Oxidative Bond Formation and Reductive Bond Cleavage at Main Group Metal Centers: Reactivity of Five-Valence-Electron MX$_2$ Radicals

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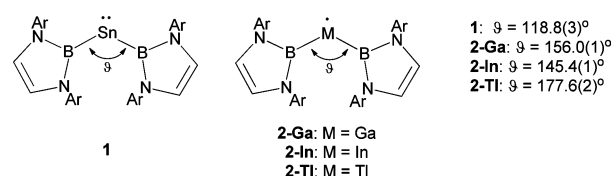[‡]School of Chemistry, Monash University, P.O. Box 23, Melbourne, Victoria 3800, Australia

S *Supporting Information*

ABSTRACT: Monomeric five-valence-electron bis(boryl) complexes of gallium, indium, and thallium undergo oxidative M−C bond formation with 2,3-dimethylbutadiene, in a manner consistent with both the redox properties expected for M^{II} species and with metal-centered radical character. The weaker nature of the M−C bond for the heavier two elements leads to the observation of reversibility in M−C bond formation (for indium) and to the isolation of products resulting from subsequent B−C reductive elimination (for both indium and thallium).

The chemistries of the Group 13 metals are dominated by the +1 and +3 oxidation states, the relative stabilities of which are described by the well-known "Inert Pair" effect.[1] Compounds with the empirical composition MX$_2$ are often mixed valence species (e.g., of the type M^{I}M^{III}X$_4$) or M$_2$X$_4$ molecules featuring a M^{II}−M^{II} bond.[2] Simple monomeric MX$_2$ species featuring the metal in the +2 oxidation state are of interest as short-lived intermediates in electron transfer processes, but isolated examples have long been confined to matrix isolation studies at very low temperatures (ca. 10 K).[2,3] Very recently, however, we reported the synthesis of the divalent radicals M{B(NDippCH)$_2$}$_2$ (M = Ga, In, Tl),[4] each of which decomposes above 130 °C.[5−7] The extremely high steric demands of the ancillary boryl substituents presents a critical steric impediment to dimerization via M−M bond formation.[8]

Bond formation processes exploiting insertion or cyclo-addition chemistry are typical of metal centers in low oxidation states and represent key steps in numerous catalytic processes.[9] One such mode of reactivity characteristic of electron-deficient Main Group systems (typically six valence electron carbenoids) involves [4+1] cycloaddition with α,β-unsaturated substrates such as *ortho*-quinones, vinyl ketones, and 1,3-dienes: double (formally oxidative) M−E bond formation typically generates a five membered metallacycle.[10,11] With synthetic routes to related five-valence-electron species now available (Chart 1),[4] we sought to investigate the potential for M−C bond formation through reactions of these radicals with unsaturated C−C bonds. Here we show that bis(boryl) complexes of gallium, indium, and thallium (**2-Ga**, **2-In**, and **2-Tl**) react with 2,3-dimethylbutadiene via oxidative M−C bond formation, and that

Chart 1. Boryl-Supported Five- and Six-Valence-Electron Main Group Metal Complexes Central to the Current Study (Ar = Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$)

1: ϑ = 118.8(3)°
2-Ga: ϑ = 156.0(1)°
2-In: ϑ = 145.4(1)°
2-Tl: ϑ = 177.6(2)°

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2-Ga: M = Ga
2-In: M = In
2-Tl: M = Tl

such processes have the potential to be reversible through homolytic bond scission. Moreover, the products isolated from the reactions of the diene with **2-In** and **2-Tl** imply that initial M−C bond formation can be followed by B−C elimination, leading to reduction of the metal center and (in the case of indium) to the formation of nanoscale clusters.

Prior to undertaking studies of novel five-valence-electron species, we first sought to establish that boryl-supported variants of *known* subvalent systems (e.g., carbenoids) *do* undergo oxidative bond formation. Accordingly, the reaction of bis(boryl)stannylene **1**[12] with 2,3-dimethylbutadiene can be shown to proceed in 1:1 stoichiometry to generate stannacyclopentene complex {(MeCCH$_2$)$_2$}Sn{B(NDippCH)$_2$}$_2$ (**3**, Scheme 1). The identity of **3** is suggested by multinuclear NMR spectroscopy and microanalysis, and confirmed by X-ray crystallography. Consistent with a [4+1] cycloaddition reaction involving formal oxidative M−C bond-forming processes, (i) the SnB$_2$ angle [123.5(1)°] is wider than that of stannylene **1** [118.8(3)°], as noted for other Sn^{IV} derivatives,[13] and (ii) the distance between the two β-carbons of the stannacycle [1.341(3) Å] is indicative of a C=C double bond.

In contrast to the precedented reactivity observed for tin complex **1**, the corresponding reactions of bis(boryl) gallium and -indium radicals **2-Ga** and **2-In** represent a first exploration of bond forming processes involving five-valence-electron MX$_2$ species. Consistent with the presence of a metal center bearing a single electron, rather than a lone pair, a 2:1 reaction stoichiometry with 2,3-dimethylbutadiene is implied by NMR and crystallographic studies of the products (Scheme 1 and

Scheme 1. Oxidative M−C Bond Formation in the Reactions of 1,2-Ga and 2-In with 2,3-Dimethylbutadiene: 1:1 and 2:1 Reaction Stoichiometries of Carbenoid and Radical Species, Respectively[a]
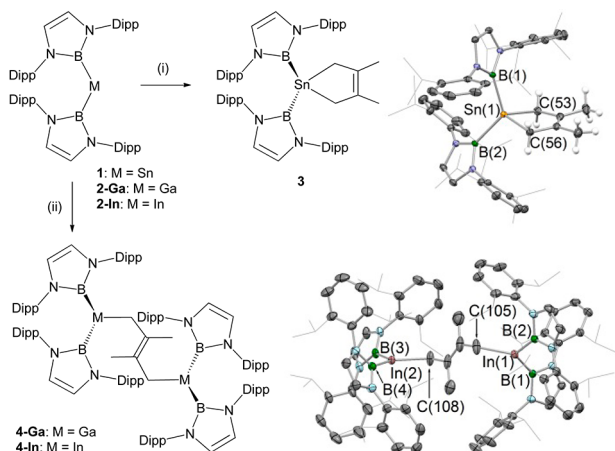
[a]Key reagents and conditions: (i) M = Sn, 2,3-dimethylbutadiene (ca. 9 equiv), C_6D_6, rt, <5 min, 85%; (ii) M = Ga or In, 2,3-dimethylbutadiene (6−9 equiv), C_6D_6, rt, <5 min, 73% (for M = In). Structures of **3** and **4-In** as determined by X-ray crystallography (see SI for structure of **4-Ga**). Key bond lengths (Å) and angles (°): for **3**, Sn(1)−B 2.274(2) and 2.272(2), Sn(1)−C 2.182(2) and 2.174(2), C(54)−C(55) 1.341(3), B(1)−Sn(1)−B(2) 123.5(1), C(53)−Sn(1)−C(56) 84.7(1); for **4-In**, In(1)−B 2.274(2) and 2.286(2), In(2)−B 2.288(2) and 2.289(2), In(1)−C(105) 2.194(3), In(2)−C(108) 2.196(3), B(1)−In(1)−B(2) 128.2(1), B(3)−In(2)−B(4) 123.9(1).

SI).[14] Thus, {(MeCCH₂)₂}[M{B(NDippCH)₂}₂]₂ (**4-Ga**: M = Ga; **4-In**: M = In) are each based around a central alkene core supporting a pair of mutually *trans* CH₂−tethered gallane/indane functions. The MB₂ angles determined crystallographically for both **4-Ga** and **4-In** (means: 123.6 and 126.9°) are very similar to that measured for tin system **3** [123.5(1)°], although in the case of **4-Ga/4-In** this represents a marked *narrowing* compared to the bis(boryl) metal precursor [156.0(1)/145.1(1)° for **2-Ga/2-In**]. Presumably the contrasting effects of metal oxidation for Group 13 and 14 systems reflect the different degrees of bending inherent in the initial five- and six-valence-electron starting materials.[15] For the Group 13 systems, changes in steric factors brought about by this narrowing lead to marked lengthening of the M-B bonds [e.g., 2.118 Å (mean) for **4-Ga** vs 2.048 Å (mean) for **2-Ga**].

Superficially, the reactivity patterns elucidated for **2-Ga** and **2-In** are therefore very similar; the more labile nature of the In−C bond, however, is reflected in two additional (contrasting) observations. First, dissolution of single crystals of **4-In** in benzene-d_6 leads to the slow establishment of an equilibrium mixture of **4-In** together with the **2-In** radical and 2,3-dimethylbutadiene. Integration of the respective diamagnetic signals in the ¹H NMR spectrum allows a value of K for the dissociation process of 1.6×10^{-6} mol² dm⁻⁶ to be determined, reflecting a conversion of 8% of **4-In** into its constituent radical/diene components at ca. 25 mM concentration (see SI). While the weaker M−C bonds typically associated with indium (cf. gallium) offer a rationale for these observations,[1] the existence of a M−C bonded species in equilibrium with a stable radical constituent generated by bond

homolysis is, to our knowledge, unprecedented in Main Group chemistry.[16−18]

Second, while solutions of **4-In** in benzene (in equilibrium with **2-In** and 2,3-dimethylbutadiene) are stable at room temperature (and **4-Ga** is thermally robust in a range of hydrocarbon media), analogous solutions in hexanes darken to a purple-brown color over a period of several hours. Cooling to 4 °C allows a small amount (<5% yield) of violet-black microcrystalline material to be isolated (together with a larger amount of unchanged **4-In**). The identification of this material as a nanoscale molecular cluster is based primarily on crystallographic studies, which reveal a species of composition In₁₉{B(NDippCH)₂}₆ (**5**, Figure 1). **5** features a central 12-
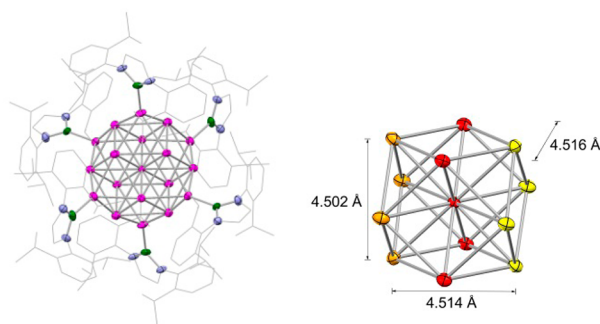

Figure 1. Two views emphasizing the metallic core of In₁₉{B-(NDippCH)₂}₆ (**5**): H atoms omitted and carbon atoms shown in wireframe format for clarity. Key: (left) nitrogen, blue; boron, green; indium, pink; (right) all atoms indium.

coordinate indium atom, and the core 13 atoms represent the smallest possible nanoscale model for a bulk CCP phase. As a polyhedral entity, these 13 non-ligated indium atoms constitute a cuboctahedron, with the six further In{B(NDippCH)₂} units capping each of the square faces [mean In−B bond length: 2.249 Å]. A related, but less regular structure has been reported by Schnöckel et al. for the [R₆Ga₁₉]⁻ anion [R = C(SiMe₃)₃].[19] In the case of **5**, the closeness with which the metallic core approaches an idealized CCP structure is reflected in the near identical values of the three "lattice parameters" (Figure 1). Indium nanoparticles have been shown to adopt both cubic ($c/a < 1.02$) and tetragonal structures ($1.06 < c/a < 1.09$), with the former apparently being favored for particles of less than 5 nm diameter (as here);[20] the bulk metal adopts a tetragonal structure.[21]

Key questions in terms of mapping patterns of reactivity are the steps in the formation of **5** from **4-In**. Although **4-In** is known to be in equilibrium with **2-In** under certain conditions, this radical is thermally robust ($T_d \approx 200$ °C in the solid state) and stable in hexane solutions of similar concentration below 50 °C. Thus, the role of the diene component in generating **5** appears crucial. In the case of **4-In**, the identity of the diene-containing co-product could not be established unequivocally; however, the chemistry of the corresponding thallium system offers some insight into potential mechanistic pathways leading to the formation of reduced metal species. Thus, the reaction of **2-Tl** with 2,3-dimethylbutadiene generates not the thallium analogue of **4-Ga/4-In**, but {(MeCCH₂)₂}[Tl{B-(NDippCH)₂}₂]{B(NDippCH)₂} (**6**, Scheme 2), featuring pendant Tl(boryl)₂ and B(NDippCH)₂ units. **6** is itself labile, being converted into the metal-free organoborane {(MeCCH₂)₂}[{B(NDippCH)₂}₂] (**7**) at longer reaction

Scheme 2. Formation of 6 and 7[a]
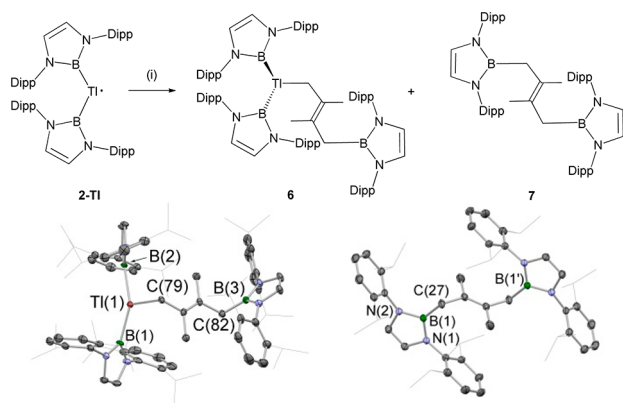
[a]Key reagents and conditions: (i) 2,3-dimethylbutadiene (2 equiv), C_6D_6, 50 °C, 4 h, 69% yield of **6**, (7% of **7**). Molecular structures of **6** and **7** as determined by X-ray crystallography. Key bond lengths (Å) and angles (°): for **6**, Tl(1)−B 2.259(1) and 2.262(3), Tl(1)−C(79) 2.299(3), B(3)−C(82) 1.570(4), B(42)−Tl(1)−B(75) 150.9(1); for **7**, B(1)−N 1.434(1) and 1.429(1), B(1)−C(27) 1.579(1).

times. The facts that (i) **6** and **7** both feature *trans*-functionalized alkene cores similar to **4-Ga** and **4-In** and (ii) B−C bond formation between adjacent (nucleophilic) alkyl and electrophilic boron-based ligands is known to be facile at transition metal centers suggest a mechanism for the formation of **6/7** involving initial generation of doubly metalated **4-Tl**, followed by successive B−C reductive elimination steps. Decomposition of the extruded [Tl^I(boryl)] unit is presumably responsible for the observed formation of thallium metal; the occurrence of similar reductive elimination chemistry for indium system **4-In** (although clearly less facile, presumably due to the differing redox properties of In^{III} vs Tl^{III}) offers a source of the [In^I(boryl)] units found in **5**. Thus, the diene effectively acts as a boryl ligand sink in the formation of this cluster.

In conclusion, we report a first exploration of the reactivity of monomeric, five-valence-electron MX$_2$ radicals (M = Ga−Tl) in bond formation processes. Bis(boryl)gallium, -indium, and -thallium systems all undergo oxidative M−C bond formation with 2,3-dimethylbutadiene, in a manner consistent both with the redox properties expected for M^{II} species, and with their metal-centered radical character. The weaker nature of the M−C bond for the heavier two elements leads to the observation of reversibility in M−C bond formation (for indium) and to the isolation of products resulting from subsequent B−C reductive elimination (for both indium and thallium). Further studies of the reactivity of these radical species are in progress and will be reported in due course.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Complete data for **3**, **4-Ga**, **4-In**, **5**, **6**, and **7**; all CIFs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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at room temperature. The color immediately changed from deep orange to yellow-orange and ^{1}H NMR showed formation of a single product. The mixture was transferred into a two-section crystallization tube and all volatiles removed *in vacuo*, producing a semicrystalline residue, which started to form well-shaped crystals (orange-yellow plates) when hexane (0.5 mL) was added. Storing the mixture at 4 °C overnight yielded **4-In**·C_6H_{14} (22.7 mg, 0.012 mmol, 73% based on In). ^{1}H NMR (C_6D_6): δ 7.23 (8 H, t, ^3J = 7.6 Hz, *p*-H of Ar), 7.13 (16 H, d, ^3J = 7.6 Hz, *m*-H of Ar), 6.27 (8 H, s, NCH), 3.22 (16 H, septet, ^3J = 6.8 Hz, C*H*Me$_2$), 1.35 (4 H, s, InCH$_2$), 1.19 (48 H, d, ^3J = 6.8 Hz, CH*Me*$_2$), 1.11 (6 H, s, InCH$_2$C*Me*), 1.00 (48 H, d, ^3J = 6.8 Hz, CH*Me*$_2$) [*n*-hexane: 1.22 (m, overlapping with CH*Me*$_2$), 0.88 (t, 6 H)]. ^{13}C{^{1}H} NMR (C_6D_6): δ 145.99 (*o*-C of Ar), 141.27 (*ipso*-C of Ar), 127.40 (*p*-CH of Ar), 124.01 (*m*-CH of Ar), 123.32 (InCH$_2$C*Me*), 122.92 (NCH), 40.95 (InCH$_2$), 28.47 (*C*HMe$_2$), 25.93 and 24.31 (CH*Me*$_2$), 22.15 (InCH$_2$*C*Me) [*n*-hexane: 31.92, 23.01, 14.31]. ^{11}B{^{1}H} (C_6D_6): δ 42.5. Anal. found (calcd for $C_{116}H_{168}B_4N_8In_2$): C, 71.35 (71.54); H, 8.51 (8.70); N, 5.89 (5.75) %. Crystallographic data (for **4-In**·$^1/_4C_6H_{14}$): $C_{223}H_{314.5}B_8In_4N_{16}$, M_r = 3765.35, monoclinic, $P2_1/n$, a = 39.8417(3), b = 13.1343(1), and c = 45.0886(4) Å, $β$ = 103.456(1)°, V = 22946.9(3) Å^3, Z = 4, $ρ_c$ = 1.090 Mg m^{-3}, T = 150 K, $λ$ = 1.54180 Å, 47 495 reflns collected, 47 495 independent [R(int) = 0.029] used in all calculations. R_1 = 0.0391, wR_2 = 0.0244 for observed unique reflns [$I > 2σ(I)$] and R_1 = 0.0444, wR_2 = 0.0257 for all unique reflns. Max and min residual electron densities: 1.47 and −1.33 e Å^{-3}. CSD reference: 1007373.

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