

Electronic delocalization in two and three dimensions: differential aggregation in indium ‘metalloid’ clusters

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Abstract: Reduction of indium boryl precursors to give two- and three-dimensional M-M bonded networks is influenced by the choice of supporting ligand. While the unprecedented nanoscale cluster $[\text{In}_{68}(\text{boryl})_{12}]^-$ (with an $\text{In}_{12}@\text{In}_{44}@\text{In}_{12}(\text{boryl})_{12}$ concentric structure), can be isolated from the potassium reduction of a bis(boryl)indium(III) chloride precursor, analogous reduction of the corresponding (benzamidinate) $\text{In}^{\text{III}}\text{Br}(\text{boryl})$ system gives a near-planar (and weakly aromatic) tetranuclear $[\text{In}_4(\text{boryl})_4]^{2-}$ system.

Metal-metal bonded compounds of aluminium and gallium have been the subject of a number of landmark studies in the last 20 years,^[1] ranging from dimetallic systems such as $\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{AlAl}\{\text{CH}(\text{SiMe}_3)_2\}_2$ ^[2] and the ‘digallyne’ $\text{Na}_2[\text{Ar}^{\text{Trip}}_2\text{Ga}_2]$ ($\text{Ar}^{\text{Trip}} = 2,6-(2,4,6-\text{Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$),^[3] through planar trinuclear systems of the type $\text{Na}_2[\text{Ar}^{\text{Mes}}_3\text{M}_3]$ ($\text{M} = \text{Al}, \text{Ga}$; $\text{Ar}^{\text{Mes}} = 2,6-(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$),^[4] all the way to large ‘metalloid’ clusters such as $[\text{Al}_{77}\{\text{N}(\text{SiMe}_3)_2\}_{20}]^{2-}$ and $[\text{Ga}_{84}\{\text{N}(\text{SiMe}_3)_2\}_{20}]^{n-}$ ($n = 3, 4$).^[5,6] Such systems have proved pivotal to the evolution of theories of chemical bonding for the heavier *p*-block elements, in particular for the formulation of delocalized bonding models in one, two and three dimensions. Thus, intense debate concerning the bond order in $\text{Na}_2[\text{Ar}^{\text{Trip}}_2\text{Ga}_2]$ and related *trans*-bent alkyne analogues ultimately led to a fuller understanding of their electronic structure and the unusual (‘transition metal like’) reactivity displayed by some such systems.^[7] In addition, planar 2π electron metallacycles have pushed the boundaries of what is understood by ‘aromatic’ character,^[8,9] and larger concentric polyhedral clusters have been identified as nanoscale models for bulk metallic phases.^[10]

Related compounds featuring the heavier metals of group 13 (i.e. indium and thallium) are much less well known, with In-In bonded systems being dominated by dinuclear In^{II} systems of the type R_2InInR_2 and tetrahedral In^{I} systems of the type

R_4In_4 .^[11] Planar systems offering the potential for Hückel-type aromaticity, and concentric polyhedral clusters are unknown: the largest polynuclear indium system yet reported to our knowledge is a compound of composition In_{19}X_6 ,^[11q] which features a cubic-close-packed In_{13} core closely related to the tetragonal structure of the metal itself.

Recently we have been exploiting the extremely sterically demanding boryl ligand $[\text{B}(\text{NDippCH})_2]$ as an ancillary donor for the stabilization of novel main group metal systems,^[11p,11q,12,13] and in the current contribution report on its use for the encapsulation of highly reduced indium clusters with widely differing degrees of nuclearity.

Reduction of the In^{III} bisboryl complex $\text{In}(\text{B}(\text{NDippCH})_2)_2\text{Cl}$ with $\text{Cp}^*_2\text{Sm}(\text{thf})$ has previously been shown to offer clean access to the In^{II} radical $[\text{In}(\text{B}(\text{NDippCH})_2)_2]^{1p}$. The corresponding chemistry using a more aggressive reductant such as potassium metal, also leads to the formation of the In^{II} complex (albeit in lower yields), but also to the formation of more highly reduced species, including indium metal itself, and a metalloid cluster of the composition $[\text{In}_{68}(\text{boryl})_{12}]^-$, which can be isolated in very low yield and characterized by X-ray crystallography (Figure 1).^[14] Aspects of the geometric structure of this cluster are reminiscent of the landmark $[\text{Al}_{77}\{\text{N}(\text{SiMe}_3)_2\}_{20}]^{2-}$ system reported by Schnöckel in 1997.^[5a] Thus, the $\text{In}_{12}@\text{In}_{44}@\text{In}_{12}(\text{boryl})_{12}$ formulation revealed crystallographically features an icosahedral In_{12} unit and surrounding In_{44} shell similar to those found in the $\text{Al}@\text{Al}_{12}@\text{Al}_{44}@\text{Al}_{20}(\text{amido})_{20}$ system. Presumably the lower nuclearity of the outermost shell (containing 12 indium atoms, as opposed to 20 aluminiums) reflects the greater steric bulk of the attached $\text{B}(\text{NDippCH})_2$ ligands, compared to $\text{N}(\text{SiMe}_3)_2$. The other substantive difference is the absence of a central metal atom in $[\text{In}_{68}(\text{boryl})_{12}]^-$, with no significant *q*-peak being located in the X-ray structure

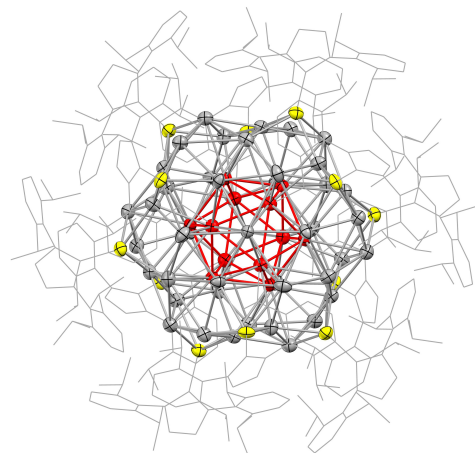


Figure 1. One of the anionic components of $[\text{Li}_9\text{In}^{\text{II}}_6(\text{B}(\text{NDippCH})_2)_6(\text{Cl})(\text{OH})_{13}]^+$ $[\text{In}_{68}(\text{B}(\text{NDippCH})_2)_{12}]^-$ in the solid state as determined by X-ray crystallography (see SI for full details). Other anion/cation pair and hydrogen atoms omitted and boryl ligands shown in wireframe format for clarity. The colour scheme reflects the $\text{In}_{12}@\text{In}_{44}@\text{In}_{12}(\text{boryl})_{12}$ structure, with the central In_{12} icosahedron shown in red, the surrounding shell of 44 non-ligated In atoms shown in grey

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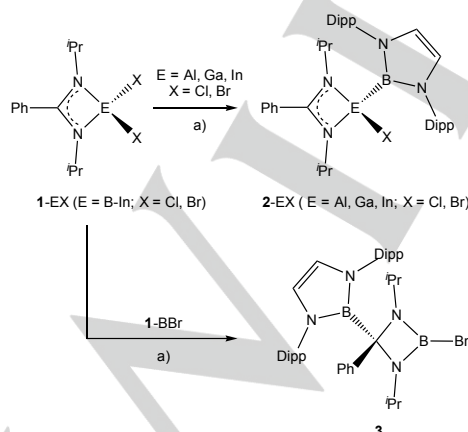
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and the outer 12 boryl-bound indium centres shown in yellow. The cluster is shown orientated along its crystallographic six-fold rotation axis. refinement close to the centre of the In_{12} icosahedron (R factor = 0.07). While a number of metalloid clusters of this type – featuring concentric shells of metal atoms – have been reported for aluminium and gallium,^[5,10] no significant precedent exists for indium, with the closest analogue being an $\text{In}_{19}(\text{boryl})_6$ system which features a cubic-close-packed In_{13} core.^[11q] The icosahedral In_{12} core of $[\text{In}_{68}(\text{boryl})_{12}]^+$ features a relatively narrow range of In-In bond lengths [3.100(1)–3.145(2) Å], and can be put in context by the corresponding distances measured for the M_{12} cores of related aluminium and gallium systems (e.g. 2.650–2.762 Å for $[\text{Al}_{22}\text{Br}_{20}(\text{thf})_{12}]$ and 2.593–2.614 Å for $[\text{Ga}_{22}\text{Br}_2\{\text{N}(\text{SiMe}_3)_2\}_{10}\text{Br}_{10}]^{2-}$) with due consideration of the metallic radii of the respective elements (Al: 1.43 Å; Ga: 1.40 Å; In: 1.58 Å).^[15]

In order to probe the potential role of the ancillary ligands in mediating the reduction process(es), we targeted the use of chelating ancillary ligands, hypothesizing that such systems might reduce the extent and/or rate of metal-metal aggregation processes. Strong N,N' -chelating mono-anionic donors such as amidinato, guanidinato and β -diketiminato ligands have previously been applied to the stabilization of low-valent main group compounds.^[16] We therefore targeted the synthesis and reduction chemistry of group 13 systems of the type (amidinato)E(boryl)X ($X = \text{Cl}, \text{Br}$).^[17,18] In the event, such systems prove to be readily accessible for $E = \text{Al}, \text{Ga}$ and In , via metathesis chemistry utilizing the corresponding amidinato element dihalide, $\{\text{PhC}(\text{N}^i\text{Pr})_2\text{EX}_2$ (1-EX) and one equivalent of Yamashita's boryllithium reagent $(\text{thf})_2\text{Li}\{\text{B}(\text{NDippCH})_2\}$ (Scheme 1).^[12] Only in the case of the boron-containing precursor 1-BBr is any divergence observed from this pattern of reactivity, with an alternative product being formed resulting from C- rather than B-centred attack by the boryl nucleophile (Scheme 1 and Figure 2).^[19] For aluminium, gallium and indium, however, the respective mono-boryl products 2-AlCl, 2-GaCl, 2-GaBr and 2-InBr can be accessed via E-B bond formation, and each has been characterized by standard spectroscopic, analytical and (with the exception of 2-GaBr) crystallographic methods. Structurally, each of 2-AlCl, 2-GaCl and 2-InBr (see Figure 2 and



Scheme 1. Reactions of benzamidinato-stabilized Group 13 halides with the boryllithium reagent $(\text{thf})_2\text{Li}\{\text{B}(\text{NDippCH})_2\}$: syntheses of boryl-aluminium, -gallium and -indium complexes of type 2, and backbone-borylated diamido-bromoborane 3. Key reagents and conditions: a) $(\text{thf})_2\text{Li}\{\text{B}(\text{NDippCH})_2\}$ (1 equiv.), benzene, 2 h, 20–55%.

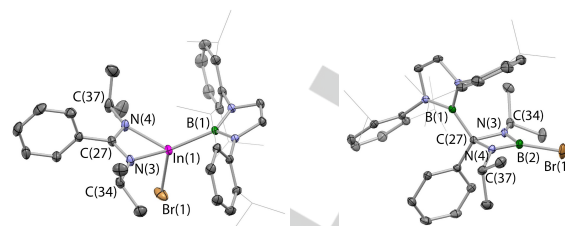
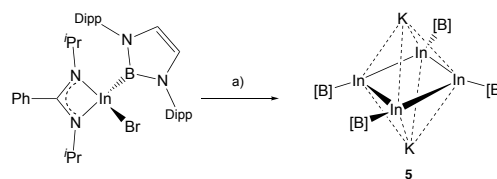


Figure 2. Molecular structures of 2-InBr (left) and 3 (right) in the solid state as determined by X-ray crystallography. Hydrogen atoms omitted and Dipp ^iPr groups shown in wireframe format for clarity; thermal ellipsoids shown at the 35% probability level. Key bond lengths (Å) and angles ($^\circ$): (for 2-InBr): In(1)–B(1) 2.223(1), In(1)–Br(1) 2.545(1), In(1)–N(3) 2.187(1), In(1)–N(4) 2.179(1), N(3)–C(27)–N(4) 114.3(1), N(3)–In(1)–N(4) 61.3(1); (for 3): B(1)–C(27) 1.614(2), B(2)–Br(1) 1.926(2), B(2)–N(3) 1.410(2), B(2)–N(4) 1.412(2), N(3)–B(2)–N(4) 95.7(1), N(3)–C(27)–N(4) 87.4(1).

ESI) features the expected N,N' -chelating benzamidinate ligand and a four-coordinate metal geometry. The E–B distances [2.114(2)/2.111(2), 2.062(2)/2.064(2) and 2.223(1) Å, respectively] are consistent with the presence of conventional 2-centre 2-electron covalent bonds, being similar to those previously reported for boryl complexes of the respective group 13 metals in the +3 oxidation state [e.g. Al: 2.150(2), 2.119(2) Å;^[16a] Ga: 2.067(3), 2.098(2) Å;^[16b] In: 2.245(7), 2.256(6) Å].^[11p]

With each of these (amidinato)boryl precursors in hand we examined their reduction chemistry towards potassium metal (Scheme 2). In the case of the chloro-aluminium and -gallium systems 2-AlCl and 2-GaCl, no molecular group 13 metal-containing products could be isolated from the reaction mixture, while in the of 2-GaBr we could isolate and structurally characterize trace amounts of a gallium containing species of stoichiometry $\text{Ga}_2(\text{boryl})_2(\text{amidinate})$, 4 (along with mainly gallium metal; see ESI). The reduction of 2-InBr under similar conditions, however, leads to the formation of a more highly reduced metal-containing system, in accordance with the established redox properties of gallium and indium.^[20] As such, NMR measurements are consistent with complete loss of the



Scheme 2. Reduction of bromo-indium complex 2-InBr with potassium to generate the cyclic tetraindium cluster $\text{K}_2[\text{In}_4\{\text{B}(\text{NDippCH})_2\}_4]$ (5). [B] = $\text{B}(\text{NDippCH})_2$. Key reagents and conditions: a) K metal (4.4 equiv.), C_6D_6 , sonication for 1 h, 21%.

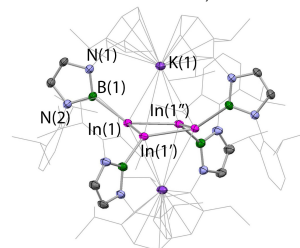


Figure 3. Molecular structure of 5 in the solid state as determined by X-ray crystallography. Hydrogen atoms omitted and ^iPr /Dipp groups shown in wireframe format for clarity; thermal ellipsoids shown at the 35% probability level. Key bond lengths (Å) and angles ($^\circ$): In(1)–In(1') 2.805(1), In(1)–In(1'')

2.838(1), In(1)-B(1) 2.316(2), In(1')-In(1)-In(1'') 89.6(1), In₄ centroid-In(1)-B(1) 148.0.

amidinato ancillary ligand. The presence of a single boryl ligand environment is also signalled by ¹H NMR measurements, but definitive characterization of the product as the cyclic tetraindium tetraboryl system K₂[In₄{B(NDippCH)₂}₄] (**5**) is dependent on the results of X-ray crystallographic studies (Figure 3). The solid-state structure features an approximately square array of four (symmetry-related) indium atoms, with each metal centre being additionally bound to a single terminal boryl ligand. The In₄ unit is near-planar, with each indium atom lying 0.12 Å out of the least-squares plane, and the internal In-In-In angles being essentially 90° [89.6(1)° in each case]. The structure is completed by two K⁺ counter-ions situated above and below the In₄ unit (K⁺In distances: 3.73 and 3.93 Å), which are sandwiched between the flanking Dipp aryl rings of diagonally opposite boryl ligands. A consequence of these K-arene contacts (3.17–3.37 Å) is a slight 'puckering' of the ligand envelope of the [In₄(boryl)₄]²⁻ unit, such that the In₄ centroid-In-B angles are non-linear [148.0°], and alternate boron atoms are positioned above/below the approximate In₄ plane.

The In-In contacts [2.805(1) and 2.838(1) Å] are similar to those found in related systems containing In-In single bonds [e.g. 2.777(1) Å for In₂{B(NDippCH)₂}₃]^[11p] and significantly shorter than the intermetallic distances associated with the boryl-ligated indium centres in clusters such as In₁₀{B(NDippCH)₂}₆ and [In₆₈{B(NDippCH)₂}₁₂] (means: 2.967 and 2.966 Å, respectively).^[11q] The near planar In₄ core of **5**, and the associated 2-charge, offers the potential for Hückel aromatic character.^[9] Although 2π electron metallo-aromatic systems have been reported previously for the lighter congeners aluminium and gallium (for example, M₂[Ga₃Ar^{Mes}₃] (M = Na, K),^[4a,b] Na₂[Al₃Ar^{Mes}₃],^[4c] and K₂[Ga₄Ar^{Trip}₂]^[21]), related systems are unprecedented for indium. Superficially, **5** is most similar to the silyl-ligated system [(thf)Na]₂[Ga₄(Si^tBu₃)₄] reported by Wiberg and co-workers, which has been described either in terms of a 2π aromatic [Ga₄(silyl)₄]²⁻ dianion, or as a Wade-Mingos five skeletal electron pair Na₂Ga₄ bicapped tetrahedron.^[22,23] In the case of **5**, the latter description (while correct in electron counting terms) is geometrically less appropriate, since the central In₄ unit is clearly a long way from being tetrahedral. Thus, the In-In-In-In torsion angles in **5** are 9.6 and 9.7°, while the corresponding parameters in the more puckered Ga₄ unit of [(thf)Na]₂[Ga₄(Si^tBu₃)₄] are 39.4°.

DFT calculations (carried out at the BP-TZP level) reveal that the HOMO of the [In₄{B(NDippCH)₂}₄]²⁻ system is indeed a delocalized π-type orbital extending in-phase over all four indium centres, with the HOMO-1 possessing In-In σ-bonding character (Figure 4). The inclusion of the K⁺ counter-cations perturbs the orbital picture slightly: thus for K₂[In₄{B(NDippCH)₂}₄], greater stabilization of the In-In π bonding MO due to the proximity of the K⁺ cations means that this orbital is the HOMO-1, with the less effectively stabilized σ-orbital now being the HOMO. Nucleus Independent Chemical Shift (NICS) values have been calculated for the potassium-free system [In₄{B(NDippCH)₂}₄]²⁻ [NICS(0) = -4.92, NICS(1) = -6.53] and can be compared with the values calculated using the same method for benzene [NICS(0) = -7.40, NICS(1) = -9.61].^[24] The π aromatic character is therefore shown to be relatively weak,^[25] presumably reflecting relatively poor pπ-

pπ overlap for indium, exacerbated by the bending of the boryl substituents away from the In₄ least-squares plane (even in the 'naked' dianion), and hence the imperfectly co-linear arrangement of indium 5p orbitals. Interestingly, a similar, moderately puckered, structure is observed for the related (6π-electron) system [Si₄(SiMe^tBu₂)₄]²⁻, for which the NICS(1) value (+6.1) implies a non-aromatic description.^[26]

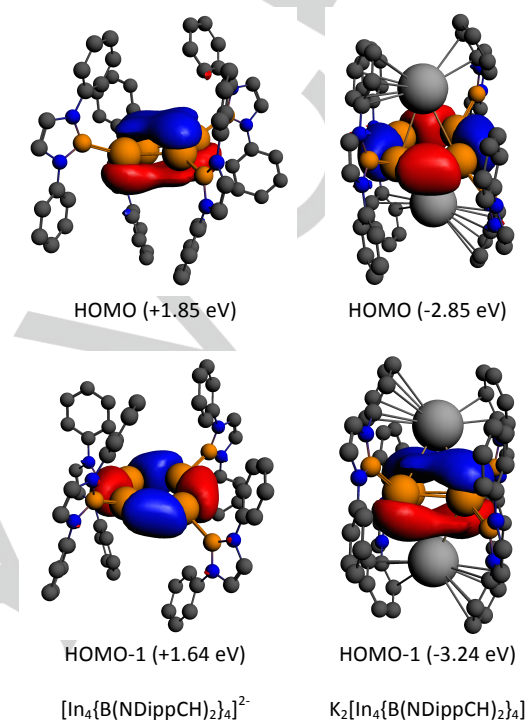


Figure 4. Electron density surfaces and energies of key molecular orbitals for [In₄{B(NDippCH)₂}₄]²⁻ (left) and K₂[In₄{B(NDippCH)₂}₄] (right) calculated by Density Functional Theory (see ESI).

In conclusion, we have shown that the highly sterically demanding boryl ligand B(NDippCH)₂ is capable of supporting two and three-dimensional aggregates featuring indium in very low oxidation states, including an unprecedented [In₆₈(boryl)₁₂]⁻ concentric cluster and a near planar 2π-electron cyclic tetramer.

Acknowledgements

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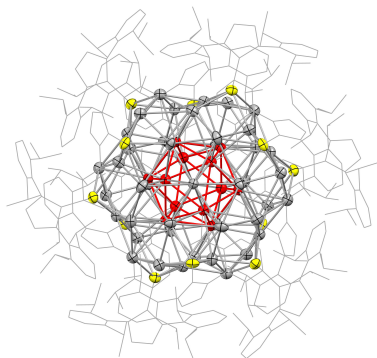
Keywords: Group 13 • indium • gallium • boryl • metal cluster

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Reduction of indium boryl complexes to give 2- and 3-D aggregates can be controlled by the choice of supporting ligand. The unprecedented nanoscale cluster $[\text{In}_{68}(\text{boryl})_{12}]^-$ ($\text{In}_{12}@\text{In}_{44}@\text{In}_{12}(\text{boryl})_{12}$) is isolated from the potassium reduction of a bis(boryl) precursor, while reduction of (amidinate) $\text{In}^{\text{III}}\text{Br}(\text{boryl})$ gives a (weakly aromatic) planar tetranuclear $[\text{In}_4(\text{boryl})_4]^{2-}$ system.



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