

Synthesis and characterisation of the first carbene and diazabutadiene–indium(II) complexes†

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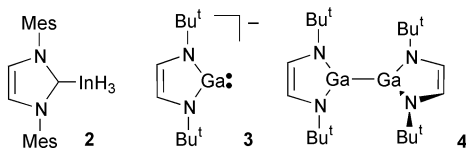
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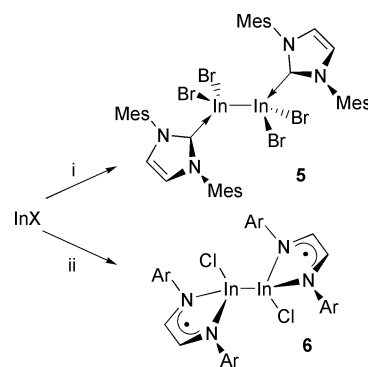
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The reactions of IMes [$:\text{CN}(\text{Mes})\text{C}_2\text{H}_2\text{N}(\text{Mes})$, Mes = mesityl] and DAB [$(\text{ArN}=\text{CH})_2$, Ar = $\text{C}_6\text{H}_3\text{Pr}^{1-2,6}$] with indium(I) halides have afforded the first carbene and diazabutadiene indium(II) complexes, $[\text{In}_2\text{Br}_4(\text{IMes})_2]$ and $[\text{In}_2\text{Cl}_2(\text{DAB})_2]$, both of which have been crystallographically characterised.

There is currently a great deal of interest in the chemistry of metastable aluminium(I) and gallium(I) halide complexes, $[\{\text{MX}(\text{L})\}_n]$ **1**, M = Al or Ga, X = halide, L = Lewis base, which are proving extremely useful as precursors to a wide variety of novel alkyl-, silyl- and amido-low oxidation state metal complexes and cluster compounds.¹ To the best of our knowledge there are no structurally characterised indium analogues of **1**, though related indium(II) complexes have been known for some time² and several have been structurally authenticated, e.g. $[\text{In}_2\text{I}_4(\text{PPr}_3)_2]$.³ We wished to prepare and characterise indium(I) halide complexes and saw N-heterocyclic carbenes (NHCs) as potentially excellent ligands for this task given that we have previously proven their stabilising properties in the formation of indium trihydride and group 13 trihalide complexes, e.g. **2**.⁴ In addition, diazabutadiene ligands have previously been utilised in the stabilisation of gallium(I) and (II) compounds, e.g. **3**⁵ (an anionic NHC analogue) and **4**,⁶ and were therefore thought of sufficient worth to be included in this study. Herein, we report the unexpected outcome of reactions of indium(I) halides with sterically encumbered examples of an NHC and a diazabutadiene ligand.



The reaction of 0.5 or 1 equivalent of IMes [$:\text{CN}(\text{Mes})\text{C}_2\text{H}_2\text{N}(\text{Mes})$ (Mes = mesityl)] with InBr in toluene at 25 °C led to the deposition of indium metal and formation of the thermally robust (decomp. 185–187 °C) carbene–indium(II) halide complex, **5**, in moderate yield (54%). Similarly, the 3:2 reaction of DAB [$(\text{ArN}=\text{CH})_2$, Ar = $\text{C}_6\text{H}_3\text{Pr}^{1-2,6}$] with InCl afforded the paramagnetic $\text{In}(\text{II})$ complex, **6** (decomp. 84–87 °C), in low yield (12%) after recrystallisation from DME (Scheme 1).‡ Presumably both compounds are formed by similar mechanisms involving $[\text{InBr}(\text{IMes})]$ and $[\text{InCl}(\text{DAB})]$ as intermediates, the former of which undergoes a disproportionation reaction to give **5** and In metal, whilst in the latter the DAB ligand is singly reduced by the metal centre prior to dimer formation. Interestingly, significant indium metal deposition was seen in the reaction that gave **6** but this does not arise from the disproportionation of this compound as it is indefinitely stable in solution at room temperature. We have not yet been able to ascertain what other products are formed in this reaction. It is worth noting here that **6** is notionally related to the gallium(II) complex, **4**, though that compound is halide free,



Scheme 1 Reagents and conditions: i, X = Br, IMes, toluene, $-\text{In}_{(s)}$; ii, X = Cl, DAB, DME.

diamagnetic and possesses doubly reduced diazabutadiene ligands.

The NMR spectroscopic data§ for both complexes were of limited value in assigning their structures and, indeed, the paramagnetic nature of **6** meant that only signals corresponding to a molecule of DAB that co-crystallises with **6** could be observed. The Raman spectra of **5** and **6**, however, display bands centred at 137 and 179 cm^{-1} respectively, which are consistent with previously reported $\text{In}-\text{In}$ stretching modes in compounds of the type $[\text{In}_2\text{X}_2(\text{L})_2]$, X = Br or Cl.² The X-band EPR spectrum of **6** was obtained and satisfactorily simulated (Fig. 1) using an isotropic g value of $g_{\text{iso}} = 2.0012$, and hyperfine splittings to two equivalent proton ($a_{\text{iso}} = 0.5$ mT) and nitrogen ($a_{\text{iso}} = 0.5$ mT) centres. These g and a_{iso} values are comparable to those reported for similar diazabutadiene anion radicals.⁷ In addition, a splitting arising from an electron interaction with the In nucleus was also observed [$a_{\text{iso}} = 2.62$ mT for ^{115}In (95.7% abundant) and $a_{\text{iso}} = 2.614$ mT for ^{113}In (4.3% abundant)]. The magnitude of these splittings confirms that the unpaired electron is largely delocalised over the NCCN fragment with negligible spin density (0.36%) on the indium centre and therefore it can be concluded that the oxidation state of the indium centres is +2.

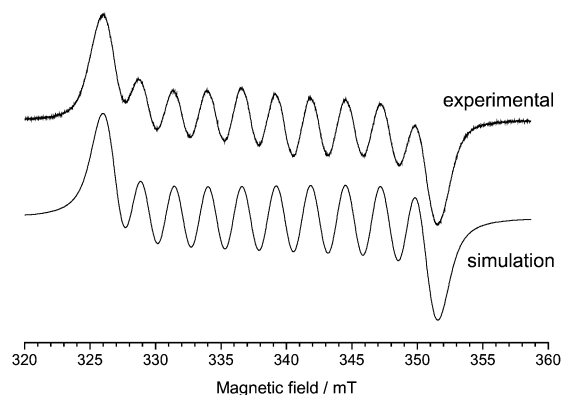


Fig. 1 X-Band EPR spectrum and computer simulation of **6** in DME at 298 K.

† Electronic supplementary information (ESI) available: synthetic details. See <http://www.rsc.org/suppdata/cc/b2/b202532a/>

The molecular structures of **5** and **6** are shown in Figs. 2 and 3, respectively. Compound **5** is dimeric and both indium centres have distorted tetrahedral geometries with the two (IMes)InBr₂ fragments staggered with respect to each other. The In–In bond length, 2.7436(7) Å, is close to those in related compounds, *e.g.* 2.745 Å in [In₂L₄(PPri₃)₂],³ and the In–Br distances are in the normal range. Compound **6** co-crystallises with a molecule of DAB that has no interaction with it. Its structure is closely

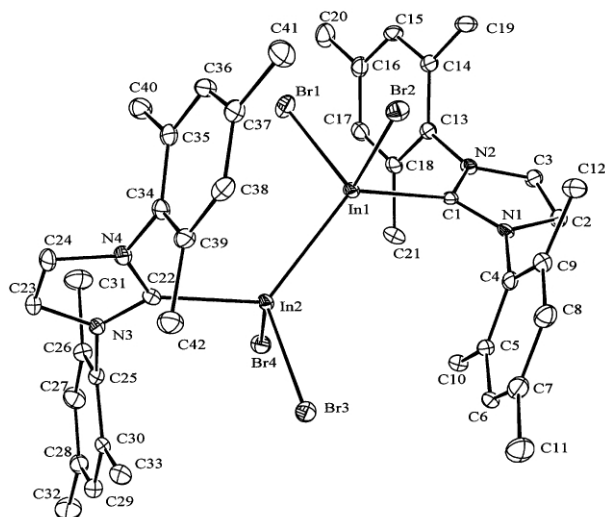


Fig. 2 Molecular structure of **5**. Selected bond lengths (Å) and angles (°): In(1)–C(1) 2.267(5), In(1)–Br(1) 2.5535(9), In(1)–Br(2) 2.5597(11), In(1)–In(2) 2.7436(7), In(2)–C(22) 2.252(6), In(2)–Br(3) 2.5567(8), In(2)–Br(4) 2.5760(12); C(1)–In(1)–Br(1) 104.33(14), C(1)–In(1)–Br(2) 95.90(14), Br(1)–In(1)–Br(2) 101.99(3), C(1)–In(1)–In(2) 122.67, Br(1)–In(1)–In(2) 105.66(2), Br(2)–In(1)–In(2) 123.39(2), C(22)–In(2)–Br(3) 100.79(14), C(22)–In(2)–Br(4) 102.31(15), Br(3)–In(2)–Br(4) 104.32(3), C(22)–In(2)–In(1) 124.62(14), Br(3)–In(2)–In(1) 118.95(2), Br(4)–In(2)–In(1) 103.14(2).

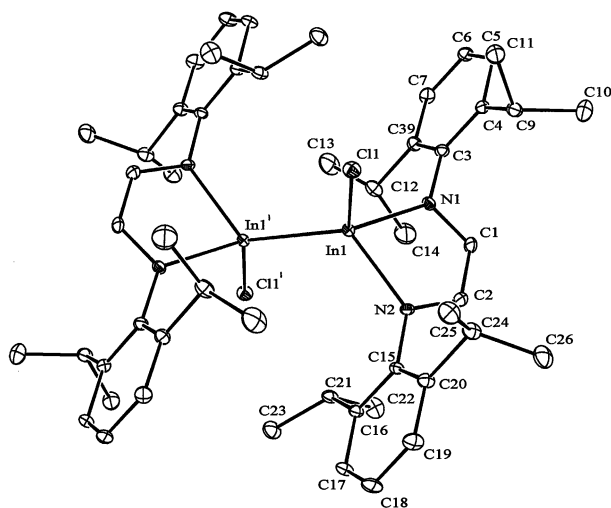


Fig. 3 Molecular structure of **6**. Selected bond lengths (Å) and angles (°): In(1)–N(1) 2.167(2), In(1)–N(2) 2.169(3), In(1)–Cl(1) 2.4094(9), In(1)–In(1') 2.7280(9), N(1)–C(1) 1.317(4), N(1)–C(3) 1.442(4), N(2)–C(2) 1.329(4), N(2)–C(15) 1.447(3); N(1)–In(1)–N(2) 78.71(9), N(1)–In(1)–Cl(1) 104.18(7), N(2)–In(1)–Cl(1) 103.98(7), N(1)–In(1)–In(1') 121.30(7), N(2)–In(1)–In(1') 122.18(7), Cl(1)–In(1)–In(1') 118.79(3), C(1)–N(1)–In(1) 110.50(19), C(2)–N(2)–In(1) 109.98(19), N(1)–C(1)–C(2) 120.4(3), N(2)–C(2)–C(1) 120.4(3).

related to that of **5** in that it possesses distorted tetrahedral indium centres with a similar In–In distance, 2.7280(9) Å. Although there are no structurally characterised diazabutadiene–indium complexes available for comparison the geometry of the In containing heterocycle is similar to that calculated for a tetrahedral indium complex incorporating a singly reduced diazabutadiene ligand, [In{N(H)C(H)C(H)N(H)}₂].⁸ In addition, the C–N and C–C bond lengths within the diazabutadiene ligand of **6** are close to those in related paramagnetic aluminium and gallium complexes and suggest a degree of delocalisation over this ligand.⁸

In conclusion, we have prepared and structurally characterised the first carbene and diazabutadiene indium(II) complexes. Given the thermal stability of **5** we are currently investigating the use of highly nucleophilic NHCs in the stabilisation of low oxidation state aluminium and gallium complexes (*cf.* **1**); and the use of **5** as a precursor to low oxidation state indium hydride complexes. In addition, attempts are being made to reduce **6** to an anionic indium(I) carbene analogue (*cf.* **3**) which are currently unknown. Our efforts in these areas will be reported in forthcoming publications.

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Notes and references

‡ *Note added at Proof:* a β -diketiminato indium(II) chloride complex, closely related to **6**, has recently been reported.⁹

§ *Spectroscopic data for 5:* ¹H NMR (400 MHz, C₆D₆) δ 2.14 (br. s, 36H, Me), 5.74 (s, 4H, NCH), 6.78 (s, 8H, ArH); IR ν /cm⁻¹ 1608m, 1536w, 1485m, 1465s, 1378s, 1260s; MS APCI *m/z* (%): 579 [InBr₂(IMes)⁺, 5], 305 [IMes⁺, 100]; **6:** IR ν /cm⁻¹ 1618m, 1449m, 1372m, 1326m, 1250s, 1101m, 819m; APCI *m/z* (%): 377 [DABH⁺, 100].

¶ *Crystal data for 5:* 2.5C₇H₈: C_{59.5}H_{67.5}Br₄In₂N₄, *M* = 1387.95, monoclinic, space group *P*2₁/*n*, *a* = 14.886(3), *b* = 15.474(3), *c* = 26.145(5) Å, β = 102.25(3)°, *V* = 5885(2) Å³, *Z* = 4, *D*_c = 1.566 g cm⁻³, *F*(000) = 2762, μ (Mo–K α) = 3.54 mm⁻¹, 150(2) K, 11582 unique reflections (*R*_{int} = 0.0819), *R* (on *F*) = 0.0528, *wR* (on *F*²) = 0.1208 (*I* > 2 σ). For **6**: DAB: C₇₈H₁₀₈Cl₂In₂N₆, *M* = 1430.24, triclinic, space group *P*1̄, *a* = 12.301(3), *b* = 13.135(3), *c* = 13.761(3) Å, α = 69.33(3), β = 64.94(3), γ = 77.37(3)°, *V* = 1878.2(7) Å³, *Z* = 1, *D*_c = 1.265 g cm⁻³, *F*(000) = 750, μ (Mo–K α) = 0.73 mm⁻¹, 150(2) K, 8542 unique reflections (*R*_{int} = 0.0573), *R* (on *F*) = 0.0408, *wR* (on *F*²) = 0.0888 (*I* > 2 σ). CCDC reference numbers 182443 and 182444. See <http://www.rsc.org/suppdata/cc/b2/b202532a/> for crystallographic data in CIF or other electronic format.

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