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Lewis Acid–Base Adducts of 1-Mesityl- and 1-Chloro-2,3,4,5-tetraphenylborole

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Electron-deficient borole compounds exhibit a pronounced Lewis acidity that is enhanced due to their antiaromatic character so that even weak donors datively coordinate to form Lewis acid–base adducts. This contribution presents the synthesis and structural characterization of Lewis acid–base adducts formed by the reaction of 1-mesityl-2,3,4,5-tetraphenylborole and 4-picoline as well as 1-chloro-2,3,4,5-tetraphenylborole with various donors. The new compounds are characterized by means of multinuclear NMR spectroscopy and single-crystal X-ray diffraction techniques and compared to related systems.

Introduction

Interest in borole chemistry arises from the antiaromatic character of the cyclic conjugated boracycle that hosts four π electrons.[1] Starting in 1969,[2] when 1,2,3,4,5-pentaphenylborole (**1**) was isolated as the first of its kind, and increasing since its structural analysis in 2008,[3] a growing number of publications emphasizes the significance of this area.[4–23] Challenges to synthesis, structural and photophysical characterization of boroles, as well as their rich and often unexpected reactivity can be ascribed to the inherent antiaromatic destabilization of boroles.[1–25] Typical reaction types that cause disruption to the antiaromatic π system include cycloaddition reactions[8,12,21,25] and the activation of small molecules such as H_2.[22] The essential strategy to isolate a borole molecule is steric and electronic shielding of the backbone in the C_4B annulus. This has hitherto been achieved by substitution with aryl or thienyl groups.[1,6,15] The substituent at the boron atom is variable over a broad range from halogen,[4,6,12] amino,[4] and aryl groups[2,5,6,14,15] to transition metals[10,23] and cyclopentadienyl moieties in transition-metal complexes.[3,11,16,17] Variation of the substituent at the boron center significantly affects the HOMO–LUMO transition, thereby resulting in different photophysical properties.[1] The vacant p_z orbital of the tricoordinate boron center in combination with antiaromatic π conjugation induces a pronounced Lewis acidity so that even weak Lewis bases such as CO,[19] ethers,[1,12] nitriles,[1] as well as stronger donors like pyridine derivatives,[4,11,12,16] N-heterocyclic carbenes (NHC),[7,12] or phosphanes[12] readily coordinate to the boron center. As a result, π conjugation within the five-membered ring is interrupted, thus leading to enhanced stability of the Lewis acid–base adducts. Such Lewis pairs are by no means unreactive but provide the basis for further reactivity studies. The pentaphenylborole–2,6-lutidine adduct [$PhBC_4Ph_4$(2,6-$Me_2C_5H_3N$)] (**2**), for example, shows remarkable thermo- and photochromic behavior.[20] Furthermore, the chloroborole–SIMes adduct [$ClBC_4Ph_4$(SIMes)] (**3**) [SIMes = *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene] serves as a precursor to a highly unusual NHC-stabilized π-boryl anion.[7] The latter exemplifies the interesting reduction properties of boroles to produce aromatic dianions with six π electrons.[5,24] The reduction sequence of free boroles involves radical anionic intermediates with five π electrons, as recently shown.[9,14] In this contribution, we report the synthesis and characterization of a Lewis acid–base adduct of 1-mesityl-2,3,4,5-tetraphenylborole with 4-picoline and, in addition, a series of different Lewis adducts of 1-chloro-2,3,4,5-tetraphenylborole.

Results and Discussion

The reduction chemistry of 1-mesityl-2,3,4,5-tetraphenylborole (**4**) has recently been studied in detail by taking advantage of a sterically shielded boron center.[14] That steric bulk around the reactive centers in Lewis acid–base pairs can lead to frustrated Lewis pairs (FLPs) has also been shown by many examples.[26] The combination of **1** and 2,6-

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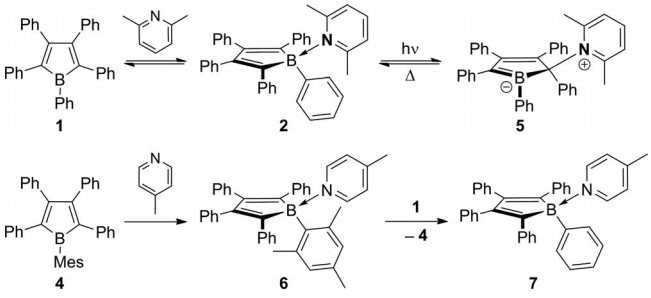
lutidine results in an equilibrium between the Lewis acid–base adduct (**2**) and the unreacted species at ambient temperature.[20] This behavior is somewhat related to FLPs. More interestingly, **2** shows a migration of the Lewis base from the boron atom to the adjacent carbon atom (compound **5**, Scheme 1) upon irradiation with UV light at –50 °C, which is thermally reversible. With this background in mind, we targeted the combination of **4** and 4-picoline, which should result in a similar spatial configuration around the boron center in the product **6**, and therefore a similar reactivity is anticipated. In addition, 4-picoline (pK_b = 8.0)[27] is less basic than 2,6-lutidine (pK_b = 7.3)[27] as deduced from experimental and theoretically predicted pK_b values in aqueous solution, which should promote FLP behavior over Lewis adduct formation.



Scheme 1. Reactivity of **1** towards 2,6-lutidine and of **4** towards 4-picoline as well as Lewis base transfer from **6** to **1**.

Surprisingly, the reaction of **4** with 4-picoline entails an immediate color change from dark green to yellow upon addition of the Lewis base to a solution of **4** at ambient temperature. This indicates the irreversible formation of the Lewis acid–base adduct [$MesBC_4Ph_4(4\text{-}MeC_5H_4N)$] (**6**) rather than an FLP. Thus, the ^{11}B NMR spectroscopic resonance of **6** was observed at δ = 4.5 ppm in the typical range of four-coordinate boron. The solid-state structure was confirmed by single-crystal X-ray diffraction (Figure 1). The B1–N1 distance of **6** [1.635(2) Å] is considerably shorter than that of **2** [1.657(3) Å],[20] thus indicating a stronger dative interaction between donor and acceptor in complex **6** than in **2**. The B1–C5′ separations of **6** [1.639(2) Å] and **2** [1.635(3) Å] are very similar.

Unexpectedly, the different behavior of **2** and **6** correlates neither with the basicity of 2,6-lutidine (pK_b = 7.3) and 4-picoline (pK_b = 8.0) nor with the Lewis acidity of the uncomplexed boroles **1** and **4** (see below).[27] It was shown earlier that the reaction of **1** and 4-picoline gives the Lewis acid–base adduct [$PhBC_4Ph_4(4\text{-}MeC_5H_4N)$] (**7**) without difficulty.[20] As expected, mixtures of **4** and 2,6-lutidine show the unaltered presence of both compounds in solution according to ^1H and ^{11}B NMR spectroscopy. Likewise, no dative interaction is observed between **4** and weak donors such as diethyl ether or thf, whereas **1** is readily complexed by the latter, which indicates a stronger relative Lewis acidity of **1** than of **4**.[1] This assumption was unequivocally confirmed by a Lewis base transfer experiment. Addition of 1 equiv. of **1** to a solution of **6** in CD_2Cl_2 results in a complete transfer of 4-picoline to **1** as deduced from ^1H and ^{11}B NMR spectroscopy as well as the characteristic dark green color of the solution that is indicative of free **4**.[14] A similar base-transfer experiment has been used to demonstrate the enhanced Lewis acidity in bis(borolyl)ferrocene [$Fe(CpBC_4Ph_4)_2$] (Cp = η^5-C_5H_4) relative to the monofunctionalized derivative [$(CpH)Fe(CpBC_4Ph_4)$].[16] Thus, we have to state that **4** and 4-picoline form no FLP (but a classical adduct) despite the fact that they constitute the weaker Lewis acid and the weaker Lewis base relative to **1** and 2,6-lutidine.

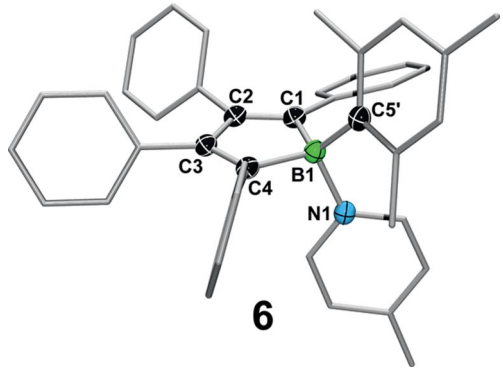
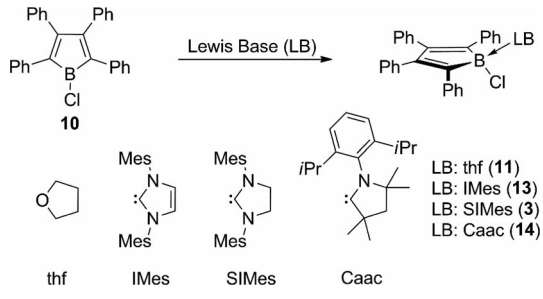


Figure 1. Molecular structure of **6** in the solid state with hydrogen atoms and thermal ellipsoids of peripheral atoms omitted for clarity. Thermal ellipsoids are set at 50% probability.

The second part of this work concerns the synthesis of Lewis adducts formed by 1-chloro-2,3,4,5-tetraphenylborole and a series of Lewis bases (Scheme 2). Coordination of ethers to haloboranes often involves cleavage of a C–O bond owing to the highly reactive nature of the Lewis acid. Contrary to our expectations, we were able to isolate the moderately stable Lewis acid–base adduct [$BrBC_4Ph_4(thf)$] (**8**) by reaction of 1-bromo-2,3,4,5-tetraphenylborole (**9**) with thf, which undergoes thf cleavage in solution only at slightly elevated temperatures.[12] The reaction of 1-chloro-2,3,4,5-tetraphenylborole (**10**) with thf gives the analogous compound [$ClBC_4Ph_4(thf)$] (**11**), which was obtained in a yield of 53% as a yellow solid. The ^{11}B NMR resonance was detected at δ = 12.4 ppm, which is similar to that of **7** (δ = 10.3 ppm). Under an inert gas, **11** shows no signs of decomposition or ether cleavage reactions in the solid state and in solution. The solid-state structure of **11** (Figure 2) obtained by single-crystal X-ray diffraction shows bond parameters very similar to those of **8**. The B1–



Scheme 2. Synthesis of Lewis adducts of different boroles with a variety of Lewis bases.

O1 atom separations [**11**: 1.573(4) Å; **8**: 1.572(2) Å] are equal within the limits of measurement. As previously shown, the aromatic system $K(thf)_2[ClBC_4Ph_4]$ (**12**) is obtained by reduction of **10** with potassium graphite in thf as a solvent. Although the isolated yields of **12** are low, it is worth noting that the boron–halogen bond remains intact, which is uncommon for haloborane species under such reducing conditions. Accordingly, formation of **11** prior to reduction is presumed to play a role in the course of the fast reaction.

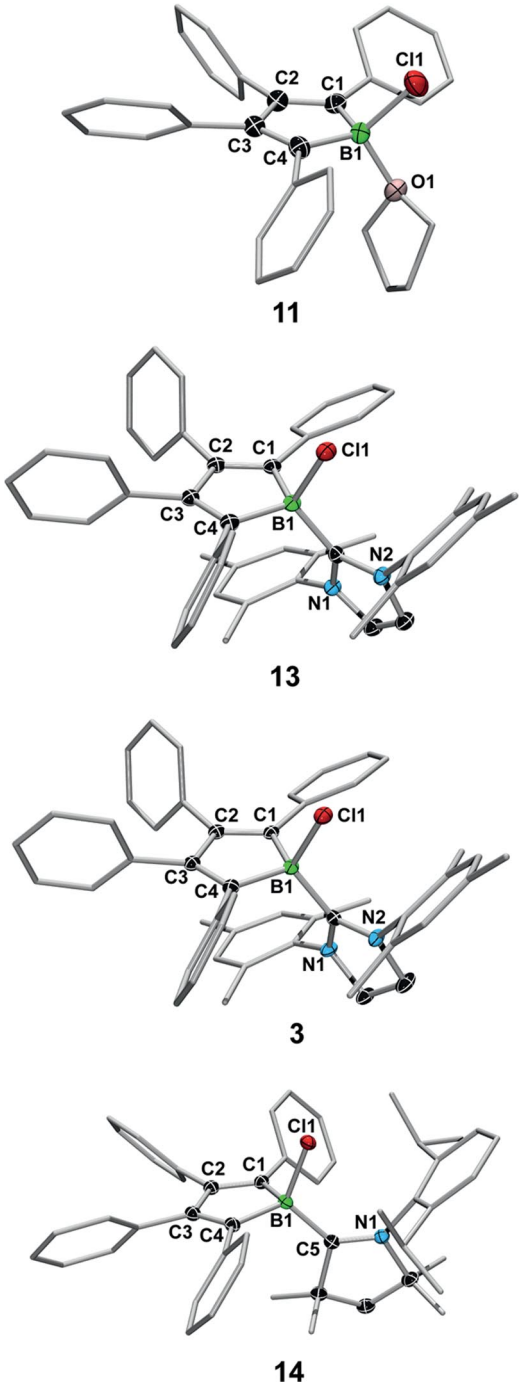


Figure 2. Molecular structures of **11**, **13**, **3**, and **13** in the solid state with hydrogen atoms and thermal ellipsoids of peripheral atoms omitted for clarity. Thermal ellipsoids are set at 50% probability.

However, when a stronger σ donor such as an N-heterocyclic carbene (NHC) is coordinated to **10**, as in $[ClBC_4Ph_4(SIMes)]$ (**3**), cleavage of the B–Cl bond and formation of an NHC-stabilized π-boryl anion can be achieved under the same reducing conditions.[7] Given the importance of 1-haloborole–carbene adducts for subsequent transformations, we sought to broaden the scope of such species and prepared an exemplary series of carbene adducts. Although the synthesis of **3** has been reported earlier,[7a] the solid-state structure is hitherto unknown and is reported here.

Reaction of **10** with *N*,*N*′-bis(2,4,6-trimethylphenylimidazol-2-ylidene (IMes) or *N*-(2,6-diisopropylphenyl)-2,2,4,4-tetramethylpyrrolidine-5-ylidene (Caac) proceeds readily as indicated by a rapid color change from deep purple to yellow when the donor is added to solutions of **10**. The Lewis pairs $[ClBC_4Ph_4(IMes)]$ (**13**) and $[ClBC_4Ph_4(Caac)]$ (**14**) show typical ^{11}B NMR spectroscopic chemical shifts at lower frequencies (**13**: δ = –3.0 ppm, **14**: δ = –1.9 ppm) relative to **10** (δ = 66.4 ppm). The ^{11}B resonances reflect those of the analogous bromo derivatives $[BrBC_4Ph_4(SIMes)]$ (**15**: δ = –6.2 ppm) and $[BrBC_4Ph_4(Caac)]$ (**16**: δ = –4.8 ppm). Analysis of the solid-state structures of **3**, **13**, and **14** was carried out by means of single-crystal X-ray diffraction. The structural data (Table 1) are unobtrusive and compare well with the structures of **15** and **16**. The longest B1–$C_{carbene}$ distance was found in **3** [1.649(2) Å], whereas the shortest value was found in **14** [1.634(3) Å]; this follows the trend previously observed between **15** [1.655(3) Å] and **16** [1.628(2) Å]. This bonding situation reflects the stronger σ-

Table 1. ^{11}B NMR spectroscopic chemical shifts [ppm], bond lengths [Å], and angles [°] of **3**, **6**, **11**, **13**, and **14**.

	6	**11**	**13**	**3**	**14**
$\delta(^{11}B)$	4.5	12.4	–3.0	–3.3	–1.9
B1–C1	1.645(2)	1.600(4)	1.626(3)	1.628(2)	1.647(2)
B1–C4	1.629(2)	1.613(4)	1.630(3)	1.631(2)	1.643(2)
B1–Cl1	–	1.866(3)	1.909(2)	1.903(2)	1.898(2)
B1–C5′	1.639(2)	–	–	–	–
C1–C2	1.358(2)	1.347(4)	1.355(3)	1.354(2)	1.355(3)
C2–C3	1.501(2)	1.515(4)	1.494(3)	1.491(2)	1.489(2)
C3–C4	1.353(2)	1.341(4)	1.343(3)	1.350(2)	1.362(2)
B1–E[a]	1.635(2)	1.573(4)	1.637(3)	1.649(2)	1.634(3)
C1–B1–C4	99.7(2)	102.3(2)	100.5(2)	100.8(2)	99.2(1)
B1–C1–C2	108.2(2)	107.4(2)	107.7(2)	107.6(2)	108.2(2)
C1–C2–C3	111.7(2)	111.6(2)	111.7(2)	111.8(2)	112.2(2)
C2–C3–C4	111.7(2)	111.5(2)	112.3(2)	112.5(2)	111.7(2)
C3–C4–B1	108.9(2)	107.3(2)	107.7(2)	107.2(2)	108.4(2)
C1–B1–Cl1	–	111.6(2)	108.0(2)	107.9(1)	107.9(1)
C4–B1–Cl1	–	115.1(2)	106.4(2)	106.6(1)	108.4(1)
C1–B1–C5	121.6(2)	–	–	–	–
C4–B1–C5	111.2(2)	–	–	–	–
C1–B1–E[a]	102.6(1)	110.7(2)	116.4(2)	116.8(2)	109.2(2)
C4–B1–E[a]	108.9(2)	112.5(2)	115.4(2)	113.4(2)	118.0(2)
Cl1–B1–E[a]	–	104.8(2)	109.3(2)	110.5(1)	113.0(1)
C5′–B1–E[a]	111.7(2)	–	–	–	–

[a] E defines the respective donor atom of the Lewis base (**6**: N1; **11**: O1; **3**, **13**, **14**: C5).

donor strength of the Caac than the used NHC donors.[28,29]

Conclusion

We have analyzed a series of Lewis acid–base adducts of boroles with different electron-pair donors. We showed that the relative Lewis acidity of [$PhBC_4Ph_4$] (**1**) is significantly increased over that of [$MesBC_4Ph_4$] (**4**). This was performed by a Lewis base transfer experiment from complex [$MesBC_4Ph_4$(4-MeC_5H_4N)] (**6**) to free borole **1**, which proved to be a spontaneous and quantitative reaction. In addition, the haloborole [$ClBC_4Ph_4$] (**10**) forms an unusual thermally stable Lewis adduct with thf and various carbenes, which were analyzed by means of single-crystal X-ray diffraction. The latter might serve as useful precursors for novel π-boryl anion derivatives potentially formed by two-electron reduction.

Experimental Section

General Considerations: All syntheses were carried out under argon with standard Schlenk and glovebox techniques. 1-Mesityl-2,3,4,5-tetraphenylborole,[14] 1-chloro-2,3,4,5-tetraphenylborole,[4] 1,1-dimethyl-2,3,4,5-tetraphenylstannole, 1,2,3,4,5-tetraphenylborole,[1] IMes, SIMes,[30] and Caac[28] were prepared according to published procedures. 4-Picoline was dried with CaH_2 and distilled under argon. Hexane, benzene, diethyl ether, and tetrahydrofuran (thf) were dried by distillation from Na/K alloy under argon and stored over molecular sieves. Likewise, dichloromethane (CH_2Cl_2) was dried by distillation from P_2O_5. $CDCl_3$ was dried with CaH_2, distilled under argon, and stored over molecular sieves. CD_2Cl_2 was degassed with three freeze–pump–thaw cycles and stored over molecular sieves. Elemental analyses were obtained with an Elementar Vario MICRO cube instrument. NMR spectra were recorded with a Bruker Avance 500 NMR spectrometer (500 MHz for ^1H, 160 MHz for ^{11}B, 126 MHz for $^{13}C\{^1H\}$). Chemical shifts are given in ppm and are referenced against external Me_4Si (^1H, ^{13}C) and [$BF_3{\cdot}Et_2O$] (^{11}B).

Synthesis of 6: A solution of 4-picoline (22.0 mg, 236 μmol) in hexane (2 mL) was added dropwise to a cooled (–40 °C) suspension of **4** (131 mg, 232 μmol) in hexane (2 mL), thus resulting in the formation of a yellow suspension. The mixture was warmed to ambient temperature and stirred for 1 h. The solid was filtered, washed with hexane (2× 1 mL), and recrystallized from thf/hexane (1:1) at –30 °C. [$MesBC_4Ph_4$(4-pic)] (**6**) (73.0 mg, 126 μmol, 54%) was obtained as a pale yellow solid. Single crystals suitable for X-ray diffraction were obtained by diffusion of hexane into a solution of **6** in thf. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.05 (s, 3 H, *o*-CH_3 Mes), 2.30 (s, 3 H, *p*-CH_3 Mes), 2.31 (s, 3 H, 4-CH_3 Pic), 2.81 (s, 3 H, *o*-CH_3 Mes), 6.58 (br. s, 1 H, *m*-C*H* Mes), 6.72–6.73 (m, 4 H, C_6H_5), 6.82–6.97 (m, 17 H, C_6H_5 and *m*-C*H* Mes), 7.00–7.02 (m, 2 H, C*H* Pic), 8.53–8.54 (m, 2 H, C*H* Pic) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 4.5 ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 21.02, 21.42, 23.76, 24.38 (*C*H_3), 124.23, 125.25, 125.89, 127.04, 127.09, 129.07, 129.28, 129.65, 130.17, 143.56 (*C*H), 134.19, 140.01, 141.36 (br.), 142.73, 143.66, 143.86, 149.60, 152.52, 158.57 (br., C_q) ppm. UV/Vis (CH_2Cl_2): λ (ε) = 327 (br. sh, 8000 L mol^{-1} cm^{-1}) nm. $C_{43}H_{38}BN$ (579.59): calcd. C 89.11, H 6.61, N 2.42; found C 88.71, H 6.79, N 2.39.

Synthesis of 7: In a J. Young NMR spectroscopy tube, 4-picoline (6.3 mg, 6.75 μmol) was added to a solution of **1** (30.0 mg, 6.75 μmol) in CH_2Cl_2 (0.6 mL), thus resulting in an immediate color change of the solution from dark blue to yellow. After slow evaporation of the solvent, the solid was washed with hexane and dried under vacuum to yield **7** (30.9 mg, 5.75 μmol, 85%) as a yellow solid. ^1H NMR (500 MHz, CD_2Cl_2): δ = 2.45 (s, 3 H, 4-CH_3 Pic), 6.65–6.67 (m, 4 H, C_6H_5), 6.84–6.90 (m, 6 H, C_6H_5), 6.95–7.03 (m, 10 H, C_6H_5), 7.15–7.22 (m, 3 H, C_6H_5), 7.28–7.29 (m, 2 H, C*H* Pic), 7.40–7.42 (m, 2 H, C_6H_5), 8.54–8.55 (m, 2 H, C*H* Pic) ppm. ^{11}B NMR (160 MHz, CD_2Cl_2): δ = 3.5 ppm. ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 21.71 (*C*H_3), 124.55, 125.67, 126.69, 127.46, 127.52, 127.63, 129.19, 130.67, 133.71, 145.83 (*C*H), 140.58, 143.35, 150.44, 154.34, 158.49 (Cq) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 355 (8340 L mol^{-1} cm^{-1}) nm. $C_{40}H_{32}BN$ (537.51): calcd. C 89.38, H 6.00, N 2.61; found C 89.93, H 6.40, N 2.87.

Lewis Base Transfer from 6 to 1: In a J. Young NMR spectroscopy tube, **1** (16.5 mg, 37.1 μmol) was added in one portion to a solution of **6** (21.5 mg, 37.1 μmol) in CD_2Cl_2 (0.6 mL). The initially yellow solution turned dark blue upon addition of **1** and within 5 min changed to dark green. ^1H and ^{11}B NMR spectra measured after 50 min show the characteristic sets of signals of **7** and **4** indicative of a quantitative transfer of 4-picoline from **6** to **1**.

Synthesis of 11: A solution of BCl_3 (4.5 mL, 2.08 M, 1.10 g, 9.36 mmol) in hexane was added dropwise to a cooled (–45 °C) solution of $Me_2SnC_4Ph_4$ (0.96 g, 1.90 mmol) in CH_2Cl_2 (6 mL) within 5 min. A dark purple solution was formed immediately. The reaction mixture was stirred at –20 °C for 3.5 h and at 0 °C for 1 h. All volatiles were removed under vacuum at 0 °C, and the residue was dissolved in CH_2Cl_2 (4 mL) at –20 °C. After the addition of thf (0.3 mL), an immediate color change from purple to orange was observed. The mixture was stirred at ambient temperature for 10 min before the solvents and the Me_2SnCl_2 byproduct were removed by sublimation (35 °C, 1×10^{-3} mbar). The orange-colored residue was dissolved in thf (3 mL), and hexane (2.5 mL) was added after filtration to obtain a yellow solid that was washed with hexane (3× 2 mL) and dried under vacuum. [$ClBC_4Ph_4$(thf)] (**11**) (0.48 g, 1.01 mmol, 53%) was obtained as a pale yellow solid. Single crystals suitable for X-ray diffraction were obtained by diffusion of hexane into a solution of **11** in thf. ^1H NMR (500 MHz, CD_2Cl_2): δ = 1.89–1.94 (m, 4 H, CH_2), 4.30–4.32 (m, 4 H, CH_2), 6.85–6.87 (m, 4 H, C_6H_5), 7.02–7.08 (m, 8 H, C_6H_5), 7.12–7.15 (m, 4 H, C_6H_5), 7.20–7.22 (m, 4 H, C_6H_5) ppm. ^{11}B NMR (160 MHz, CD_2Cl_2): δ = 12.4 ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ = 25.33, 74.74, (*C*H_2), 125.64, 126.38, 127.71, 128.04, 129.40, 130.23 (*C*H), 138.89, 141.23, 144.17 (br.), 151.71 (C_q) ppm. $C_{32}H_{28}BClO$ (474.84): calcd. C 80.94, H 5.94; found C 81.09, H 6.02.

Synthesis of 13: Benzene (20 mL) was added to a mixture of **10** (400 mg, 0.99 mmol) and IMes (302 mg, 0.99 mmol) at ambient temperature. After stirring for 20 min, the solvent was removed under vacuum to give a brown solid, which was washed with hexane (20 mL) and extracted with diethyl ether (100 mL). The diethyl ether solution was dried under vacuum to give [$ClBC_4Ph_4$(IMes)] (**13**) as a yellow solid (351 mg, 0.50 mmol, 51%). Single crystals suitable for X-ray diffraction were obtained by diffusion of hexane into a solution of **13** in CH_2Cl_2. ^1H NMR (500 MHz, CD_2Cl_2): δ = 1.78 (s, 12 H, *o*-CH_3 Mes), 2.42 (s, 6 H, *p*-CH_3 Mes), 6.56–6.60 (m, 4 H, C*H* Mes), 6.89–6.95 (m, 14 H, C_6H_5), 6.96 (s, 2 H, $CH_{imidazoline}$), 7.11–7.14 (m, 6 H, C_6H_5) ppm. ^{11}B NMR (160 MHz, CD_2Cl_2): δ = –3.0 ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ = 18.66, 21.23 (*C*H_3), 124.77, 124.87, 125.30, 126.97, 127.22, 129.31, 130.50, 130.57 (*C*H), 134.68, 136.12, 139.82, 140.96, 142.50, 151.10

(C_q) ppm. $C_{49}H_{44}BClN_2$ (707.16): calcd. C 83.22, H 6.27, N 3.96; found C 82.81, H 6.11, N 3.24.

Synthesis of 14: Benzene (10 mL) was added to a mixture of **10** (200 mg, 0.50 mmol) and *N*-(2,6-diisopropylphenyl)-2,2,4,4-tetramethylpyrrolidine-5-ylidene (141 mg, 0.50 mmol) at ambient temperature. After stirring for 20 min, the solvent was removed under vacuum to give a brown solid, which was washed with hexane (10 mL) and extracted with diethyl ether (50 mL). The diethyl ether solution was dried under vacuum to give [ClBC$_4$Ph$_4$(Caac)] (**14**) as a yellow solid (161 mg, 0.23 mmol, 46%). Single crystals suitable for X-ray diffraction were obtained by diffusion of hexane into a solution of **14** in CH_2Cl_2. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.64 (d, ^3J = 6.45 Hz, 6 H, CH_3 dipp), 1.04 (d, ^3J = 6.50 Hz, 6 H, CH_3 dipp), 1.25 (s, 6 H, CH_3), 1.89, (s, 6 H, CH_3), 2.28 (s, 2 H, CH_2), 2.38–2.46 (m, 2 H, C*H* *i*Pr), 6.63–6.65 (m, 4 H, C_6H_5), 6.84–6.89 (m, 6 H, C_6H_5), 6.99–7.08 (m, 6 H, C_6H_5 and C*H* dipp), 7.10–7.15 (m, 6 H, C_6H_5), 7.29–7.32 (m, 1 H, C*H* dipp) ppm. ^{11}B NMR (160 MHz, CD_2Cl_2): δ = –1.9 ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ = 23.83, 26.84, 29.87, 30.22 (*C*H$_3$), 51.13 (*C*H$_2$), 29.51, 124.90, 125.00, 125.28, 126.92, 127.12, 129.11, 130.40, 130.83 (*C*H), 55.32, 80.53, 134.43, 140.13, 144.37, 146.00, 152.25 (C_q) ppm. $C_{48}H_{51}BClN$ (688.20): calcd. C 83.77, H 7.47, N 2.04; found C 84.26, H 7.49, N 2.08.

Crystal Structure Data: The crystal data of **3**, **11**, **13**, and **14** were collected with a Bruker X8-APEX II diffractometer with a CCD area detector and multilayer-mirror-monochromated Mo-K_α radiation. The crystal data of **6** were collected with a Bruker APEX diffractometer with CCD area detector and graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods, refined with the SHELX software package[31] and expanded by using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized geometric positions and included in the structure factor calculations. CCDC-908226 (**3**), -908227 (**6**), -908228 (**11**), -908229 (**13**), and -908230 (**14**) 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.

Crystal Data for 3: $C_{49}H_{46}BClN_2$; M_r = 709.14; yellow block, 0.20 × 0.20 × 0.10 mm; monoclinic, space group $P2_1/n$; a = 11.972(2) Å, b = 14.729(3) Å, c = 22.019(5) Å; α = 90°, β = 91.166(10)°, γ = 90°; V = 3882.2(14) Å^3; Z = 4, $\rho_{calcd.}$ = 1.213 g cm^{-3}; μ = 0.136 mm^{-1}; F(000) = 1504; T = 100(2) K; R_1 = 0.0476, wR^2 = 0.1078; 7701 independent reflections ($2\theta \leq 52.28°$) and 484 parameters.

Crystal Data for 6: $C_{43}H_{38}BN$; M_r = 579.55; yellow needles, 0.19 × 0.07 × 0.06 mm; hexagonal, space group $R\bar{3}$; a = 41.2393(15) Å, b = 41.2393(15) Å, c = 11.6474(5) Å; α = 90°, β = 90°, γ = 120°; V = 17154.7(11) Å^3; Z = 18; $\rho_{calcd.}$ = 1.010 g cm^{-3}; μ = 0.057 mm^{-1}; F(000) = 5544; T = 100(2) K; R_1 = 0.0708, wR^2 = 0.1095; 7828 independent reflections ($2\theta \leq 52.84°$) and 410 parameters.

Crystal Data for 11: $C_{32}H_{28}BClO$; M_r = 474.80; yellow block, 0.14 × 0.16 × 0.33 mm; orthorhombic, space group $Pca2(1)$; a = 10.9923(14) Å, b = 11.8853(15) Å, c = 19.727(3) Å; α = 90°, β = 90°, γ = 90°; V = 2577.3(6) Å^3; Z = 4; $\rho_{calcd.}$ = 1.224 g cm^{-3}; μ = 0.171 mm^{-1}; F(000) = 1000; T = 173(2) K; R_1 = 0.0717, wR^2 = 0.1485; 6486 independent reflections ($2\theta \leq 56.92°$) and 316 parameters.

Crystal Data for 13: $C_{49}H_{44}BClN_2$; M_r = 707.12; colorless block, 0.20 × 0.19 × 0.18 mm; monoclinic, space group $P2_1/n$; a = 11.9493(6) Å, b = 14.6325(9) Å, c = 22.0119(13) Å; α = 90°, β = 91.340(3)°, γ = 90°; V = 3847.7(4) Å^3; Z = 4; $\rho_{calcd.}$ = 1.221 g cm^{-3}; μ = 0.137 mm^{-1}; F(000) = 1496; T = 173(2) K; R_1 = 0.0694, wR^2 = 0.0993; 8218 independent reflections ($2\theta \leq 53.64°$) and 484 parameters.

Crystal Data for 14: $C_{48}H_{51}BClN$; M_r = 688.16; yellow block, 0.316 × 0.213 × 0.178 mm; monoclinic, space group $P2_1/n$; a = 9.712(9) Å, b = 18.521(16) Å, c = 21.201(18) Å; α = 90°, β = 96.53(3)°, γ = 90°; V = 3789(6) Å^3; Z = 4; $\rho_{calcd.}$ = 1.206 g cm^{-3}; μ = 0.136 mm^{-1}; F(000) = 1472; T = 273(2) K; R_1 = 0.0410, wR^2 = 0.1066; 7504 independent reflections ($2\theta \leq 52.3°$) and 468 parameters.

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