **II** it is likely that half the highly nucleophilic carbene will be readily protonated by the water forming an imidazolium cation. This would leave the

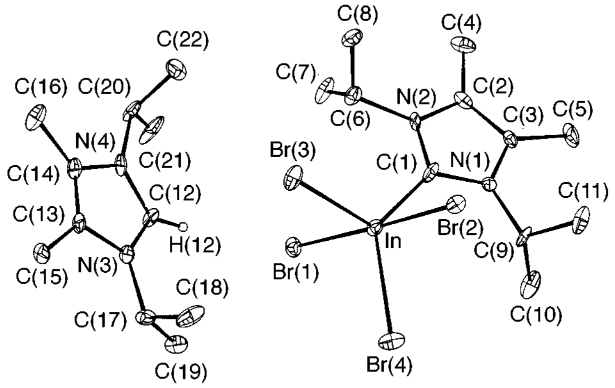


Fig. 4 Molecular structure of compound **9**. Details as in Fig. 1

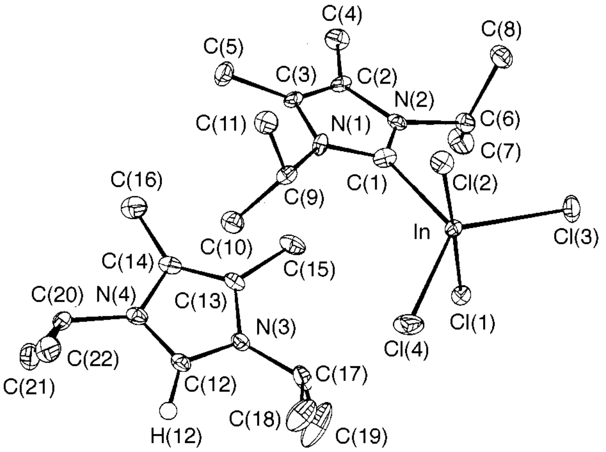


Fig. 5 Molecular structure of compound **10**. Details as in Fig. 1

generated hydroxide ion to combine with the $[InX_2(thf)_n]^+$ cation to form a dihalogenohydroxoindium species, **12**, whilst the remaining unprotonated carbene complexes the $[InX_4]^-$ anion. Unfortunately no species such as **12** could be identified in the reaction mixture but logic dictates that a product resembling it must be generated.

The solution-state ^{1}H and ^{13}C NMR spectroscopic data for compounds **9** and **10** are similar and, surprisingly, each displays only one set of heterocyclic resonances. It is likely, therefore, that there is a fluxional process underway which probably involves a rapid decomplexation/complexation of the carbene ligand with a concomitant proton exchange with the imidazolium cation. Indeed, the ^{1}H NMR spectra of **9** and **10** show broad resonances at low field (δ 10.05 and 9.54 respectively) in the expected region for imidazolium protons. Further evidence for the postulated exchange process comes from the ^{115}In NMR spectra which show narrow peaks at δ 179 (peak width at half peak height 651 Hz) and 423 (peak width 770 Hz) which compare very well with the literature values for unco-ordinated $[InBr_4]^-$, δ 176, and $[InCl_4]^-$, δ 430, in solution.[12] It seems very unlikely that if the $[InX_4(carbene)]^-$ anions existed without any fluxional process taking place the observed resonances would be so narrow due to the high quadruple moment of ^{115}In. Cooling dichloromethane solutions of **9** and **10** to −70 °C led only to a slight broadening of the resonances in their ^{1}H NMR spectra which suggests that the fluxional process is rapid, even at this temperature.

The molecular structures of the isostructural compounds **9** and **10** are depicted in Figs. 4 and 5 respectively (see also Tables 4 and 5). Each can be considered as a salt comprising a $[InX_4(carbene)]^-$ anion and a imidazolium cation. No interaction between the ions or any other intermolecular contacts were observed for either compound. During the refinement of the structure of **10** the proton, H(12), was located in Fourier-difference maps and refined isotropically; in **9** this proton was placed in a calculated position. The indium centres in the anions of both compounds have been calculated[15] as having a slightly distorted trigonal-bipyramidal environment with X(1) and X(2) in the apical positions and C(1), X(3) and X(4) in the equatorial sites. It is noteworthy that whilst the anions $[InX_4]^-$ have been previously structurally characterised in the free (four-co-

Table 4 Selected intramolecular distances (Å) and angles (°) for compound **9** with e.s.d.s in parentheses

N(1)–C(1)	1.367(12)	N(1)–C(3)	1.432(12)
N(1)–C(9)	1.481(11)	N(2)–C(1)	1.362(11)
N(2)–C(2)	1.404(12)	N(2)–C(6)	1.493(12)
N(3)–C(12)	1.325(11)	N(3)–C(13)	1.415(12)
N(3)–C(17)	1.479(12)	N(4)–C(12)	1.339(12)
N(4)–C(14)	1.430(12)	N(4)–C(20)	1.510(12)
In–C(1)	2.200(11)	In–Br(3)	2.5394(14)
In–Br(4)	2.5399(14)	In–Br(2)	2.7365(13)
In–Br(1)	2.7387(13)	C(2)–C(3)	1.368(13)
C(2)–C(4)	1.485(13)	C(3)–C(5)	1.462(13)
C(13)–C(14)	1.314(13)	C(13)–C(15)	1.495(13)
C(14)–C(16)	1.459(13)		
C(1)–N(1)–C(3)	110.5(8)	C(1)–N(1)–C(9)	123.2(9)
C(3)–N(1)–C(9)	126.3(8)	C(1)–N(2)–C(2)	111.0(8)
C(1)–N(2)–C(6)	123.1(8)	C(2)–N(2)–C(6)	125.8(8)
C(12)–N(3)–C(13)	108.5(8)	C(12)–N(3)–C(17)	126.3(8)
C(13)–N(3)–C(17)	125.3(8)	C(12)–N(4)–C(14)	108.6(8)
C(12)–N(4)–C(20)	126.6(8)	C(14)–N(4)–C(20)	124.8(8)
C(1)–In–Br(3)	120.0(3)	C(1)–In–Br(4)	120.3(3)
Br(3)–In–Br(4)	119.70(5)	C(1)–In–Br(2)	88.3(3)
Br(3)–In–Br(2)	89.41(4)	Br(4)–In–Br(2)	92.38(4)
C(1)–In–Br(1)	90.6(3)	Br(3)–In–Br(1)	89.73(4)
Br(4)–In–Br(1)	89.63(5)	Br(2)–In–Br(1)	177.99(4)
N(2)–C(1)–N(1)	105.5(9)	N(2)–C(1)–In	128.1(7)
N(1)–C(1)–In	126.4(7)	C(3)–C(2)–N(2)	107.3(9)
C(3)–C(2)–C(4)	127.0(10)	N(2)–C(2)–C(4)	125.7(9)
C(2)–C(3)–N(1)	105.6(8)	C(2)–C(3)–C(5)	128.3(10)
N(1)–C(3)–C(5)	126.0(9)	N(3)–C(12)–N(4)	108.4(9)
C(14)–C(13)–N(3)	108.4(9)	C(14)–C(13)–C(15)	130.6(10)
N(3)–C(13)–C(15)	121.0(9)	C(13)–C(14)–N(4)	106.2(9)
C(13)–C(14)–C(16)	131.9(11)	N(4)–C(14)–C(16)	121.8(9)

Table 5 Selected intramolecular distances (Å) and angles (°) for compound **10** with e.s.d.s in parentheses

In–C(1)	2.212(6)	In–Cl(4)	2.396(2)
In–Cl(3)	2.399(2)	In–Cl(1)	2.565(2)
In–Cl(2)	2.565(2)	N(1)–C(1)	1.360(6)
N(1)–C(3)	1.399(7)	N(1)–C(9)	1.475(7)
N(2)–C(1)	1.338(7)	N(2)–C(2)	1.415(7)
N(2)–C(6)	1.497(6)	N(3)–C(12)	1.339(7)
N(3)–C(13)	1.375(7)	N(3)–C(17)	1.486(8)
N(4)–C(12)	1.330(7)	N(4)–C(14)	1.389(7)
N(4)–C(20)	1.497(7)	C(2)–C(3)	1.347(8)
C(2)–C(4)	1.475(8)	C(3)–C(5)	1.506(8)
C(13)–C(14)	1.351(8)	C(13)–C(15)	1.496(8)
C(14)–C(16)	1.482(8)		
C(1)–In–Cl(4)	119.9(2)	C(1)–In–Cl(3)	120.0(2)
Cl(4)–In–Cl(3)	120.13(6)	C(1)–In–Cl(1)	88.5(2)
Cl(4)–In–Cl(1)	90.14(6)	Cl(3)–In–Cl(1)	91.11(5)
C(1)–In–Cl(2)	90.77(14)	Cl(4)–In–Cl(2)	88.88(6)
Cl(3)–In–Cl(2)	90.57(6)	Cl(1)–In–Cl(2)	178.31(5)
C(1)–N(1)–C(3)	109.9(5)	C(1)–N(1)–C(9)	123.0(5)
C(3)–N(1)–C(9)	127.0(4)	C(1)–N(2)–C(2)	111.2(5)
C(1)–N(2)–C(6)	121.6(5)	C(2)–N(2)–C(6)	127.1(5)
C(12)–N(3)–C(13)	109.4(5)	C(12)–N(3)–C(17)	124.6(5)
C(13)–N(3)–C(17)	126.0(5)	C(12)–N(4)–C(14)	109.9(5)
C(12)–N(4)–C(20)	124.2(5)	C(14)–N(4)–C(20)	125.9(5)
N(2)–C(1)–N(1)	105.7(5)	N(2)–C(1)–In	127.2(4)
N(1)–C(1)–In	127.0(4)	C(3)–C(2)–N(2)	105.5(5)
C(3)–C(2)–C(4)	128.8(5)	N(2)–C(2)–C(4)	125.7(5)
C(2)–C(3)–N(1)	107.6(5)	C(2)–C(3)–C(5)	127.6(5)
N(1)–C(3)–C(5)	124.8(5)	N(4)–C(12)–N(3)	107.2(6)
C(14)–C(13)–N(3)	107.4(5)	C(14)–C(13)–C(15)	130.2(6)
N(3)–C(13)–C(15)	122.4(5)	C(13)–C(14)–N(4)	106.1(5)
C(13)–C(14)–C(16)	131.4(6)	N(4)–C(14)–C(16)	122.5(5)

ordinate) and diligated (six-co-ordinate) state, *e.g.* $[InCl_4(py)_2]^-$ (py = pyridine),[19] the anions in **9** and **10** represent the first examples of five-co-ordinate $[InX_4L]^-$ species, L = monodenate neutral ligand. As in **7** and **8** there is a significant difference in the $In-X_{ax}$ (2.738, **9**; 2.565 Å averages, **10**) and $In-X_{eq}$ interactions (2.539, **9**; 2.397 Å averages, **10**) though all bond lengths are in the expected range. The In−C(1) bond lengths are similar and compare favourably to those in **7** and **8**, as does the geometry of the co-ordinated carbene heterocycles.

It can be seen in the imidazolium cations of compounds **9** and **10** that the methyl substituents on the isopropyl groups are turned away from the methyls in the 4 and 5 positions of the ring while the opposite is true for the anions, presumably for steric reasons. The geometries of the imidazolium rings are similar to those in other imidazolium salts, *e.g.* $[HCN(Ph)C_2H_2N(Ph)][ClO_4]$,[20] but significantly different to those of the co-ordinated imidazolylidene rings. Most notably, the N(4)−C(12)−N(3) angles [108.4(9), **9**; 107.2(6)°, **10**] are more open than the N(1)−C(1)−N(2) angles [105.5(9), **9**; 105.7(5)°, **10**]. The results of previous studies suggest that this is because of a greater π delocalisation in imidazolium ions relative to both free and metal-co-ordinated imidazolylidene rings.[9]

Conclusion

The first co-ordination complexes between a carbene and an indium centre have been reported. This study has highlighted the propensity of indium to achieve higher co-ordination numbers than those of aluminium and gallium for which only 1 : 1 carbene complexes are known. Surprisingly, the structures of the 2 : 1 complexes, **7** and **8**, have trigonal-bipyramidal geometries with two halides axial and one equatorial. The high nucleophilicity of the carbene ligand, **II**, is evidenced by its co-ordination of the InX_4 anion in **9** and **10**. We are currently investigating the use of the neutral indium halide complexes reported herein as precursors to stable carbene–InH_3 complexes.

Experimental

General remarks

All manipulations were carried out using standard Schlenk and glove-box techniques under an atmosphere of high-purity argon or dinitrogen. The solvents tetrahydrofuran and diethyl ether were distilled over Na/K alloy then freeze/thaw degassed prior to use. Dichloromethane was distilled from CaH_2 prior to use. Proton, ^{13}C and ^{115}In NMR spectra were recorded on either a Bruker WM-250 or AM 400 spectrometer in CD_2Cl_2 and referenced to the residual ^1H resonances of the solvent used (^1H), the ^{13}C resonance of the deuteriated solvent (^{13}C) or to external $[In(H_2O)_6]^{3+}$ (^{115}In) respectively. Mass spectra were recorded using a VG-autospec/Cs^+ ions/25 kV/3-nitrobenzyl alcohol matrix (FAB) instrument and conditions. Microanalyses were obtained from the University of Wales, Cardiff Microanalytical Service. The microanalysis for compound **7** was carried out on a sample from which the dichloromethane of crystallisation had been removed *in vacuo*. Reproducible microanalyses on **9** could not be obtained due to the persistent presence of a small amount of **6** which could not be removed by repeated attempts at fractional crystallisation. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. The carbene starting material $:\overline{CN(Pr^i)C_2Me_2N}Pr^i$ was prepared by a published procedure.[21] All other reagents were used as received with the exception of $InCl_3$ and $InBr_3$ which were sublimed prior to use.

Syntheses

$[InCl_3\{\overline{CN(Pr^i)C_2Me_2N}Pr^i\}]$ 5. A solution of $\overline{CN(Pr^i)C_2Me_2N}Pr^i$ (0.50 g, 2.77 mmol) in thf (10 cm^3) was added to a solution of $InCl_3$ (0.61 g, 2.77 mmol) in thf (40 cm^3) at 20 °C over 10 min. The resulting solution was stirred at room temperature for 3 h and volatiles were removed *in vacuo* to yield an oily white solid. This was washed with Et_2O (30 cm^3) and the residue recrystallised from a CH_2Cl_2–Et_2O mixture to yield compound **5** as colourless crystals, yield 0.83 g, 74%, m.p. 143–145 °C. ^1H NMR (250 MHz, CD_2Cl_2, 298 K): δ 1.77 [d, 12 H, $CH(CH_3)_2$, $^3J_{HH}$ 6.7], 2.46 (s, 6 H, Me) and 4.65 [spt, 2 H, $CH(CH_3)_2$, $^3J_{HH}$ 6.7 Hz]. ^{13}C-{^1H} NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 10.5 (Me), 24.5 [$CH(CH_3)_2$], 52.9 [$CH(CH_3)_2$] and 128.8 (C=C). FAB mass spectrum: *m/z* 181 ($M + H - InCl_3$, 100%). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1631m, 1555w, 1225m, 1113m, 936w and 730m (Found: C, 32.86; H, 5.16; N, 7.02. Calc. for $C_{11}H_{20}Cl_3InN_2$: C, 33.00; H, 5.04; N, 7.00%).

$[InBr_3\{\overline{CN(Pr^i)C_2Me_2N}Pr^i\}]$ 6. A solution of $\overline{CN(Pr^i)C_2Me_2N}Pr^i$ (0.48 g, 2.66 mmol) in thf (10 cm^3) was added to a solution of $InBr_3$ (0.91 g, 2.66 mmol) in thf (30 cm^3) at 20 °C over 10 min. The resulting solution was stirred at room temperature for 3 h and volatiles were removed *in vacuo* to yield an oily white solid. This was washed with Et_2O (30 cm^3) and the residue recrystallised from a CH_2Cl_2–Et_2O mixture to yield compound **6** as colourless crystals, yield 0.61 g, 43%, m.p. 141–143 °C. ^1H NMR (250 MHz, CD_2Cl_2, 298 K): δ 1.54 [d, 12 H, $CH(CH_3)_2$, $^3J_{HH}$ 6.5], 2.32 (s, 6 H, Me) and 5.33 [spt, 2 H, $CH(CH_3)_2$, $^3J_{HH}$ 6.5 Hz]. ^{13}C-{^1H} NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 10.6 (Me), 22.1 [$CH(CH_3)_2$], 54.9 [$CH(CH_3)_2$] and 127.3 (C=C). FAB mass spectrum: *m/z* 535 (M^+, 2), 355 ($InBr_3^+$, 3) and 181 (carbene + H^+, 100%). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1622m, 1555w, 1220m, 1111m, 906w and 723m (Found: C, 24.88; H, 3.76; N, 5.31. Calc. for $C_{11}H_{20}Br_3InN_2$: C, 24.82; H, 3.79; N, 5.27%).

$[InCl_3\{\overline{CN(Pr^i)C_2Me_2N}Pr^i\}_2]\cdot CH_2Cl_2$ 7. A solution of $\overline{CN(Pr^i)C_2Me_2N}Pr^i$ (0.50 g, 2.77 mmol) in thf (10 cm^3) was added to a solution of $InCl_3$ (0.31 g, 1.40 mmol) in thf (40 cm^3) at 20 °C over 10 min. The resulting solution was stirred at room temperature for 3 h and volatiles were removed *in vacuo* to yield an oily white solid. This was washed with thf (30 cm^3) and the residue recrystallised from a CH_2Cl_2–Et_2O mixture to yield compound **7** as colourless crystals, yield 0.31 g, 38%, m.p. 163–165 °C. ^1H NMR (250 MHz, CD_2Cl_2, 298 K): δ 1.35 [d, 24 H, $CH(CH_3)_2$, $^3J_{HH}$ 6.4], 2.18 (s, 12 H, Me) and 4.35 [spt, 4 H, $CH(CH_3)_2$, $^3J_{HH}$ 6.4 Hz]. ^{13}C-{^1H} NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 8.7 (Me), 22.0 [$CH(CH_3)_2$], 54.3 [$CH(CH_3)_2$] and 127.0 (C=C). FAB mass spectrum: *m/z* 400 (M^+ − carbene, 6) and 181 (carbene + H^+, 100). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1770w, 1629m, 1550m, 1242m, 1115m and 726s (Found: C, 46.43; H, 7.48; N, 9.79. Calc. for $C_{22}H_{40}Cl_3InN_4$: C, 45.51; H, 6.95; N, 9.66%).

$[InBr_3\{\overline{CN(Pr^i)C_2Me_2N}Pr^i\}_2]\cdot CH_2Cl_2$ 8. A solution of $\overline{CN(Pr^i)C_2Me_2N}Pr^i$ (0.50 g, 2.77 mmol) in thf (10 cm^3) was added to a solution of $InBr_3$ (0.20 g, 0.56 mmol) in thf (40 cm^3) at 20 °C over 10 min. The resulting solution was stirred at room temperature for 3 h and volatiles were removed *in vacuo* to yield an oily white solid. This was washed with thf (30 cm^3) and the residue recrystallised from a CH_2Cl_2–Et_2O mixture to yield compound **8** as colourless crystals, yield 0.31 g, 69%, m.p. 177–179 °C. ^1H NMR (250 MHz, CD_2Cl_2, 298 K): δ 1.69 [d, 24 H, $CH(CH_3)_2$, $^3J_{HH}$ 6.8], 2.28 (s, 12 H, Me) and 4.53 [spt, 4 H, $CH(CH_3)_2$, $^3J_{HH}$ 6.8 Hz]. ^{13}C-{^1H} NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 8.9 (Me), 23.0 [$CH(CH_3)_2$], 51.2 [$CH(CH_3)_2$] and 126.2 (C=C). FAB mass spectrum: *m/z* 716 ($M + H^+$, 3), 455 [(carbene)$InBr_2^+$, 11] and 181 (carbene + H^+, 100%). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1765w, 1630m, 1550w, 1219m, 1113s, 905m and 729s (Found: C, 35.17; H, 5.41; N, 7.20. Calc. for $C_{23}H_{42}Br_3Cl_2InN_4$: C, 34.68; H, 5.32; N, 7.04%).

Table 6 Crystal data for $[InBr_3\{CN(Pr^i)C_2Me_2NPr^i\}]$ **6**, $[InX_3\{CN(Pr^i)C_2Me_2NPr^i\}_2]\cdot CH_2Cl_2$, X = Cl **7** or Br **8** and $[HCN(Pr^i)C_2Me_2NPr^i]$-$[InX_4\{CN(Pr^i)C_2Me_2NPr^i\}]$ X = Br **9** or Cl **10**

	6	**7**	**8**	**9**	**10**
Chemical formula	$C_{11}H_{20}Br_3InN_2$	$C_{23}H_{42}Cl_5InN_4$	$C_{23}H_{42}Br_3Cl_2InN_4$	$C_{22}H_{41}Br_4InN_4$	$C_{22}H_{41}Cl_4InN_4$
M	534.84	666.68	800.06	796.05	618.21
Space group	*Pbca*	$P2_1/n$	$P2_1/n$	$Pca2_1$	$Pca2_1$
a/Å	16.5220(5)	14.895(4)	15.180(9)	17.034(3)	16.860(2)
b/Å	12.0530(13)	9.990(4)	10.068(3)	10.668(2)	10.412(2)
c/Å	17.704(3)	20.382(4)	20.696(12)	17.004(3)	16.815(2)
β/°	90.0	94.15(4)	93.23(5)	90.0	90.0
U/Å^3	3525.6(7)	3025(2)	3158(3)	3095(1)	2951.8(8)
Z	8	4	4	4	4
D_c/g cm^{-3}	2.015	1.464	1.683	1.708	1.391
μ(Mo-Kα)/cm^{-1}	81.25	12.42	47.32	59.43	11.79
DIFABS absorption correction, T_{max}, T_{min}	1.11, 0.82	1.23, 0.79	1.15, 0.79	1.23, 0.80	1.08, 0.92
F(000)	2032	1368	1584	1560	1272
Reflections collected	12 664	11 374	9875	10 988	12 137
No. unique relections	2839	4487	4324	4260	4347
Crystal size/mm	0.20 × 0.15 × 0.15	0.20 × 0.20 × 0.25	0.12 × 0.10 × 0.10	0.15 × 0.30 × 0.20	0.20 × 0.25 × 0.25
θ Range/°	2.30–25.01	1.76–24.95	1.97–25.08	1.91–25.05	1.96–25.03
R^a (all data)	0.0429	0.1027	0.0901	0.0519	0.0414
$[I > 2\sigma(I)]$	0.0284	0.0618	0.0432	0.0351	0.0308
wR^b (all data)	0.0651	0.1601	0.0879	0.1260	0.1023
$[I > 2\sigma(I)]$	0.0640	0.1516	0.0820	0.0755	0.0691

[a] $R = \Sigma(\Delta F)/\Sigma(F_o)$. [b] $wR = [\Sigma w(\Delta F^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2]$, where $P = [\max(F_o^2) + 2\ (F_c^2)]/3$ and $a = 0.0266$ for compound **6**, 0.076 for **7**, 0.022 for **8**, 0.013 for **9** and 0.016 for **10**.

$[HCN(Pr^i)C_2Me_2NPr^i][InBr_4\{CN(Pr^i)C_2Me_2NPr^i\}]$ 9. A solution of $CN(Pr^i)C_2Me_2NPr^i$ (0.50 g, 2.77 mmol) in thf (10 cm^3) was added over 10 min to a solution of $InBr_3$ (0.98 g, 2.77 mmol) and water (0.025 g, 1.38 mmol) in thf (40 cm^3) at 20 °C. The resulting solution was stirred at room temperature for 3 h and volatiles were removed *in vacuo* to yield an oily white solid. This was washed with Et_2O (30 cm^3) and the residue recrystallised from a CH_2Cl_2–Et_2O mixture to yield compound **9** as colourless crystals, yield 0.36 g, 16%, m.p. 145–148 °C. ^1H NMR (250 MHz, CD_2Cl_2, 298 K): δ 1.65 [d, 24 H, $CH(CH_3)_2$, $^3J_{HH}$ 6.8], 2.26 (s, 12 H, Me), 4.56 [spt, 4 H, $CH(CH_3)_2$, $^3J_{HH}$ 6.8 Hz] and 10.05 [br s, 1 H, NC(H)N]. ^{13}C-{^1H} NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 8.8 (Me), 22.9 [$CH(CH_3)_2$], 51.2 [$CH(CH_3)_2$], 126.5 (C=C) and 131.8 [NC(H)N]. ^{115}In NMR (54.801 MHz, CD_2Cl_2, 298 K): δ 179 (width 651 Hz, half peak height). FAB mass spectrum: *m*/*z* 455 [(carbene)$InBr_2^+$, 3] and 181 (carbene + H^+, 100%). IR (Nujol): ṽ/cm^{-1} 1642s, 1573s, 1228m 1110m and 760m (Found: C, 31.84; H, 4.96; N, 6.66. Calc. for $C_{22}H_{41}Br_4InN_4$: C, 33.34; H, 5.22; N, 7.07%).

$[HCN(Pr^i)C_2Me_2NPr^i][InCl_4\{CN(Pr^i)C_2Me_2NPr^i\}]$ 10. A solution of $CN(Pr^i)C_2Me_2NPr^i$ (0.50 g, 2.77 mmol) in thf (10 cm^3) was added over 10 min to a solution of $InCl_3$ (0.61 g, 2.77 mmol) and water (0.025 g, 1.38 mmol) in thf (40 cm^3) at 20 °C. The resulting solution was stirred at room temperature for 3 h and volatiles were removed *in vacuo* to yield an oily white solid. This was washed with Et_2O (30 cm^3) and the residue recrystallised from a CH_2Cl_2–Et_2O mixture to yield compound **10** as colourless crystals, yield 0.38 g, 44%, m.p. 175–178 °C. ^1H NMR (250 MHz, CD_2Cl_2, 298 K): δ 1.65 [d, 24 H, $CH(CH_3)_2$, $^3J_{HH}$ 6.7], 2.28 (s, 12 H, Me), 4.54 [spt, 4 H, $CH(CH_3)_2$, $^3J_{HH}$ 6.7 Hz] and 9.54 [br s, 1 H, NC(H)N]. ^{13}C-{^1H} NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 8.8 (Me), 22.8 [$CH(CH_3)_2$], 51.3 [$CH(CH_3)_2$], 126.5 (C=C) and 131.8 [NC(H)N]. ^{115}In NMR (54.801 MHz, CD_2Cl_2, 298 K): δ 423 (width 770 Hz, half peak height). FAB mass spectrum: *m*/*z* 181 (carbene + H^+, 100%). IR (Nujol): ṽ/cm^{-1} 1628s, 1555s, 1231m and 1113m (Found: C, 42.19; H, 6.47; N, 8.66. Calc. for $C_{22}H_{41}Cl_4InN_4$: C, 42.85; H, 6.71; N, 9.09%).

Crystallography

Crystals of compounds **6**–**10** were grown by slow diffusion of Et_2O into a dichloromethane solution of the relevant compound and were mounted in silicone oil. Intensity data were measured on a FAST[22] area-detector diffractometer using Mo-Kα radiation (λ 0.71069 Å) at 150(2) K. The structure of **8** was solved by the heavy-atom method while direct methods were used to solve the structures of **6**, **7**, **9** and **10** (SHELXS 86[23]). Refinement of all structures was by full-matrix least squares on F^2 using all unique data (SHELXL 93[24]). Neutral-atom complex scattering factors were employed.[25] Empirical absorption corrections were carried out by the DIFABS method.[26] The Flack parameters in the refinement of **9** [−0.01(1)] and **10** [0.00(3)] were very close to zero, indicating that the absolute configurations have been determined correctly for both these compounds. Crystal data, details of data collections and refinement are given in Table 6. Anisotropic thermal parameters were refined for all non-hydrogen atoms. The hydrogen atoms in all structures were included in calculated positions (riding model) with the exception of H(12) in **10** which was located from difference maps and refined isotropically.

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