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Heavy metal boryl chemistry: complexes of cadmium, mercury and lead†

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Synthetic routes to the first boryl complexes of cadmium and mercury are reported *via* transmetallation from boryllithium; the syntheses of related group 14 systems highlight the additional factors associated with extension to more redox-active post-transition elements.

Transition metal boryl complexes have attracted much recent attention,[1] in part due to their implication in unique C–H functionalization chemistry.[2,3] More recently, the synthesis of reagents possessing nucleophilic character at boron[4,5] has enabled the extension of such chemistry to the f- and early d-block elements.[6,7] In addition, the large steric profile and strong σ-donor properties of the {(HCNDipp)$_2$B} ligand has led to its use as a bespoke ancillary substituent in the synthesis of main group carbenoid systems capable of facile E–H bond activation (E = H, C).[8]

While reagents such as {(HCNDipp)$_2$B}Li(thf)$_2$ are known to be strong reducing agents as well as powerful nucleophiles, the modulation of reactivity achieved for related alkyl/aryl systems by employing a less polar M–C bond,[9] suggests that post transition metal boryl complexes represent synthetically valuable targets. Thus, for example, zinc boryl complexes have been reported and their conjugate addition to α, β unsaturated ketones explored.[10] While related systems have been reported for the B-metal triads Cu, Ag, Au,[10a] and Ga, In, Tl,[11] well-defined group 12 boryl complexes are confined to two zinc species (Fig. 1).[10a]

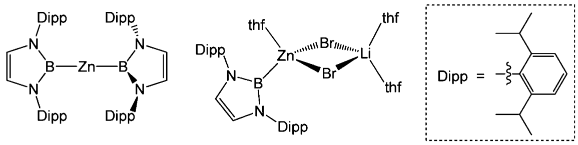
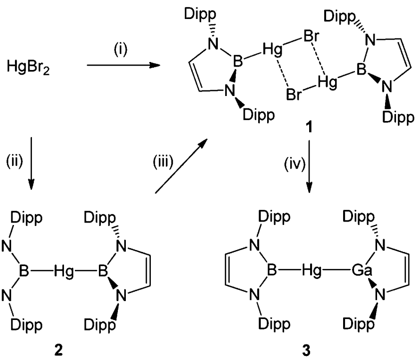


Fig. 1 Previously reported group 12 metal boryl complexes.[10a]

In the current study we targeted the first examples of cadmium and mercury boryls using a salt metathesis approach, and sought to explore whether this synthetic methodology could be extended to the more redox active metal lead. Moreover, in addition to homoleptic systems, routes to unsymmetrical (linear) complexes of the type (boryl)MX were sought, as these offer a convenient platform on which to study the σ donor properties of boryl ligands, free from complications involving π back bonding. Existing examples of Hg–B single bonds are confined to *exo*-polyhedral linkages associated with borane clusters;[12] simple 2-centre 2-electron Cd–B and Pb–B bonds are hitherto unknown.[13]

The reactions of {(HCNDipp)$_2$B}Li(thf)$_2$ with HgBr$_2$ in non-polar solvents such as benzene provide a versatile access point to a range of donor-free mercury boryl systems (Scheme 1). Thus, reactions in 1 : 1 and 2 : 1 stoichiometries generate complexes of the composition {(HCNDipp)$_2$B}HgBr (**1**) and {(HCNDipp)$_2$B}$_2$Hg (**2**), respectively. Conversion of **1** into **2** can be effected by the addition of a second equivalent of {(HCNDipp)$_2$B}Li(thf)$_2$ to **1**, and the reverse transformation by mixing equimolar quantities of **2** and HgBr$_2$. The composition of both mercury boryl complexes is suggested by multinuclear



Scheme 1 Syntheses of borylmercury complexes **1–3**. Key reagents/conditions: (i) {(HCNDipp)$_2$B}Li(thf)$_2$ (0.85 equiv.), benzene, RT, 5 min, 36%; (ii) {(HCNDipp)$_2$B}Li(thf)$_2$ (2.00 equiv.), benzene-d$_6$, RT, 5 min, 43%; (iii) HgBr$_2$ (1.0 equiv.), benzene-d$_6$, RT, 5 min, 96%; (iv) [{(HCNDipp)$_2$Ga}K(OEt$_2$)]$_2$ (1.0 equiv.), benzene-d$_6$, RT, 5 min, 35%.

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† Electronic supplementary information available: Synthetic and characterizing data for all new compounds; CIFs for **1–4**, **7** and **8**. CCDC 950737, 950743, 950744 and 968284–968286. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc00697f

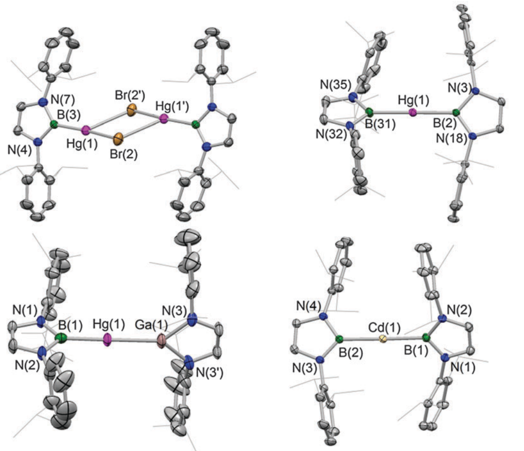
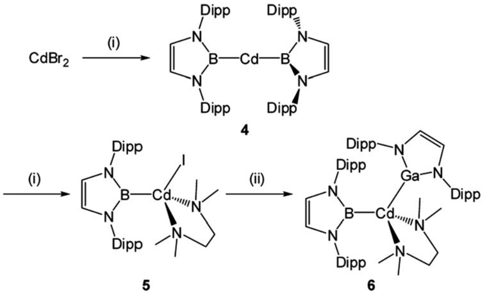


Fig. 2 Molecular structures of **1** (upper left), **2** (upper right), one of the components of the asymmetric unit of **3** (lower left) and **4** (lower right). Here and elsewhere: H atoms omitted and ^{i}Pr groups shown in wireframe format for clarity; thermal ellipsoids set at the 40% probability level. Key bond lengths (Å) and angles (°) for **1**: Hg(1)–B(3) 2.116(5), Hg(1)–Br(2) 2.486(1), Hg(1)–Br(2′) 3.295(1), B(3)–Hg(1)–Br(2) 169.0(1). Key metrical parameters for **2–4** are listed in Table 1.



Scheme 2 Syntheses of Cd complexes **4–6**. Key reagents/conditions: (i) $\{(HCNDipp)_2B\}Li(thf)_2$ (2.00 equiv.), benzene-d$_6$, RT, 12 h, 90%; (ii) $\{(HCNDipp)_2B\}Li(thf)_2$ (1.00 equiv.), thf, −78 °C to 0 °C, 5 h, 46%; (iii) $[\{(HCNDipp)_2Ga\}K(tmeda)]_2$ (0.50 equiv.), thf, −78 °C to 20 °C, 12 h, 70%.

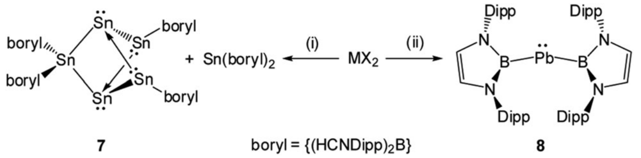
NMR and micro-analytical measurements and is confirmed by X-ray crystallography (Fig. 2). The monomeric structure of **2** features the linear two-coordinate geometry commonly associated with Hg(II) [∠(B–Hg–B) = 179.0(1)°], and comparison of the Hg–B bond lengths [2.150(3), 2.151(3) Å] with the sum of the respective covalent radii (2.16 Å),[14] is consistent with descriptions as 2-centre 2-electron single bonds. Similar bond lengths have been reported by Hawthorne and co-workers for the Hg–B bonds associated with cyclic mercura-carborand systems.[12c]

In the case of **1**, by contrast, the solid state structure is based around loosely bound centro-symmetric $[\{(HCNDipp)_2B\}HgBr]_2$ dimers, featuring a planar Hg_2Br_2 core [∠(Br–Hg–Br) = 80.3(1)°; ∠(Hg–Br–Hg) = 99.7(1)°] and (superficially at least) a T-shaped mercury centre. Comparison of the two different Hg–Br distances [*d*(Hg(1)–Br(2)) = 2.486(1) Å; *d*(Hg(1)–Br(2′)) = 3.295(1) Å] is consistent with weak association of the (boryl)HgBr units (*cf.* 2.52/3.40 Å for the sum of the respective covalent/van der Waals radii).[14] The B(3)–Hg(1)–Br(2) angle [169.0(1)°] is, however, 10° more acute than the B–Hg–B angle determined for the strictly two-coordinate **2**, consistent with a small but significant distortion from linearity imposed by the secondary Hg···Br contacts.

The synthetic utility of **1** in giving access to further examples of heteroleptic mercury boryl systems can be demonstrated by its reaction with the anionic gallyl equivalent $[\{(HCNDipp)_2Ga\}K(OEt_2)]_2$,[15,16] which yields the mixed group 13 donor species $\{(HCNDipp)_2B\}Hg\{Ga(NDippCH)_2\}$ (**3**) *via* salt metathesis chemistry. The synthesis of **3** is significant in that reactions of mercury(II) dihalides with the same gallyl anion lead to the reductive formation of mercury metal, rather than metathesis.[17] In common with **2**, the structure of **3** features a linear co-ordination geometry at mercury [∠(B–Hg–Ga) = 179.1(1)°], with the shorter Hg–B distance [2.116(5) Å] measured for **3** being consistent with the weaker *trans* influence of the gallyl ligand compared to its boryl counterpart. Such an assertion is consistent with observations made previously for square planar systems, based on analyses of ^{195}Pt–^{31}P coupling constants.[18] The Hg–Ga linkage – the first of its kind involving three-coordinate gallium – features a bond length [2.476(1) Å] reflective of the difference in the covalent radii of gallium and boron (Δd = 0.38 Å). The only other example of a Hg–Ga bond, found in $[\{HC(CMeNDipp)_2\}Ga(SC_6F_5)]_2Hg$, is markedly longer [2.534(1) Å], presumably due to the tetra-coordinate nature of the gallium centres.[19]

While Hg–B bonds have some precedent (albeit not for simple mono-boron ligand systems),[12] unsupported Cd–B and Pb–B bonds are hitherto unknown.[13] As such, we hypothesized that salt metathesis chemistry utilizing $\{(HCNDipp)_2B\}Li(thf)_2$ and appropriate cadmium or lead electrophiles might allow access to a range of novel bond types. In the case of cadmium, both bromide and iodide precursors prove to be amenable to such chemistry (Scheme 2). Moreover, the presence of an additional neutral donor – such as tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylene-diamine) modulates the observed reactivity, providing control of product stoichiometry. Thus, in the absence of such a donor, the reaction of cadmium dibromide with $\{(HCNDipp)_2B\}Li(thf)_2$ generates bis(boryl)cadmium complex **4**, irrespective of stoichiometry, with the bromo(boryl) system analogous to **1** presumably being more labile to substitution than (sparingly soluble) $CdBr_2$. In the case of the more soluble precursor $(tmeda)CdI_2$, the use of one equiv. of boryllithium allows for the controlled introduction of a single boryl ligand yielding a heteroleptic system of the type (tmeda)Cd(boryl)I (*i.e.* **5**).[17] Further substitution can then be effected, for example using a gallylpotassium reagent to give **6**.

By contrast, in the case of lead dihalide precursors (and to some extent their tin analogues), redox chemistry provides a competing reaction pathway to straightforward salt metathesis (Scheme 3). Thus, although the primary product of the reaction of $SnCl_2$ is $\{(HCNDipp)_2B\}_2Sn$ (as reported previously),[8a] a small



Scheme 3 Syntheses of Sn and Pb complexes **7** and **8**. Key reagents/conditions: (i) $\{(HCNDipp)_2B\}Li(thf)_2$ (2.00 equiv.), Et_2O, RT, 1 h, *ca.* 4% [+51% $Sn(boryl)_2$];[8a] (ii) $\{(HCNDipp)_2B\}Li(thf)_2$ (2.02 equiv.), benzene, RT, 5 min, 46%.

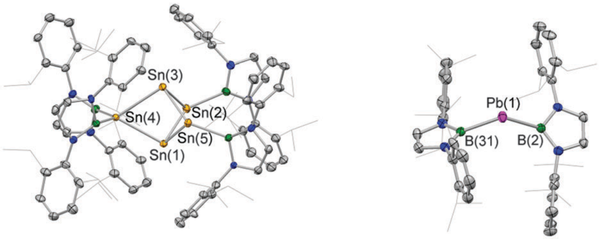


Fig. 3 Molecular structures of **7** (left), **8** (right). Key bond lengths (Å) and angles (°) for **7**: Sn(2)–B 2.290(5), Sn(5)–B 2.278(6), Sn(4)–B 2.595(7)/2.526(7), Sn(1)–Sn(2) 2.796(1), Sn(1)–Sn(4) 2.883(1), Sn(1)–Sn(5) 2.865(1), Sn(3)–Sn(2) 2.852(1), Sn(3)–Sn(4) 2.888(1), Sn(3)–Sn(5) 2.799(1). Key metrical parameters for **8** are listed in Table 1.

quantity of a pentanuclear tin cluster species (**7**) is also obtained. **7** features four boryl ligands and consequently a mean metal oxidation state of 0.8; three different tin environments are revealed crystallographically featuring either zero [Sn(1) and Sn(3)], one [Sn(2) and Sn(5)] or two metal-bound boryl ligands [Sn(4)] (Fig. 3).[20] In the case of lead(II) bromide, by contrast, the only isolable product is the bis(boryl)lead complex, **8**, but the propensity for reduction is signalled by the formation of metallic lead and the relatively low yield of **8** (46%).

The structures of the bis(boryl) complexes of both cadmium (**4**) and lead (**8**) have been determined crystallographically, confirming the expected linear [177.5(1)°] and bent geometries [118.3(1)°] at the respective metal centres (Fig. 2 and 3). Salient structural parameters are included in Table 1 (along with those of related systems) allowing the following general trends to be identified for post-transition metal boryl complexes: (i) the stronger σ-donor properties of the boryl ligand over gallyl and (less surprisingly) bromide counterparts; (ii) M–B bond lengths within individual groups (*i.e.* 12 and 14) which conform to the trends predicted on the basis of covalent radii, as expected for 2-centre 2-electron single bonds; and (iii) the over-arching influence of the steric demands of the boryl substituent. The latter factor leads to shorter M–B bonds for linear *vs.* bent bis(boryl) derivatives, even to the extent of out-weighing the influence of covalent radius (*e.g.* for Cd, In, Sn and Hg, Tl, Pb), and presumably results from enhanced steric 'buttressing' between pendant Dipp groups as the B–M–B angle narrows.

Steric considerations also appear to be a factor in modulating the *reactivity* of heavier p-block bis(boryl) systems, thus for example, mercury system **2** is surprisingly unreactive towards a range of substrates, while the more accessible lead centre in **8** is extremely labile, and its tin counterpart shows a wide range of controlled reactivity involving both insertion and addition processes. Studies of this chemistry will be reported shortly.

Table 1 M–B bond lengths and B–M–B angles for bis(boryl) and related complexes of the heavier group 12, 13 and 14 metals

	r(M–B)/Å	∠(B–M–X)/°	r_{cov}[14] (M)
Zn(boryl)$_2$[10a]	2.052(3), 2.053(3)	178.5(1)	1.22
Cd(boryl)$_2$ (**4**)	2.205(2), 2.207(2)	177.5(1)	1.44
Hg(boryl)$_2$ (**2**)	2.150(3), 2.151(3)	179.0(1)	1.32
BrHg(boryl) (**1**)	2.116(5)	169.0(1)	1.32
(Gallyl)Hg(boryl) (**3**)	2.116(5)	179.1(1)	1.32
In(boryl)$_2$[11a]	2.242(3), 2.246(3)	145.4(1)	1.42
Tl(boryl)$_2$[11a]	2.167(5), 2.173(6)	177.6(2)	1.45
Sn(boryl)$_2$[8a]	2.285(8), 2.294(8)	118.8(3)	1.39
Pb(boryl)$_2$ (**8**)	2.363(4), 2.372(4)	118.3(1)	1.46

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