

Synthesis of B/Ga and B/In Heteronuclear Bidentate Lewis Acids: Formation of Intramolecular π -Arene-Gallium(III) and -Indium(III) Complexes

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Abstract: Reaction of 1,8-dilithionaphthalene · TMEDA (TMEDA = tetramethylethylenediamine) with dimesitylboron fluoride in diethyl ether followed by treatment with THF affords the Li(THF)₄ salt of dimesityl-1,8-naphthalenediylborate (**1**). Compound **1** · Li(THF)₄ undergoes a ring-opening reaction with trimethyltin chloride to afford high yields of 1-(dimesitylboron)-8-(trimethyltin)naphthalenediyl (**2**), a compound in which a boryl and a stannyl moiety coexist at the *peri* positions of a naphthalene core. Compound **2** has been characterized by multinuclear NMR spectroscopy, elemental analysis, and

X-ray single-crystal analysis which reveal the existence of a sterically crowded structure. Compound **2** is a useful starting material for the synthesis of other heteronuclear naphthalene derivatives. Thus, the transmetalation reaction of **2** with GaCl₃ or InCl₃ in THF results in high yields of 1-(dichlorogallium)-8-(dimesitylboron)naphthalenediyl (**3**) and 1-(dichloroindium)-8-(dimesitylboron)naphthalenediyl (**4**), respectively. These unprecedented boron/gallium and bor-

on/indium heteronuclear bidentate Lewis acids have been characterized by multinuclear NMR spectroscopy, elemental analysis, and X-ray single-crystal analysis. Owing to the presence of a short contact between the *ipso*-carbon atom of a mesityl group and the heavy Group 13 element (C_{ipso} -Ga 2.279(4) Å for **3**, C_{ipso} -In 2.442(6) Å for **4**), compounds **3** and **4** are best described as intramolecular π -arene complexes and are the first examples of such complexes. As shown by ¹H and ¹³C NMR spectroscopy, this π interaction subsists in solution.

Keywords: boron · gallium · indium · Lewis acids · pi interactions

Introduction

With applications in the field of catalysis,^[1–6] molecular recognition,^[7–14] and material science,^[15, 16] polyfunctional Lewis acids that incorporate Group 13 elements are becoming a useful class of compounds. The majority of the derivatives so far prepared are bifunctional boron^[1, 2, 4, 5, 8, 11–13] or aluminum^[4, 10, 17–20] complexes in which the Group 13 moieties are linked by a rigid organic backbone. In recent years, however, polyfunctional Lewis acids that contain gallium or indium at the active sites of these derivatives have been discovered.^[9, 14, 15, 20–24] In the light of these past synthetic achievements, it is noteworthy that heteronuclear polyfunctional Lewis acids that involve two different Group 13 elements have never been prepared. Lessons learned from the chemistry of polydentate Lewis bases show that the preparation of ligands that contain mixed donor atoms allows tuning the

affinity and properties of the ligand.^[25] Thus, in an effort to prepare charge-reverse analogues of such ligands, we have engaged into a study aimed at the synthesis of bidentate derivatives in which a boryl unit coexists with a gallium or indium center.

The sequential introduction of Group 13 elements on an organic backbone is a nontrivial task. While neutral 1,8-boron-bridged naphthalene derivatives are known,^[26, 27] we recently reported the synthesis of an anionic example of such compounds, namely dimesityl-1,8-naphthalenediylborate (**1**),^[28] and showed that it undergoes ring-opening reactions with organoboron halides. It occurred to us that similar ring-opening reactions might take place with other main group halides thus enabling the preparation of mixed Group 13 bidentate Lewis acids. Herein, we show that the reaction of **1** with trimethyltin chloride yields 1-(dimesitylboron)-8-(trimethyltin)naphthalenediyl (**2**) as a new stannylated naphthalene derivative,^[29] which is converted by transmetalation with gallium and indium trichloride into 1-(dichlorogallium)-8-(dimesitylboron)naphthalenediyl (**3**) and 1-(dichloroindium)-8-(dimesitylboron)naphthalenediyl (**4**), respectively. The heteronuclear bifunctional Lewis acids **3** and **4** display intramolecular π coordination of an aromatic ligand to the heavier Group 13 element.

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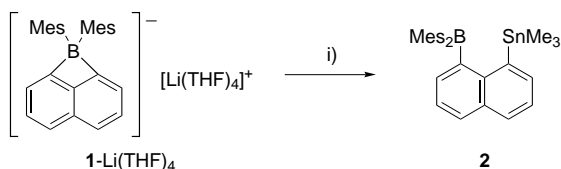
Results and Discussion

Synthesis and properties of dimesityl-1,8-naphthalenediylborate:

The reaction of 1,8-dilithionaphthalene·TMEDA (TMEDA = tetramethylethylenediamine)^[30] with one molar equivalent of dimesitylboron fluoride in diethyl ether afforded a colorless precipitate which could be converted into the Li(py)₄ and Li(THF)₄ salt of dimesityl-1,8-naphthalenediylborate (**1**) upon treatment with pyridine (py) and THF, respectively. While we have previously described the synthesis of **1**-Li(THF)₄ and **1**-Li(py)₄,^[28] the present procedure is noteworthy because it involves the more convenient use of 1,8-dilithionaphthalene·TMEDA as a starting material and affords salts of **1** in higher yields and higher purity.

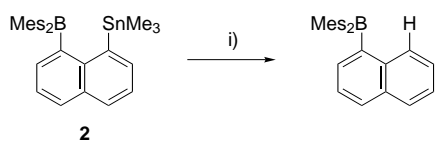
Ring-opening reaction of dimesityl-1,8-naphthalenediylborate: synthesis, structure, and reactivity of 1-(dimesitylboron)-8-(trimethyltin)naphthalenediyl:

The direct reaction of **1**-Li(THF)₄ with gallium or indium trihalides gave rise to intractable mixtures of products. By contrast, the reaction of **1**-Li(THF)₄ with one molar equivalent of trimethyltin chloride in diethyl ether afforded the 1-(dimesitylboron)-8-(trimethyltin)naphthalenediyl (**2**) as a colorless crystalline solid in 85% yield (Scheme 1). Compound **2** is soluble in all common



Scheme 1. Synthesis of compound **2**. i) Me₃SnCl, Et₂O (– LiCl, – 4THF).

organic solvents such as pentane, hexane, toluene, diethyl ether, and THF. It is water-sensitive and undergoes rapid hydrolysis to afford dimesityl- α -naphthylborane^[31] and trimethyltin hydroxide (Scheme 2), the identity of which was inferred from the observation of a single resonance signal in



Scheme 2. Hydrolysis of compound **2**. i) H₂O (– Me₃SnOH).

the ¹¹⁹Sn NMR spectrum at $\delta = 113.3$ ppm in C₆D₆.^[32] Compound **2** constitutes a new example of a Group 13/Group 14 heteronuclear *peri*-substituted naphthalene complex. Thus, it resembles boron–silicon derivatives^[33] and gallium–tin derivatives^[22] that have been previously reported. Compound **2** crystallizes in the orthorhombic space group *P*2₁2₁2₁ with four molecules in the unit cell. The molecular structure of **2** is shown in Figure 1. Unit cell data and refinement details are listed in Table 1. The structure of **2** presents a number of features characteristic of sterically hindered *peri*-substituted naphthalene derivatives.^[34] The B–C(1)–C(9) (129.9(5)°) and Sn–C(8)–C(9) (133.6(4)°) angles substantially deviate from the

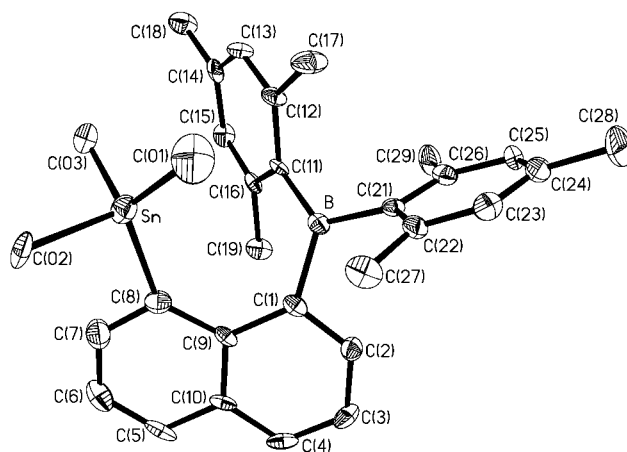


Figure 1. Structure of **2** in the crystal (ORTEP view; 50% ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: B–C(1) 1.610(9), B–C(11) 1.565(9), B–C(21) 1.566(8), C(1)–C(9) 1.453(8), C(8)–C(9) 1.458(9), Sn–C(8) 2.161(6), Sn–C(01) 2.168(8), Sn–C(02) 2.181(6), Sn–C(03) 2.082(8); C(1)–B–C(11) 122.2(5), C(1)–B–C(21) 115.5(5), C(11)–B–C(21) 121.5(5), B–C(1)–C(2) 111.4(5), B–C(1)–C(9) 129.9(5), C(1)–C(9)–C(8) 125.1(5), Sn–C(8)–C(7) 108.0(5), Sn–C(8)–C(9) 133.6(4), C(8)–Sn–C(01) 122.7(3), C(8)–Sn–C(02) 103.9(2), C(8)–Sn–C(03) 105.4(3), C(01)–Sn–C(02) 100.8(3), C(01)–Sn–C(03) 116.0(3), C(02)–Sn–C(03) 106.1(3).

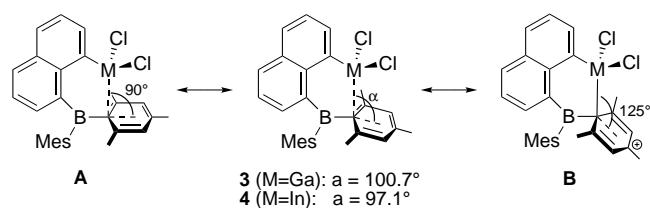
Table 1. Crystallographic data for **2–4**.

	2	3	4
formula	C ₃₁ H ₃₇ SnB	C ₂₈ H ₂₈ Cl ₂ GaB	C ₂₈ H ₂₈ Cl ₂ InB
<i>M_w</i> [g mol ^{−1}]	539.11	515.93	561.03
crystal system	orthorhombic	monoclinic	monoclinic
crystal size [mm]	0.22 × 0.15 × 0.08	0.20 × 0.12 × 0.10	0.08 × 0.05 × 0.02
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	8.341(1)	8.2520(8)	8.1607(7)
<i>b</i> [Å]	9.520(1)	20.037(2)	20.319(2)
<i>c</i> [Å]	33.958(5)	14.949(2)	15.182(1)
β [°]	−98.115(2)	99.111(2)	
<i>V</i> [Å ³]	2696.6(7)	2447.0(4)	2485.6(4)
<i>Z</i>	4	4	4
ρ_{calcd} [Mg m ^{−3}]	1.328	1.400	1.499
μ [mm ^{−1}]	0.964	1.357	1.180
<i>F</i> (000)	1112	1064	1136
θ range [°]	2.22 to 29.03	2.03 to 25.00	1.69 to 28.30
index ranges	−10 ≤ <i>h</i> ≤ 10 −12 ≤ <i>k</i> ≤ 9	−23 ≤ <i>k</i> ≤ 23 −40 ≤ <i>l</i> ≤ 44	−16 ≤ <i>k</i> ≤ 25 −17 ≤ <i>l</i> ≤ 15 −20 ≤ <i>l</i> ≤ 19
reflections measured	23072	12728	15640
completeness to θ_{max}	95.2	99.5	92.9
independent reflns/ <i>R</i> _{int}	6645/0.0821	4280/0.0489	5741/0.0672
parameters	298	289	289
GooF (<i>F</i> ²)	0.976	1.030	0.864
<i>R</i> 1 (<i>F</i>) [<i>I</i> > 2 σ (<i>I</i>)]	0.0533	0.0550	0.0492
<i>wR</i> 2 (<i>F</i>) [<i>I</i> > 2 σ (<i>I</i>)]	0.1222	0.1329	0.1025
largest diff. peak/hole [e Å ^{−3}]	1.124/−0.656	1.771/−0.395	1.804/−0.461

ideal value of 120°. The core of the naphthalene backbone is twisted as reflected by the dihedral angle of 7.8° formed between the planes defined by C(1)–C(9)–C(8) and C(4)–C(10)–C(5). The stannyl and boryl moieties are displaced above and below the plane of the naphthalene backbone by 0.63 and 0.70 Å, respectively. A final structural remark concerns the orientation of the dimesitylboryl moiety whose

2.170 Å) thus indicating the presence of a strong interaction. This coordination induces a tetrahedralization of the heavy Group 13 center as shown by the value of the sum of the C(1)–M–Cl(1), C(1)–M–Cl(2), and Cl(1)–M–Cl(2) angles ($\Sigma_{\text{angles}} = 335.4^\circ$ for **3** and 338.5° for **4**). The coordination geometry at the boron center is essentially trigonal planar ($\Sigma_{\text{angles}} = 359.5^\circ$ for **3** and 359.6° for **4**). The boron–carbon bond involving the bridging mesityl group (B–C(21) 1.613(6) Å for **3** and 1.608(9) Å for **4**) does not appear significantly elongated when compared to the bond which involves the terminal mesityl ligand (B–C(11) 1.591(6) Å for **3** and 1.597(9) Å for **4**).

While arene complexes of univalent gallium and indium cations are known,^[38] the existence of short π -arene contacts is unprecedented in the chemistry of gallium(III) and indium(III) derivatives.^[39] To ascertain the nature of the bonding in compounds **3** and **4**, it is instructive to review related phenomena observed in the chemistry of aluminum(III). First, triphenylaluminum^[40] exists as a dimer wherein a phenyl ligand adopts a symmetrically bridging situation. Distortions of the bridging phenyl in this dimer indicate that the four coordinate carbon atom adopts a non-negligible sp_3 character, as in the case of Wheland intermediates.^[41] Yet, another situation is encountered in the benzene or toluene adducts of $Al(C_6F_5)_3$, which are best described as π -arene complexes with an sp_2 -hybridized bridging carbon atom.^[42] Extending the bonding encountered in these aluminum complexes to the case of **3** and **4** leads to the formulation of **A** and **B** as the two extreme canonical forms (Scheme 4). The M–C(21)–C(24)



Scheme 4. Canonical forms for compounds **3** and **4** as π -arene complexes (**A**) or Wheland intermediates (**B**).

angles in **3** (100.7°) and **4** (97.1°) are close to that expected for **A** suggesting that they are best described as intramolecular π -arene complexes. Metrical parameters within the mesityl substituents confirm this view as the bridging mesityl ligand is only moderately distorted as shown by the value of the C(26)–C(21)–C(22) angle ($116.2(3)^\circ$ for **3** and $116.0(5)^\circ$ for **4**) which is only slightly smaller than the C(16)–C(11)–C(12) angle ($117.9(4)^\circ$ for **3** and $118.3(6)^\circ$ for **4**). In accordance with this observation, the C(21)–C(22) and C(21)–C(26) distances of 1.453(6) and 1.447(5) Å for **3** and 1.449(8) and 1.460(8) Å for **4** are only slightly elongated when compared to the C(11)–C(12) and C(11)–C(16) distances (1.427(5) and 1.413(5) Å for **3**; 1.417(8) and 1.406(8) Å for **4**) found in the terminal mesityl group.

As in the case of **2**, the ^{11}B NMR spectra of **3** and **4** in C_6D_6 display single signals at $\delta = 70.8$ and $\delta = 70.5$ ppm, respectively. The 1H and ^{13}C NMR spectra in C_6D_6 , which reveal the existence of chemically distinct mesityl groups indicate that

the structure observed in the crystalline form of **3** and **4** subsists in solution. Each mesityl group adopts a non-freely rotating structure and gives rise to two aryl-CH and three methyl resonance signals. The ^{13}C NMR spectrum of **3** and **4** exhibit a resonance ($\delta = 120.0$ ppm for **3** and 125.2 ppm for **4**) which appears at the high field end of the aromatic region and which can be assigned to the mesityl *ipso*-carbon atom coordinated to the heavy Group 13 element. For reference, the resonance for the mesityl *ipso*-carbon atom of trimesitylboron in C_6D_6 is observed at $\delta = 144.8$ ppm. As shown by variable-temperature 1H NMR experiments for **3** and **4** in $[D_{10}]o$ -xylene, elevation of the temperature to $130^\circ C$ does not lead to coalescence of any of the signals thus indicating the robustness and rigidity of the structure.

Conclusion

While it has been established previously that the ring-opening reactions of **1** can serve for the synthesis of unsymmetrically substituted diboranes, the synthesis of **2** demonstrates that such reactions can also be used for the preparation of heteronuclear *peri*-substituted naphthalene complexes. Compound **2** is a useful starting material that undergoes remarkably smooth transmetalation reactions with heavy Group 13 halides. These reactions proceed by elimination of Me_3SnCl and produce high yields of the B/Ga and B/In heteronuclear bidentate Lewis acids **3** and **4**. The structures of the latter reveal the existence of an intramolecular π complexation of the heavier Group 13 elements by one of the mesityl substituent. The ^{13}C NMR spectrum of these compounds corroborates this conclusion and indicates that this interaction is robust enough to subsist in solution. Interestingly, these are the first examples of gallium(III) and indium(III) π -arene complexes.

Experimental Section

General methods: All experiments were carried out under a dry inert atmosphere of N_2 using standard Schlenk technique or a glove box (Unilab, M. Braun). The solvents were purified by distillation from appropriate drying agents under N_2 . Dimesitylboron fluoride, trimethyltin chloride, gallium trichloride, and indium trichloride were purchased from Aldrich and used without further purification. 1,8-Dilithionaphthalene·TMEDA was prepared according to a published procedure.^[30] The microanalyses were performed by Atlantic Microlab, Norcross, GA. The melting points were measured on samples in sealed capillaries and are uncorrected.

NMR spectroscopy: NMR spectra were recorded on a Varian Unity Inova 400 FT NMR spectrometer (399.67 MHz for 1H ; 128.23 MHz for ^{11}B , 100.50 MHz for ^{13}C , 149.04 MHz for ^{119}Sn) by using internal deuterium lock. Chemical shifts δ are given in ppm, and are referenced against external Me_4Si (1H , ^{13}C), $BF_3 \cdot Et_2O$ (^{11}B), and Me_4Sn (^{119}Sn).

Crystallography: Crystals of 1-(dimesitylboron)-8-(trimethyltin)naphthalenediyl (**2**) were grown from a pentane solution at $-20^\circ C$, and of 1-(dichlorogallium)-8-(dimesitylboron)naphthalenediyl (**3**) and 1-(dichloroindium)-8-(dimesitylboron)naphthalenediyl (**4**) from toluene/pentane solutions at $-20^\circ C$, respectively. Due to the reactive nature of the compounds, the crystals were handled under a blanket of dry mineral oil during mounting. The crystals selected for data collection were mounted on a glass fiber with apiezon grease, and rapidly transferred into the cold N_2 stream of the low-temperature accessory. Intensity data for the crystals were collected on a Siemens SMART CCD diffractometer by using

graphite-monochromated Mo_{Kα} radiation ($\lambda = 0.71073 \text{ \AA}$) and 0.3°-wide ω scans with a crystal to detector distance of 5.0 cm. The structures were solved by direct methods^[43] and refined by full-matrix least-squares against F^2 .^[44] Crystallographic data are given in Table 1. CCDC-178273 (**2**), CCDC-178274 (**3**), and CCDC-178275 (**4**) contain the supplementary data crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Dimesityl-1,8-naphthalenediylborate (1): A solution of dimesitylboron fluoride (1.05 g, 3.90 mmol) in diethyl ether (10 mL) was added dropwise to a solution of 1,8-dithionaphthalene · TMEDA (1.00 g, 3.90 mmol) in diethyl ether (25 mL) at -78 °C, and the resulting mixture was stirred at -78 °C for 2 h and at room temperature for 15 h. The precipitate was filtered off, washed with diethyl ether (2 × 5 mL), and dried in vacuo. Subsequent treatment with THF, followed by recrystallization afforded **1** · Li(THF)₄ (1.70 g, 2.54 mmol, 65 %).^[28]

1-(Dimesitylboron)-8-(trimethyltin)naphthalenediyl (2): A solution of trimethyltin chloride (0.24 g, 1.19 mmol) in diethyl ether (5 mL) was added to a suspension of **1** · Li(THF)₄ (0.80 g, 1.19 mmol) in diethyl ether (5 mL) at -20 °C, and the resulting reaction mixture stirred at room temperature for 15 h. The solvent was evaporated in vacuo and the residue extracted with pentane (3 × 5 mL). The solvent was again evaporated in vacuo and the residue washed with cold pentane (1 mL) and dried under vacuum yielding **2** (0.55 g, 1.02 mmol, 85 %) as a colorless solid. M.p. 183–184 °C; ¹H NMR (399.67 MHz, C₆D₆, 25 °C, TMS): $\delta = 0.16$ (s, ¹J(¹³C,H) = 129 Hz, ²J(¹¹⁷Sn,H) = 52/54 Hz, 9H); Sn(CH₃)₃, 1.88 (s, 12H; *o*-CH₃), 2.15 (s, 6H; *p*-CH₃), 6.72 (s, ¹J(¹³C,H) = 155 Hz, 4H; *m*-H), 7.12 (dd, ³J(H,H) = 8 + 7 Hz, 1H; H-3), 7.27 (dd, ³J(H,H) = 8 + 7 Hz, ⁴J(^{117/119}Sn,H) = 6 Hz, 1H; H-6), 7.61 (dd, ³J(H,H) = 8 Hz, ⁴J(H,H) = 2 Hz, ⁵J(^{117/119}Sn,H) = 6 Hz, 1H; H-5), 7.67 (dd, ³J(H,H) = 8 Hz, ⁴J(H,H) = 2 Hz, ³J(^{117/119}Sn,H) = 9 Hz, 1H; H-4), 7.75 (dd, ³J(H,H) = 7 Hz, ⁴J(H,H) = 2 Hz, ³J(^{117/119}Sn,H) = 56/58 Hz, 1H; H-7), 8.03 ppm (dd, ³J(H,H) = 7 Hz, ⁴J(H,H) = 2 Hz, 1H; H-2); ¹³C{¹H} NMR (100.50 MHz, C₆D₆, 25 °C, TMS): $\delta = -3.89$ (¹J(^{117/119}Sn,¹³C) = 329/345 Hz; Sn(CH₃)₃), 21.24 (*p*-CH₃), 24.75 (*o*-CH₃), 125.14 (³J(^{117/119}Sn,¹³C) = 53 Hz; C-6), 125.63 (C-2), 129.98 (*mesityl m*-C), 130.67 (⁴J(^{117/119}Sn,¹³C) = 13 Hz; C-5), 135.00 (²J(^{117/119}Sn,¹³C) = 41 Hz; C-10), 135.44 (⁴J(¹¹⁷Sn,¹³C) = 6 Hz; C-4), 139.25 (²J(^{117/119}Sn,¹³C) = 29 Hz; C-7), 139.65 (*mesityl p*-C), 139.69 (C-3), 143.04 (*mesityl o*-C), 143.45 (*mesityl i*-C), 144.79 (¹J(^{117/119}Sn,¹³C) = 478/500 Hz; C-8), 144.89 (⁴J(^{117/119}Sn,¹³C) = 37 Hz; C-9), 151.82 ppm (C-1); ¹¹B{¹H} NMR (128.23 MHz, C₆D₆, 25 °C, BF₃ · Et₂O): $\delta = 67.2$ ppm; ¹¹⁹Sn{¹H} NMR (149.04 MHz, C₆D₆, 25 °C, SnMe₄): $\delta = -32.4$ (¹J(¹³C-¹¹⁹Sn) = 500 Hz, ¹J(¹³CH₃,¹¹⁹Sn) = 347 Hz); elemental analysis calcd (%) for C₃₁H₃₇SnB (539.15): C 69.06, H 6.92; found: C 68.97, H 6.87.

1-(Dichlorogallium)-8-(dimesitylboron)naphthalenediyl (3): A solution of gallium trichloride (0.10 g, 0.56 mmol) in THF (2 mL) was added to a solution of **2** (0.30 g, 0.56 mmol) in THF (3 mL) at -20 °C and the resulting mixture was stirred at room temperature for 12 h. The solvent was evaporated in vacuo, the residue washed with pentane (3 × 3 mL), and dried in vacuo yielding **3** (0.24 g, 0.47 mmol, 84 %) as a pale yellow solid. M.p. 205 °C (decomp); ¹H NMR (399.67 MHz, C₆D₆, 25 °C, TMS): $\delta = 1.39$ (s, 3H; CH₃), 1.66 (s, 3H; CH₃), 1.96 (s, 3H; CH₃), 2.16 (s, 3H; CH₃), 2.27 (s, 3H; CH₃), 2.27 (s, 3H; CH₃), 6.58 (s, 1H; *m*-H), 6.62 (s, 1H; *m*-H), 6.64 (s, 1H; *m*-H), 6.73 (s, 1H; *m*-H), 7.08 (dd, ³J(H,H) = 8 + 7 Hz, 1H; H_{naph}), 7.24 (dd, ³J(H,H) = 8 + 7 Hz, 1H; H_{naph}), 7.58 (dd, ³J(H,H) = 8 Hz, ⁴J(H,H) = 2 Hz, 1H; H_{naph}), 7.68 (dd, ³J(H,H) = 8 Hz, ⁴J(H,H) = 1 Hz, 1H; H_{naph}), 7.83 (dd, ³J(H,H) = 7 Hz, ⁴J(H,H) = 1 Hz, 1H; H_{naph}), 8.03 (dd, ³J(H,H) = 7 Hz, ⁴J(H,H) = 2 Hz, 1H; H_{naph}); ¹³C{¹H} NMR (100.50 MHz, C₆D₆, 25 °C, TMS): $\delta = 21.26$ (CH₃), 21.45 (CH₃), 21.85 (CH₃), 24.63 (CH₃), 24.99 (CH₃), 27.78 (CH₃), 120.01 (*mesityl i*-C ··· Ga), 125.93, 126.92, 127.62, 129.36, 130.90, 133.43, 134.11, 134.81, 136.35, 136.83, 138.70, 139.33, 140.71, 141.29, 141.53, 141.84, 144.44, 145.56, 154.02, 155.16, 161.31 (all C_{arom}); ¹¹B{¹H} NMR (128.23 MHz, C₆D₆, 25 °C, BF₃ · Et₂O): $\delta = 70.8$; elemental analysis calcd (%) for C₂₈H₂₈Cl₂GaB (515.97): C 65.18, H 5.47; found: C 65.00, H 5.60.

1-(Dichloroindium)-8-(dimesitylboron)naphthalenediyl (4): A solution of indium trichloride (0.12 g, 0.56 mmol) in THF (2 mL) was added to a solution of **2** (0.30 g, 0.56 mmol) in THF (3 mL) at -20 °C and the resulting mixture stirred at room temperature for 12 h. The solvent was evaporated in vacuo, the residue washed with pentane (3 × 3 mL), and dried in vacuo yielding **4** (0.29 mg, 0.52 mmol, 94 %) as a pale yellow solid. M.p. 200 °C

(decomp); ¹H NMR (399.67 MHz, C₆D₆, 25 °C, TMS): $\delta = 1.48$ (s, 3H; CH₃), 1.63 (s, 3H; CH₃), 2.02 (s, 3H; CH₃), 2.14 (s, 3H; CH₃), 2.16 (s, 3H; CH₃), 2.24 (s, 3H; CH₃), 6.62 (s, 1H; *m*-H), 6.65 (s, 2H; *m*-H), 6.67 (s, 1H; *m*-H), 7.03 (dd, ³J(H,H) = 11 + 9 Hz, 1H; H_{naph}), 7.13 (dd, ³J(H,H) = 10 + 9 Hz, 1H; H_{naph}), 7.54 (m, 2H; H_{naph}), 7.62 (dd, ³J(H,H) = 11 Hz, ⁴J(H,H) = 2 Hz, 1H; H_{naph}), 7.75 (dd, ³J(H,H) = 10 Hz, ⁴J(H,H) = 2 Hz, 1H; H_{naph}); ¹³C{¹H} NMR (100.50 MHz, C₆D₆, 25 °C, TMS): $\delta = 21.27$ (CH₃), 21.66 (CH₃), 21.76 (CH₃), 24.14 (CH₃), 24.71 (CH₃), 27.08 (CH₃), 125.22 (*mesityl i*-C ··· In), 125.95, 126.94, 127.62, 129.47, 131.12, 134.02, 134.29, 135.40, 135.96, 138.55, 138.79, 138.99, 139.60, 139.88, 141.38, 142.47, 145.26, 147.58, 149.81, 151.84, 152.72 (all C_{arom}); ¹¹B{¹H} NMR (128.23 MHz, C₆D₆, 25 °C, BF₃ · Et₂O): $\delta = 70.5$; elemental analysis calcd (%) for C₂₈H₂₈Cl₂InB (561.05): C 59.94, H 5.03; found: C 59.58, H 5.07.

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