Boryl Complexes

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# Organoaluminum Boryl Complexes**

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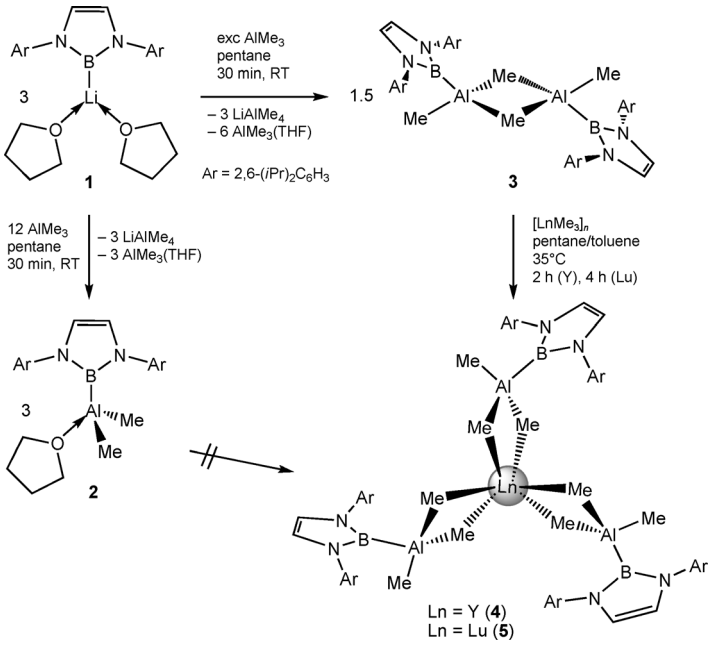
Metal-mediated borylations play a key role in many organocatalytic transformations, hence making isolable metal boryl complexes interesting targets in experimental and mechanistic organometallic chemistry.[1] Crucially, the electron-deficient nature of boron moieties/reagents inherently impeded the development of reaction routes utilizing (pre-isolated) carbanion-like nucleophilic boryls.[2] It was the seminal discovery by Yamashita and Nozaki in 2006 of the stable boron-centered anionic nucleophile $(THF)_2Li\{B(NArCH)_2\}$ (**1**, $Ar = C_6H_3iPr_2$-2,6)[3] which has since triggered intriguing metal boryl chemistry.[4–8] The synthesis of lithium boryl **1** was originally achieved by reduction of the N-heterocyclic carbene (NHC) analogue[9] 2-bromo-1,3,2-diazaborole with lithium naphthalenide[3] while its nucleophilic character was demonstrated by reactions with organic electrophiles, such as PhCHO, MeOTf, and *n*BuCl.[3a,c,5b] Moreover, several N-heterocyclic boryl transition-metal complexes were accessed with **1** by nucleophilic borylation, that is, metal–ligand (halo, alkoxo) displacement, and derivatives of Ti, Hf,[6] Cu,[5b,7a,d] Ag, Au,[7a] and Zn[5b,7b] X-ray structurally authenticated. Additionally, the corresponding magnesium complexes $BrMg\{B(NArCH)_2\}(THF)_2$ and $Mg\{B(NArCH)_2\}_2(THF)_2$ were synthesized by bromo/boryl exchange employing $MgBr_2$ and **1**.[5b,8] The series of metal boryl complexes has recently been extended to the rare-earth metals when Mountford et al. and Hou et al. independently prepared the first Group 3 and lanthanide boryl compounds $[Ln\{B(NArCH)_2\}(CH_2SiMe_3)_2(THF)_n]$ ($Ln = Sc$,[10,11] Y, Lu,[10] Gd,[11] $n = 1$ (Sc), 2 (Y, Lu, Gd)) according to a "charge-neutralization reaction" exploiting $[Ln(CH_2SiMe_3)_2(THF)_n]^+[BPh_4]^-$ salts as precursors and precipitation of $LiBPh_4$.[12]

Interestingly, until now $(THF)_2Li\{B(NArCH)_2\}$ (**1**) seems to be the only reagent employed for studying transformations of such anionic boryl moieties. Given that the polarity and hence reactivity of the metal–carbon bond in carbanionic species crucially depends on the metal center and because of the importance of organoaluminum-mediated (catalytic) transformations[13] we became interested in assessing the synthesis and possible reactivity of aluminum boryl complexes.

Spurred on by the nucleophilic character of lithium boryl **1**, we examined its reactivity toward Lewis acid $AlMe_3$ (Scheme 1, details of the synthesis are given in the Supporting Information). The envisaged reaction sequence would require two equivalents $AlMe_3$ to bind the two molecules of coordinated THF forming $AlMe_3(THF)$,[14] and an additional two equivalents of $AlMe_3$ should displace lithium through formation of insoluble $LiAlMe_4$[15] generating putative $Me_2Al\{B(NArCH)_2\}$.




***Scheme 1.*** Synthesis of, and reaction pathways from, dimethylaluminum boryl complexes and the formation of rare-earth-metal heteroaluminate complexes.

We could isolate and crystallographically characterize two aluminum boryl complexes, $(THF)Me_2Al\{B(NArCH)_2\}$ (**2**) and solvent-free $\{(\mu\text{-}Me)MeAl[B(NArCH)_2]\}_2$ (**3**).[16] NMR spectroscopic studies revealed that the interaction of the Lewis acidic boron and aluminum centers with THF is highly competitive (Supporting Information Figure S1 and S2). The proposed equilibrium $AlMe_3 + \mathbf{2} \rightleftarrows THF(AlMe_3) + 0.5\,\mathbf{3}$ is very much shifted to the left side with a strong bonding of the

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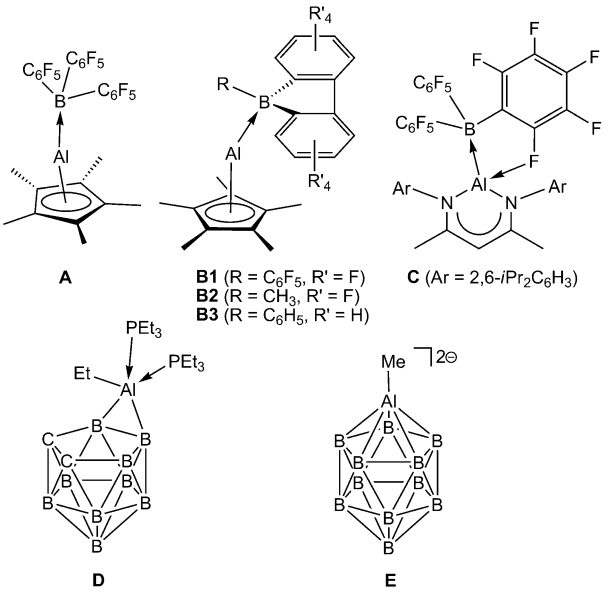
THF to the $AlMe_2$ group of the boryl complex **2**. Consequently, the stoichiometric amount of four equivalents of $AlMe_3$ gave predominantly complex **2**, and using more than 20 equivalents of $AlMe_3$ could not suppress formation of complex **2**. Not surprisingly, complex **2** is obtained quantitatively by the addition of an excess of THF to **3**.

There are few examples of unsupported direct Al–B bonds, which, however, involve the coordination of a nucleophilic aluminum compound to an electron-deficient boron center. Complex $[(\eta^5\text{-}C_5Me_5)Al\rightarrow B(C_6F_5)_3]$ (**A**), reported by Cowley and co-workers in 2000, was the first example showing an aluminum(I)–boron donor–acceptor bond.[17] Related complexes were later described by Piers et al.,[18] studying various perfluorinated and phenyl-substituted borafluorenes (**B**) and by H. W. Roesky et al., employing a ketimidinate instead of a cyclopentadienyl ancillary ligand (**C**).[19] The aluminum center of **C** $[LAl\rightarrow B(C_6F_5)_3]$ (L = HC(CMeNAr)$_2$) displays both Lewis base and acid character as shown by an additional close Al–F interaction (2.156(3) Å).[19] Importantly, both direct and H-supported multiple Al–$B_n$ bonds have been reported as early as 1970 by Hawthorne et al. in neutral and anionic boron clusters (e.g., **D** = *nido*-$B_9C_2H_{12}AlEt(PEt_3)_2$; **E** = $Na_2$[*closo*-$B_{11}H_{11}AlMe$]), mainly utilizing protonolysis methods with acidic carboranes and boranes and alkylaluminum compounds.[20–23]




The aluminum boryl complexes **2** and **3** have four-coordinate aluminum centers, as a result of THF coordination and dimerization through methyl groups, respectively (Figure 1). The Al–B bond lengths of 2.150(2) and 2.119(3) Å are in the same range as in complexes **A** (2.169(3) Å),[17] **B** (2.115(2)–2.149(7) Å),[18] and **C** (2.183(5) Å).[19] Note that in complexes **2** and **3**, unlike in complexes **A**–**C**, the boron atom serves as a donor and not as an acceptor. The remarkably short Al–B bond (2.119(3) Å) in complex **3**, which is also shorter than the closest Al–B

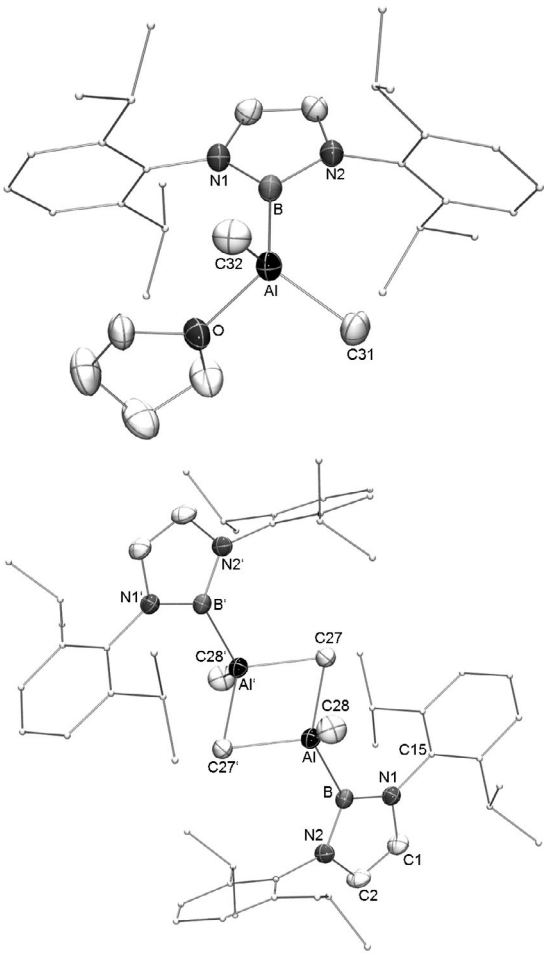



***Figure 1.*** Molecular structures of **2** (top) and **3** (bottom) with atomic displacement parameters set at the 50% level. Hydrogen atoms are omitted for clarity and the carbon atoms of the aromatic parts are shown with reduced radius. Selected bond lengths [Å] and angles [°]: **2**: B–Al 2.150(2), B–N1 1.454(3), B–N2 1.449(3), Al–C31 1.974(2), Al–C32 1.981(2), Al–O 1.940(2); N1-B-N2 101.7(2), B-Al-C31 115.34(9), B-Al-C32 117.87(9), B-Al-O 106.26(8). **3**: B–Al 2.119(3), B–N1 1.442(3), B–N2 1.447(3), Al–C27 2.124(3), Al–C28 1.964(3), Al···Al′ 2.609(2); N1-B-N2 102.6(2), B-Al-C27 111.8(2), B-Al-C28 124.3(2), C27-Al-C28 101.3(2), C27-Al-C27′ 104.41(9).

contacts found in aluminum carborane complexes (**D**, 2.128(5) Å),[20d] accounts for an especially strong bonding situation. The terminal Al–C(methyl) bond in complex **3** (Al–C28 = 1.964(3) Å) is slightly longer than the corresponding ones in $Al_2Me_6$ (1.949(2) and 1.956(2) Å),[24] but shorter than those in the amine amido complex [2-{($C_6H_3i\text{Pr}_2$-2,6)NCMe$_2$}-6-{($C_6H_3i\text{Pr}_2$-2,6)NHCMe$_2$}$C_5H_3N$]$AlMe_2$ (1.981(2) and 1.976(2) Å).[25]

At ambient temperature, the $^1$H NMR spectrum of donor-free **3** shows only one (relatively broad) singlet at $\delta = -0.57$ ppm ([$D_8$]toluene, 26 °C) for the aluminum-bonded methyl groups indicating high fluxionality on the NMR time scale. A variable-temperature NMR study confirmed decoalescence of this methyl resonance into two separate signals even at −10 °C ($Al_2Me_6$: −20 °C, Supporting Information, Figure S3). Inhibited rotation around the Ar–N bond owing to the steric demand of the isopropyl groups results in two

distinct methyl resonances, while the 2,6-diisopropylphenyl rings themselves are equivalent in the $^1$H NMR spectrum.[3a] The $^{11}$B{$^1$H} NMR spectrum of **3** shows a singlet at $\delta =$ 27.9 ppm (**2**, $\delta = 31.9$ ppm), which is shifted downfield compared to the $^{11}$B signals of complexes **A** ($\delta = -32.9$ ppm)[17] and **C** ($\delta = -26.52$ ppm)[19] featuring four-coordinate boron atoms.

To further study the properties of complex **3** and in particular its fluxional behavior we tested its reactivity toward amorphous $[LnMe_3]_n$ (Ln = Y, Lu).[14a] Note that we have previously shown that such polymeric, insoluble rare-earth metal methyl derivatives straightforwardly add $Al_2Me_6$ or $Al_2Et_6$ to give alkylaluminate complexes $[Ln(AlR_4)_3]$ which are soluble in hexane or toluene.[26] Treatment of a suspension of $[LnMe_3]_n$ (Ln = Y, Lu) in a mixture of toluene/pentane with 1.5 equivalents of **3** led to a clear solution, from which single crystals of the Ln-centered complexes $Ln[(\mu\text{-}Me)_2AlMeB(NArCH)_2]_3$ (Ln = Y, **4**; Lu, **5**) were grown at −40 °C (Scheme 1).[16] The 1.7 nm-sized molecular structure of **5** revealed a hexamethyl coordination of the Lu center and peripheral aluminum-bonded boryl ligands (Figure 2). Crucially, the donor-coordinated complex **2** does not react with $[LnMe_3]_n$ under these conditions, corroborating the enhanced Lewis acidity of the aluminum center in $[AlMe_2(boryl)]$ and hence a very strong Al–THF interaction in **2**.

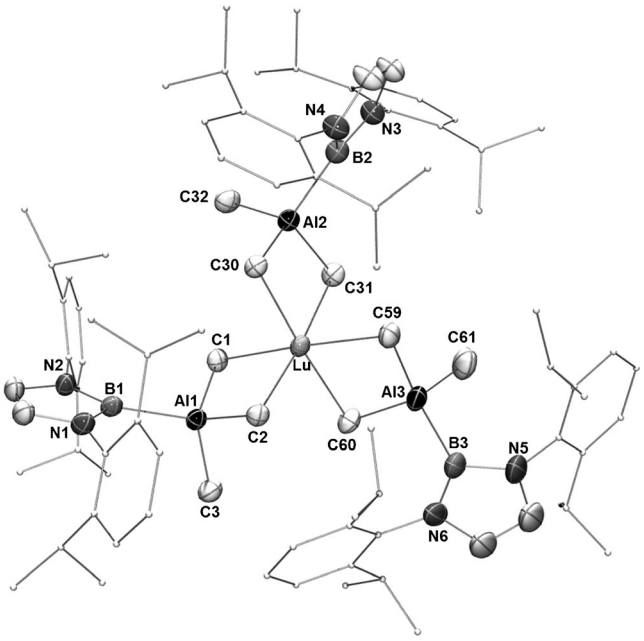
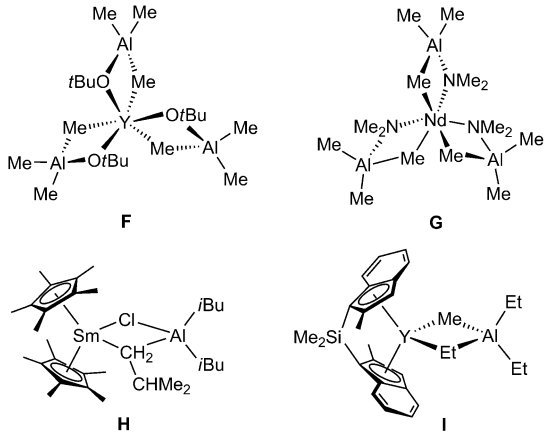



***Figure 2.*** ORTEP representation of the molecular structure of **5** with atomic displacement parameters set at the 50% level. Hydrogen atoms are omitted for clarity and the carbon atoms of the aromatic parts are shown with reduced radius. Disorders in the Ar$^{iPr}$ groups are not shown. Selected bond lengths [Å] and angles [°]: B1–Al1 2.153(3), B2–Al2 2.152(3), B3–Al3 2.153(4), Al1–C1 2.099(3), Al1–C2 2.100(3), Al1–C3 1.982(3), Al2–C30 2.100(3), Al2–C31 2.104(3), Al2–C32 1.973(3), Al3–C59 2.099(3), Al3–C60 2.091(3), Al3–C61 1.980(4), Lu–C1 2.472(3), Lu–C2 2.466(3), Lu–C30 2.479(3), Lu–C31 2.491(3), Lu–C59 2.478(3), Lu–C60 2.503(3); C1-Lu-C2 86.03(9), C1-Al1-C2 106.7(2), C2-Al1-C3 105.3(2), C30-Lu-C31 85.85(9), C30-Al2-C31 107.3(2), C30-Al2-C32 108.0(2), C59-Lu-C60 85.3(1), C59-Al3-C60 107.3(2), C59-Al3-61 107.7(2).

The Ln–$AlMe_3$X heteroaluminate bonding in complexes **4** and **5** (X = boryl) certainly reflects a strong interaction between boron and aluminum, but can be further rationalized on the basis of additional electronic and steric arguments. For monoanionic X featuring strongly electronegative donor atoms (OR, $NR_2$, Cl), X appears exclusively bonded to the Ln center forming heterobridged moieties[27] as exemplified for **F**,[28] **G**,[29] and **H**.[30] In the case of heteroaluminates with different alkyl groups, the bulkier X is found in the terminal position, that is, bonded solely to aluminum (**I**).[31] The heteroaluminate bonding motif in complexes **4** and **5** (X = very bulky boryl) corresponds to that of **I**, suggesting a carbanion-like behavior of the nucleophilic boryl ligand.[2,3] The Lu–C(methyl) and Al–B bond lengths compare well to those found in $Lu(AlMe_4)_3$ (2.455(2)–2.471(2) Å) and complex **3**. The $^{11}$B chemical shift of $\delta = +28.6$ ppm for **5** confirms a three-coordinate boron center.




The $^1$H NMR spectra of complexes **4** and **5**, recorded at ambient temperature, show only one signal for the $AlMe_3$ groups in the upfield region at $\delta = -0.68$ ppm ([D$_8$]toluene, 26 °C, **4**, Ln = Y, Figures 3 and S4) and $\delta = -0.32$ ppm ($C_6D_6$, 26 °C, **5**, Ln = Lu, Figure S5), respectively. For both complexes, the signals for bridging and terminal methyl groups split at lower temperatures with 2:1 integral ratios (**4**: ca. −40 °C, Figure 3; **5**: ca. −10 °C, Figure S6). The signals of the bridging methyl groups decoalescence further at lower temperatures (**4**: ca. −50 °C, Figure 3; **5**: ca. −25 °C, Figure S6).

In accordance with the literature,[32] the decoalescence temperature $T_c$ is lower for the complex with the larger metal center, in this case, yttrium. This observation can be explained by an increased steric hindrance of the lutetium center and therefore less-rapid alkyl exchange between bridging and terminal methyl groups of the $AlMe_3$ moieties.

In conclusion, boryllithium $(THF)_2Li\{B(NArCH)_2\}$ (Ar = $C_6H_3iPr_2$-2,6) reacts with $AlMe_3$ by methyl–boryl ligand exchange and formation of the boryl aluminum complex $(THF)Me_2Al\{B(NArCH)_2\}$. Because of a highly Lewis acidic aluminum center, removal of coordinated THF and formation of $\{Me_2Al[B(NArCH)_2]\}_2$ is difficult (it only occurs in the

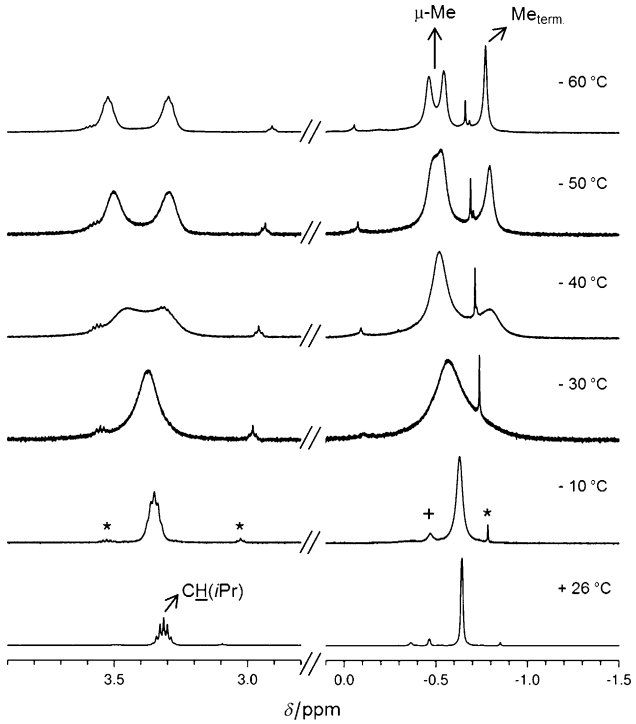



***Figure 3.*** Low-temperature $^1$H NMR spectra of **4**. The spectra show the splitting of the signals for the methine protons of the isopropyl groups and for the $AlMe_3$ groups into three signals at lower temperatures ($Me_{term.}$ = terminal methyl groups). Impurities are marked with asterisks and crosses (* = **2**, + = **3**).

presence of large excess of $AlMe_3$). However, the absence of THF is necessary to add the organoaluminum boryl complex to $[LnMe_3]_n$ (Ln = Y, Lu). The obtained rare-earth metal-centered complexes $Ln[(\mu\text{-}Me)_2AlMeB(NArCH)_2]_3$ have aluminum-bonded terminal boryl ligands, which nicely demonstrates their carbanion-type behavior. Current work in our group focuses on the synthesis of other Group 13 boryl complexes, their derivatization, and reactivity.

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[16] Compound **2** ($C_{32}H_{50}AlBN_2O$, $M_r = 516.53\ g\,mol^{-1}$), crystallizes from a toluene/pentane mixture in the monoclinic space group $P2_1/n$ with $a = 12.2128(5)$, $b = 10.7074(3)$, $c = 25.0255(10)$ Å, $\beta = 100.683(3)°$, $V = 3215.8(2)$ Å$^3$, and $\rho_{calcd} = 1.067\ g\,cm^{-3}$ for $Z = 4$. Data were collected at 173(2) K on a STOE IPDSII system. The structure was solved by direct methods, and least-square refinement of the model based on 6578 (all data) and 5866 reflections ($I > 2.0\sigma(I)$) converged to a final $R1 = 0.0676$ and $wR2 = 0.1424$, respectively. Compound **3** ($C_{56}H_{84}Al_2B_2N_4$, $M_r = 888.85\ g\,mol^{-1}$) crystallizes from a toluene/pentane mixture in the monoclinic space group $P2_1/n$ with $a = 14.9446(14)$, $b = 12.2129(9)$, $c = 16.0766(15)$ Å, $\beta = 100.669(7)°$, $V = 2883.5(4)$ Å$^3$, and $\rho_{calcd} = 1.024\ g\,cm^{-3}$ for $Z = 2$. Data were collected at 173(2) K on a STOE IPDSII system. The structure was solved by direct methods, and least-square refinement of the model based on 5244 (all data) and 4193 reflections ($I > 2.0\sigma(I)$) converged to final $R1 = 0.0697$and $wR2 = 0.1336$, respectively. Compound **5** ($C_{87}H_{135}Al_3B_3LuN_6$, $M_r = 1553.35\ g\,mol^{-1}$), crystallizes from a toluene/pentane mixture in the monoclinic space group $P2_1/n$ with $a = 10.2852(2)$, $b = 23.0503(4)$, $c = 40.8693(8)$ Å, $\beta = 93.5930(10)°$, $V = 9670.1(3)$ Å$^3$, and $\rho_{calcd} = 1.067\ g\,cm^{-3}$ for $Z = 4$. Data were collected at 173(2) K on a Bruker APEXII system. The structure was solved by direct methods, and least-square

  

refinement of the model based on 28387 (all data) and 26431 reflections ($I > 2.0\sigma(I)$) converged to a final $R1 = 0.0472$ and $wR2 = 0.1065$, respectively. Compound **4** ($C_{87}H_{135}Al_3B_3YN_6$, $M_r = 1467.32\ g\,mol^{-1}$) crystallizes from a toluene/pentane mixture in the monoclinic space group $P2_1/n$ with $a = 10.36(3)$, $b = 23.22(7)$, $c = 41.82(12)$ Å, $\beta = 93.49(4)°$. Because of the poor quality of the crystals, data collection was not completed and hence not deposited. Crystals of compounds **2**, **3**, **4**, and **5** are all colorless. CCDC-865456 (**2**), 865457 (**3**), and 865458 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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