Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Diradical Anion of Potassium Aggregate: Reduction of Dimer Boroxide Complex

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Supporting Information

ABSTRACT: Crystalline aggregates containing metal cation clusters "wrapped" by reduced hydrocarbon anions have been presented. Initially, a dimeric complex (2) possessing a bimetallic K_2O_2 core was synthesized from the reaction between an anthracene substituted boronic acid (2-(anthracen-9yl)phenyl)(hydroxy)(mesityl)borane (1-H) and KN(SiMe₃)₂ in THF solution. The B-O bond length (1.281(4) Å) in complex 2 is comparable to those observed in oxoboranes, indicating this may be a double bond, which is supported by its Wiberg bond order (1.9) predicted by density functional theory



calculations. Subsequently, potassium aggregate complexes, diradical 3 and dihydro anion 4, were obtained through the reduction reactions of dimeric complex 2 and 1-H, respectively. They exhibit similar K₃O₂B₂ aggregate structures, but differ significantly in the geometry of the anthracene units. Complex 3 features a triplet diradical character with planar anthracene units that carry the unpaired electrons, while the anthracene groups in complex 4 display a puckered structure due to the addition of hydrogen atoms.

INTRODUCTION

Metal ketyls, as important intermediates in a variety of organic carbonyl-involved reactions, have received continuous attention since their discovery in the previous century¹⁻⁴ (Scheme 1a). Extensive studies have led to the emergence of a number

Scheme 1. Diagram of the Reduction of Ketones (a) and Their Boron Isoelectronic Analogues (b)



of structurally characterized stable alkali-metal, $^{5-9}$ alkaline-earth-metal, 10 transition-metal, 11,12 and rare-earth metal $^{13-16}$ ketyls complexes. These radical species are synthetically useful and have been used in various organic and organometallic reactions as strong reductants. In contrast, their boroncontaining isoelectronic analogues (Scheme 1b) are elusive. On the other hand, boroxide ligands have been applied in coordination chemistry¹⁷ with different main group met-als¹⁸⁻²² and transition metals²³⁻²⁸ and exhibited distinct catalytic properties.^{21,28} Although hundreds of these species have been well investigated in their neutral form, the study of the structure of the corresponding reduced radical and anionic species is rare.

Crystalline aggregates consisting of charged organic molecules held together by metal-cluster-mediated Coulomb interactions have attracted substantial interest owing to their unusual structural, chemical, and electronic properties. In the reduction chemistry of aromatic hydrocarbons,^{29,30} such as biphenyl,³¹ pyrene,^{32,33} and anthracene,³⁴ crystalline aggregates containing metal cation clusters "wrapped" by corresponding reduced hydrocarbon radical anions have also been extensively investigated.^{35–38} They exhibited various structural features and have been applied to electron transfer reactions and polymerization.²⁹ These exciting aggregation behaviors were mainly caused by cation- π interaction, which plays an important role in the formation and stability of the reduced species. On the basis of our previous works,^{39,40} by choosing the anthracene moiety as the substituent group, which is favorable to form an aggregation unit through cation- π interaction, we herein present the reduction behaviors of its boroxide-substituted derivative 1-H and the corresponding dimer complex 2, and describe the electronic and aggregation characteristics of the reduced species 3 and 4. The experimental results show that 3 displays a K₃O₂B₂ cluster structure with planar anthracene moieties and exhibits triplet diradical character, while the closed-shell species 4 features a similar K₃O₂B₂ aggregate structure with puckered anthracene

Received: July 30, 2018

Scheme 2. Synthesis of Compound 1-H



units, accompanied by a loss of aromaticity in the central ring of the anthracene group.

RESULTS AND DISCUSSION

Synthesis, Structure, and Characterization of Compounds 1-H and 2. (2-(Anthracen-9-yl)phenyl)(hydroxy)-(mesityl)borane (1-H) was obtained in moderate yield (40%) from the reaction between "BuLi lithiated 9-(2-bromophenyl)anthracene in THF and freshly prepared mesityl-5,5-dimethyl-1,3,2-dioxaborinane at -78 °C (Scheme 2). The ¹¹B NMR resonance of 1-H appears at 48.2 ppm, indicating the formation of diarylborinic acid. In the ¹H NMR spectrum, the peak at 5.22 ppm confirms the existence of protons of boric acid. In addition, the precursor 1-H was further verified with X-ray diffraction (Figure S1). The lengths of B1-O1 and B2-O2 bonds are 1.354(4) Å and 1.356(4) Å, respectively, which are in the range of those reported B–O distances in $Ar'_{2}BOH$ (1.335(2)–1.368(5) Å).^{18,41–44} Treatment of 1-H with $KN(SiMe_3)_2$ in THF solution afforded a yellowish solid 2 (Scheme 3). The ¹¹B NMR resonance of **2** appears at δ = 38.0 ppm. This is obviously shifted upfield compared to other reported metal boroxide complexes ([$(\mu-Mes_2BO)AlR_2$]₂, R =

Scheme 3. Synthetic Route of Complexes 2-4



Me and Et, 57.3 ppm;¹⁹ $[(\mu-Mes_2BO)ZnEt]_2$, 51.0 ppm;²⁷ $(Mes_2BO)ZnEt\cdot2,2'$ -bipy, 48.5 ppm²⁷), which may be caused by the strong π -electron donation from the oxygen atom to the boron center in the B–O double bond.

Crystals of 2 suitable for an X-ray structure determination were grown from a saturated THF solution at room temperature. Similar to previously reported complexes,¹⁸ complex 2 (Figure 1a) displays a dimeric structure with two boroxide ligands connected by a bimetallic K₂O₂ core. Each K⁺ has cation- π interaction with both anthracene (2.99 Å) and Mes (3.15 Å) groups, besides coordination with a THF molecule. It is worth noting that the distance between B and O is 1.281(4) Å, which is similar to the B=O bond distances (1.296(3)-1.314(3) Å, Figure S2) in oxoboranes,⁴⁵⁻⁴⁷ indicating this may be a double bond. This is supported by its Wiberg bond order (1.9) predicted by density functional theory (DFT) calculations at the CAM-B3LYP/6-31G(d) level of theory (see Supporting Information for details). The LUMO and LUMO+1 of 2 are localized on the two anthracene units and are nearly energetically degenerated (Figure 2a), indicating a diradical state may be formed upon direduction of 2.

Synthesis, Structure, and Characterization of Complex 3. Recently, a series of reduction reactions of neutral complexes bridged by metal cations or metal clusters were reported⁴⁸⁻⁵² to produce reduced species with interesting radical characters, encouraging us to explore if 2 has a similar property. First, cyclic voltammetry of complex 2 was recorded in THF with 0.1 M "Bu₄NPF₆ as the supporting electrolyte. A quasi-reversible reduction event occurs at -2.14 V vs Fc/Fc⁺ (Figure 1b), which is close to that of anthracene (E = -2.48 V vs Fc/Fc^+),⁵³ indicating that the anthracene moiety of dimer 2 probably accepts electrons to form a stable radical anion under this condition. Next, the chemical reduction of 2 was performed in freshly distilled THF at room temperature. The solution gradually changed from colorless to dark-blue when 2.2 equiv of potassium chips and 1.0 equiv of [2,2,2]-cryptand were added. The dark-blue solids of 3 were obtained with a moderate yield (71%) from a frozen THF solution. Although 3 is highly sensitive to air and moisture, it is thermally stable under argon at room temperature.

The X-band EPR spectra of **3** (Figure 3) in THF solution were recorded at both 298 and 115 K. The room temperature spectrum (Figure 3a) shows a complex but nicely resolved signal (centered at g = 2.0045) that is maintained for several days, indicating the formation of a highly persistent radical anion. The simulation analysis successfully reproduced the

Article



Figure 1. (a) Thermal ellipsoid (50%) drawing of crystals 2. All H atoms, free solvent THF molecules are omitted for clarity. Selected bond lengths (Å): B1–O1 1.281(4), B1–C1 1.620(4), B1–C21 1.635(4), K1–O1 2.554(2), K1–O1A 2.626(2). (b) Cyclic voltammogram of 2 (1×10^{-3} M) in THF, containing 0.1 M ⁿBu₄NPF₆ measured at 100 mV s⁻¹ at room temperature.



Figure 2. (a) LUMO and LUMO+1 for 2. The molecular orbital energies are given in the parentheses. (b) Spin density distribution for both the open-shell singlet (OS) and triplet (T) states of diradical anion $3a^{--}$. All hydrogen atoms are omitted for clarity.



Figure 3. EPR spectra of 3 in THF measured at (a) 298 K ($1 \times 10^{-4} \text{ mol/L}$) and (b) 115 K ($5 \times 10^{-3} \text{ mol/L}$). The central peak in (b) shows the signal derived from monoradical impurities, and the inset shows the $\Delta m_s = 2$ resonance.

spectrum (Figures 3a and S3). The hyperfine coupling constants (a(H1) = 6.0 G, a(H2) = 3.0 G, and a(H3) = 1.20 G) are similar to other anthracene derivatives' radical anions.⁵⁴ This coupling pattern suggests that the unpaired electrons are highly delocalized over the anthracene moieties of boroxide anion ligands. The frozen solution (THF, 115 K) EPR spectrum (g = 2.0037, Figure 3b) of complex 3 confirmed that it is a triplet diradical species, and each anthracene group carries one unpaired electron. From the zero-field splitting parameters (D = 6 mT; E = 0 mT), the distance between the two unpaired electrons (the average spin-spin distance) was calculated to be 7.74 Å, which is close to the distance (7.22 Å) between the geometric centers of the two anthracene moieties in the crystal structure of 3. Further evidence for the triplet diradical nature of 3 was the observation of a half-field signal at

1686 G corresponding to the forbidden $\Delta m_{\rm s} = 2$ transition. In addition, DFT calculations show that $3a^{--}$ has a triplet ground state, but the energy gap between the open-shell singlet state (OS) and the triplet state (T) is rather small ($\Delta E_{\rm OS-T} = 0.002$ kcal mol⁻¹). The two states show nearly identical structures (all atom positional root-mean-square deviation (RMSD) < 0.006 Å). The spin density resides almost exclusively on the anthracene moieties and delocalizes over the whole anthracene backbone (Figure 2b).

Crystals of **3** suitable for single-crystal X-ray diffraction were obtained from the THF solution at room temperature. Figure 4a displays its crystal structure. A list of its important structure parameters, as well as those of **1-H** and **2**, is given in Table S1. According to X-ray diffraction, complex **3** consists of a discrete $[K(cryptand)]^+$ ion and a diradical $K_3O_2B_2$ cluster anion, in



Figure 4. Thermal ellipsoid (40%) drawing of anion **3a**⁻⁻⁻ (a) and **4a**⁻ (b). Except for four H atoms of C14 and C43 in **4a**⁻, other H atoms, free THF molecules are omitted for clarity. Selected bond lengths (Å): in **3a**⁻⁻⁻ B1–O1 1.295(6), B2–O2 1.308(6), C1–B1 1.600(7), C21–B1 1.622(8), C30–B2 1.599(7), C50–B2 1.607(8), C13–C14 1.378(8), C14–C15 1.410(9), C42–C43 1.390(7), C43–C44 1.393(8); in **4a**⁻: B1–O1 1.310(7), B2–O2 1.302(7), C1–B1 1.599(7), C21–B1 1.635(7), C30–B2 1.603(8), C50–B2 1.637(7), C13–C14 1.467(8), C14–C15 1.470(8), C42–C43 1.482(7), C43–C44 1.498(7).

which the K₃O₂B₂ core contains potassium cation clusters "wrapped" by two boroxide radical dianions. The cluster core has approximately 3-fold rotational symmetry with the axis bisecting the two O atoms (Figure S4). All three K⁺ ions are involved in the cation- π bonding to anthracene units in a way that each anthracene group accommodates two K⁺ ions. K1 and K2, while each being coordinated to one THF molecule, bond to two oxygen atoms (O1 and O2) and form cation- π bonds with anthracene and Mes groups from different boroxide ligands. The third K⁺ center K3 also bonds to the two oxygen atoms, but it is sandwiched between two anthracene moieties with no interaction with the Mes groups. Meanwhile, this coordination of K3 ion also causes the change of dihedral angle of two anthracene units, which is up to 60.46° (Figure S5). Regarding the structure of boroxide ligands, the B1-O1 and B2-O2 bonds (1.295(6) and 1.308(6) Å) undergo an obvious elongation going from complexes 2 to 3, while the B1(or B2)-C(Mes) bond clearly shortens. But the lengths of B1-O1 and B2-O2 bonds are still in the range of double bonds. The structure of the anthracene subunit in complex 3 exhibits a small difference relative to complex 2 (see Table S2 for details). The skeleton remains planar with experimental error, and the largest deviation of individual centers from the mean plane amounts to about 0.08 Å.

Synthesis, Structure, and Characterization of Complex 4. The reactivity of 3 was tested by adding 1.0 equiv of "Bu₃SnH, Ph₃SiH, and 1,4-cyclohexadiene to its THF solution at room temperature, respectively, and monitoring if the corresponding dihydro anion would be formed. However, no hydrogen abstraction was observed, probably due to the low activity of these hydrogen donor reagents. Subsequently, a new experiment was designed to directly reduce the boronic compound 1-H using 2.2 equiv of the potassium chips. The solution changed from colorless to yellowish to dark-blue and then immediately turned dark-red. The product was identified as dihydro anion 4. It should be noted that the crystals obtained from the yellow solution were identified as complex 2 through X-ray diffraction. In addition, the EPR spectrum of the blue solution was measured at both room temperature and 115 K, and displays the same signal as that of diradical 3 (Figure S8). These experimental results along with the color change of the reaction thus implies the formation of 4 is a three-step process with complexes 2 and 3 as intermediates. The dark-red crystals of 4 were obtained from the THF solution with 53% isolated yield (Scheme 3). The ¹¹B NMR resonance appears at δ = 38.2 ppm, which is almost identical to dimer 2, indicating an insignificant environment change around the boron center. In the ¹H NMR spectrum, the chemical shifts of anthracene moieties in 4 are obviously upfield relative to the dimer 2, which is caused by the effect of more negative charges in the anthracene units. The signals of the four hydrogen atoms bound to C14 and C43 were not observed due to the overlap with THF signals. However, combining the ¹³C NMR and DEPT (Figure S23) spectra, the existence of peaks at 99.6 ppm (C7 and C36) and 39.7 ppm (C14 and C43) could clearly demonstrate the formation of 4.5

Although it is difficult to unambiguously determine the backbone structure of 4 from the spectroscopic data, X-ray measurements confirmed its structure. The X-ray analysis revealed complex 4 possesses a similar K₃O₂B₂ core structure (Figures 4b and S6) to complex 3, but there are two distinct structural changes. First, the average (1.480 Å) of the lengths of C13-C14, C14-C15, C42-C43, and C43-C44 bonds in the anthracene units obviously increases due to the addition of hydrogen atoms, which leads to the hybridization mode change of C14 and C43 atoms from sp² to sp³. Meanwhile, these changes result in the formation of a puckered anthracene geometry (Figure S7), which simultaneously gives rise to the change of aromaticity. This puckered geometry of the anthracene units also creates a more crowded coordination environment around the K2 center, causing the departure of the coordinated THF.

The UV-vis-NIR absorption spectra of 1-H, 2, 3, and 4 obtained in THF solution are shown in Figure 5. The neutral ligand 1-H displays three intense absorption bands in the range of 350-400 nm. The intensity of these bands was increased after the formation of complex 2. In addition to these bands, the dark blue diradical anion 3 exhibits a broad and less intense absorption (main peaks: 556, 604, 667, and 758 nm) in the range of 500-900 nm, which are similar to other anthracene substituted radical anions.^{56,57} In contrast, the dihydro anion 4 manifested a strong absorption at 477 nm, as well as a rather weak and wide peak (600-850 nm) that was due to the existence of a small amount of residual 3. On the basis of TD-DFT calculations (Figures S9-S13, Tables S3-S6), we attribute the maximum absorptions of these complexes to ligand-based $\pi - \pi^*$ transitions. For compounds 1-H and 2, the transitions are either HOMO \rightarrow LUMO or HOMO-1 \rightarrow

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Figure 5. UV–vis-NIR spectra of compounds **1-H**, **2**, **3**, and **4** in THF solution (**1-H** and **2**: 2×10^{-4} mol/L; **3** and **4**: 6×10^{-4} mol/L). In the spectrum of **4**, there is a wide peak in the range of 600–850 nm, which is caused by the existence of a small quantity of diradical **3**.

LUMO+1, whereas more complex transitions are found for 3 and 4 with $\pi - \pi^*$ transition being the main contributor.

CONCLUSION

In conclusion, we herein have described the stabilization of a triplet diradical anion $3a^{--}$ and its dihydro anion $4a^{--}$. The former was synthesized through the reduction of dimer boroxide complex 2, while the latter was prepared via directly reducing the boronic compound 1-H. Both complexes 3 and 4 possess a similar $K_3O_2B_2$ aggregate structure, but the geometries of the anthracene units are different. The former is planar while the latter has a puckered structure. According to the experimental and computational results, a clear change in the geometry and aromaticity of the anthracene moiety was revealed from dimeric potassium boroxide complex 2 to diradical anion $3a^{--}$ to cluster anion $4a^{--}$. Further studies on the chemical reaction of these reduced species are underway.

EXPERIMENTAL SECTION

General Procedures. All reactions and manipulations were carried out under an argon atmosphere by using standard Schlenk techniques and a glovebox. CDCl₃ was dried by 4 Å molecular sieve (2-3 days). C₆D₆ and THF-d₈ were dried over Na/K alloy without benzophenone (2-3 days). Prior to use, the solvents were dried by refluxing with sodium and benzophenone and degassed by applying three freeze-pump-thaw cycles. The 9-iodoanthracene,58 mesitylboronic acid,⁵⁹ and 2-mesityl-5,5-dimethyl-1,3,2-dioxaborinane⁶⁰ were synthesized according to literature methods, respectively. The ¹H and ¹³C NMR spectra were performed using a JEOL JNM-ECS-400 or INOVA 600NB (Bruker) at room temperature in ppm downfield from Me₄Si. The ¹¹B NMR spectra were also recorded using a JEOL JNM-ECS-400 at room temperature in ppm downfield from external aqueous BF3. Et2O. The cyclic voltammetry experiment was conducted in an argon-filled atmosphere using a CHI 760e Electrochemical Workstation. Freshly distilled THF was used as solvent, and "Bu₄NPF₆ (10⁻¹ M) was used as electrolyte. A standard three-electrode cell configuration was employed using a glassy carbon working electrode, a Pt wire counter electrode, and an saturated calomel serving as the reference electrode. Formal redox potentials were referenced to the ferrocene/ferrocenium redox couple [E(Fc/ Fc^+) = 0 V]. The ESI mass spectra were recorded on a Thermo Scientific Orbitrap Elite mass spectrometer (LTQ Orbittrap Elite). The IR spectra were performed with a Nicolet 360 FTIR spectrometer in the region 4000-400 cm⁻¹ using KBr pellets. UVvis-NIR spectra were recorded on Agilent Carry 5000 UV-vis-NIR

spectrometer. Elemental analyses for C, H, and N were carried out with a German Elementary Vario EL cube instrument.

X-ray Crystallography. The data were collected with a SuperNova (Dual) X-ray diffractometer equipped with Cu/Mo K α radiation ($\lambda = 1.54184/0.71073$ Å) at a different temperature (1-H, 295 K; 2 and 4, 173 K; 3, 292 K). Data reduction was performed using CrysAlisPro (Version 1. 171. 37. 35). The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.^{61,62} Crystals structures were solved by direct methods using Olex 2-1.2. Subsequent difference Fourier analyses and least-squares refinement with SHELXL-2014/7 program package⁶³⁻⁶⁵ allowed for the location of the atom positions. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms were found in difference maps and refined using a riding model. More details on the crystallographic studies as well as atomic displacement parameters are given in CIF files deposited with the CCDC. The crystallographic details for compounds 1-H, 2, 3, and 4 are summarized in Table S1. The data have been deposited in the Cambridge Crystallographic Data Centre (CCDC), deposition numbers CCDC 1849078-1849081 for compounds 1-H, 2, 3, and 4. Although we attempted several times to measure the crystals of dimer 2, the largest electron residual peak (1.31 e Å⁻³) still exists. We also tried to refine it many times, but it still has not been solved. However, this electron residual peak does not affect the geometry of 2. Despite repeated measurements, the quality of the crystals of 3 was still not good enough due to the nature of twins. The uncertainties are relatively large and only allow for a qualitative discussion.

Computational Details. All the geometry optimizations were carried out at the (U)CAM-B3LYP/6-31G(d) level of theory. The obtained stationary points were characterized by frequency calculations. The symmetry-broken approach was applied for open-shell singlet calculations. The molecular orbitals, spin densities, and Wiberg bond order were calculated at the level of (U)CAM-B3LYP/6-31G(d) on the optimized geometries. The spin contamination errors were corrected by the approximate spin-projection method⁶⁶ when evaluating the singlet–triplet energy gaps (ΔE_{OS-T}). The Wiberg bond order was calculated with the Multiwfn program.⁶⁷ The UV–vis absorption spectra were calculated using the time-dependent DFT (TD-DFT) method at the (U)CAM-B3LYP/6-31G(d) level, and the polarized continuum model (PCM) was adopted for solvent (THF) effects. All calculations were performed with the Gaussian 09 program suite.⁶⁸

EPR Measurement. Solution EPR measurement was recorded at both room temperature and 115 K with a Bruker ER200DSRC10/12 spectrometer. Samples containing 10^{-4} M (298 K) or 5×10^{-3} (115 K) of 3 were prepared in a J. Young EPR tube inside a glovebox. Room temperature EPR spectrum was obtained with a microwave power of 6.13 mW, modulation amplitude of 0.8 G, time constant of 81.92 ms, and sweep time of 75 s. The frozen EPR spectrum was obtained with a microwave power of 0.8 G, time constant of 81.92 ms, and sweep time of 75 s. The Frozen EPR spectrum was obtained with a microwave power of 2.51 mW, modulation amplitude of 0.8 G, time constant of 81.92 ms, and sweep time of 75 s. The EPR spectrum was simulated using EasySpin with hyperfine coupling constants.

Synthesis of 9-(2-Bromophenyl)anthracene. To a mixture of 9-iodoanthracene (3.04 g, 10.0 mmol), 2-bromophenylboronic acid (2.10 g, 10.5 mmol), Pd(PPh₃)₄ (0.289 g, 0.25 mmol), K₂CO₃ (2.76 g, 20.0 mmol) were added a dioxane/H₂O (8:1, 45 mL) degassed mixed solvent. The reaction mixture was stirred at 110 °C for 24 h. Then, the organic layer was extracted with CH₂Cl₂ (3 × 40 mL) and dried over MgSO₄. Purification by flash column chromatography (SiO₂, hexane) yielded a colorless solid (1.39 g, 42%). M.p.: 136–138 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.44 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.39 (m, 3H), 7.30 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz): δ 139.7, 135.6, 133.0, 132.9, 131.4, 129.9, 129.5, 128.6, 127.5, 127.3, 126.2, 125.9, 125.6, 125.3. Elemental analysis: Calcd for C₂₀H₁₃Br: C 72.09, H 3.93%; Found: C 72.21, H 3.86%.

Synthesis of (2-(Anthracen-9-yl)phenyl)(hydroxy)(mesityl)borane (1-H). 9-(2-Bromophenyl)anthracene (3.32 g, 10.0 mmol) was dissolved in fresh distilled THF (100 mL), and the solution was cooled to -78 °C. "BuLi (6.90 mL, 11.0 mmol, 1.6 M in hexanes) was added slowly to the solution, and the mixture was stirred at -78 °C for 3 h. Then, 2-mesityl-5,5-dimethyl-1,3,2-dioxaborinane (2.32 g, 10.0 mmol) in THF (30 mL) was added, and the mixture was allowed to warm to room temperature. Subsequently, the reaction was quenched by 1.0 M aq. HCl (30 mL). The obtained biphasic mixture was stirred for 2 h at room temperature. The organic layer was collected, and the aqueous layer extracted with CH_2Cl_2 (3 × 50 mL). All combined organic layers were dried over Na₂SO₄, and the solvent was removed to obtain an orange oil. Purification by flash column chromatography (SiO₂, hexane/ethyl acetate, 20:1 and hexane/ethyl acetate, 10:1) yielded 1-H as a white solid (1.60 g, 40%). M. p.: 184-186 °C. UV-vis-NIR (THF): 333, 350, 368, and 388 nm. ¹H NMR $(CDCl_3, 400 \text{ MHz}): \delta 8.50 \text{ (s, 1H, Ar-H)}, 8.04 \text{ (d, } J = 8.0 \text{ Hz}, 2\text{H}, \text{Ar-H})$ H), 7.80 (d, J = 8.0 Hz, 1H, Ar-H), 7.64 (td, J = 7.2, 1.6 Hz, 1H, Ar-H), 7.57 (s, 1H, Ar-H), 7.55 (s, 1H, Ar-H), 7.45-7.53 (m, 3H, Ar-H), 7.31-7.37 (m, 3H, Ar-H), 6.58 (s, 2H, Mes-H), 5.22 (s, 1H, B-OH), 2.19 (s, 3H, Mes-CH₃), 1.95 (s, 6H, Mes-CH₃); ¹³C NMR (CDCl₃, 100 MHz): δ 144.3, 138.8, 137.3, 136.8, 131.9, 131.5, 130.6, 128.7, 127.8, 127.3, 127.1, 126.8, 126.0, 125.5, 22.2 (Ar-CH₃), 21.3 (Ar-CH₃); ¹¹B NMR (128.3 MHz, CDCl₃, ppm, 293 K): δ 48.2 ppm. IR (KBr, cm⁻¹): 3513 (s), 3048, 2906, 2854, 1943 (w), 1822 (w), 1722, 1603, 1557, 1439, 1363, 1557, 1439, 1363, 1326, 1285 (s), 1160, 1113, 1069, 944, 891, 848, 800, 737, 666. MS (ESI): calculated for $[C_{29}H_{25}BO + Na]^+: 423.1891;$ found: 423.1893. Elemental analysis: Calcd for C29H25BO: C 87.01, H 6.29%; Found: C 86.89, H 6.17%.

Synthesis of {[K(THF)]⁺·[1⁻]}₂ (2). Under anaerobic and anhydrous conditions, compound 1-H (0.20 g, 0.50 mmol) was dissolved in THF (~35 mL) at room temperature. KN(SiMe₃), (0.52 mL, 0.52 mmol, 1.0 M in hexanes) was added slowly to the solution, and the mixture was stirred for 3 h. The yellowish solution was filtered to remove the insoluble substance. Then the filtrate was concentrated in vacuo, and the yellowish solid was obtained. The crude product was washed three times with hexanes, allowing for isolation of product 2. X-ray-quality yellow crystals of 2 were obtained in THF solution at room temperature. Yield: 0.454 g (89%). M. p.: 169-171 °C. UVvis-NIR (THF): 335, 351, 369, and 389 nm. ¹H NMR (C₆D₆, 400 MHz): δ 7.96 (s, 1H, Ar-H), 7.68 (d, J = 8.0 Hz, 2H, Ar-H), 7.63 (d, J = 12 Hz, 2H, Ar-H), 7.46 (d, J = 4.0 Hz, 1H, Ar-H), 7.38 (t, J = 8.0 Hz, 1H, Ar-H), 7.30 (t, J = 8.0 Hz, 1H, Ar-H), 7.12 (d, J = 8.0 Hz, 2H, Ar-H), 7.06 (d, J = 8.0 Hz, 1H, Ar-H), 6.95 (t, J = 8.0 Hz, 2H, Ar-H), 6.17 (s, 2H, Mes-H), 3.55 (t, J = 8.0 Hz, 8H, O-CH₂-), 2.14 (s, 3H, Mes-CH₃), 1.41 (m, 14H, overlap of O-CH₂-CH₂- and Mes-CH₃); ¹³C NMR (C₆D₆, 100 MHz): δ 148.9, 146.8, 143.4, 142.7, 137.2, 136.6, 134.4, 132.1, 131.8, 131.0, 129.1, 128.1, 127.8, 126.3, 125.4, 125.2, 68.4 (THF), 26.4 (THF), 23.5 (Ar-CH₃), 21.8 (Ar-CH₃); ¹¹B NMR (128.3 MHz, C₆D₆, ppm, 293 K): δ 38.0 ppm. IR (KBr, cm⁻¹): 3431 (br), 3045, 2918, 2861, 1939 (w), 1613, 1439 (s), 1411, 1153, 1060, 943, 882, 848, 801, 741 (s), 673. Calcd for $C_{66}H_{64}B_2K_2O_4$ ·THF: C 76.91, H 6.64%; Found: C 76.92, H 6.49%.

Synthesis of [K(cryptand)]⁺·3a⁻⁻⁻ (3). Under anaerobic and anhydrous conditions, a mixture of 2 (0.204 g, 0.20 mmol), [2,2,2]cryptand (0.075 g, 0.20 mmol) and potassium chips (0.017 g, 0.44 mmol) in THF (~30 mL) was stirred at room temperature. The color of the mixture solution changed from yellowish to dark-blue. Then the blue solution was filtered to remove the dark insoluble substance. The filtrate was concentrated in vacuo, and the dark-blue solid was obtained. The crude product vas washed three times with hexanes, allowing for isolation of product 3. X-ray-quality dark-blue crystals of 3 were obtained in THF solution at room temperature. Yield: 0.209 g (71%). M.p.: 80 °C (decompose). UV–vis-NIR (THF): 556, 604, 667, and 758 nm. IR (KBr, cm⁻¹): 3430 (br), 3040, 2963, 2880 (s), 1599 (w), 1444 (s), 1356, 1302, 1257, 1103 (s), 943, 840, 741. Calcd for C₈₄H₁₀₀B₂K₄N₂O₁₀: C 68.37, H 6.83, N 1.90%; Found: C 68.13, H 6.69, N 1.79%.

Synthesis of $[K(cryptand)]^{+}4a^{-}$ (4). Under anaerobic and anhydrous conditions, a mixture of 1-H (0.160 g, 0.40 mmol), [2,2,2]-cryptand (0.075 g, 0.20 mmol) and potassium chips (0.033 g, 0.84 mmol) in THF (~20 mL) was stirred at room temperature. The color

of the mixture solution changed from colorless to yellowish to darkblue to dark-red. Then the dark-red solution was filtered to remove the dark insoluble substance. The filtrate was concentrated in vacuo, and the dark-red solid was obtained. The crude product was washed three times with hexanes, allowing for isolation of product 4. X-rayquality dark-red crystals of 4 were obtained in cooling THF solution. Yield: 0.149 g (53%). M.p.: 81.8 °C (turn black). UV-vis-NIR (THF): 477 nm. ¹H NMR (THF- d_{8} , 600 MHz): δ 7.33 (d, J = 6.0 Hz, 2H, Ar-H), 7.12 (t, J = 6.0 Hz, 2H, Ar-H), 7.02 (d, J = 6.0 Hz, 2H, Ar-H), 6.82 (t, J = 6.0 Hz, 2H, Ar-H), 6.74 (s, 4H, Mes-H), 6.33 (d, J = 6.0 Hz, 4H, Ar-H), 6.18 (t, J = 6.0 Hz, 4H, Ar-H), 5.60 (d, J =6.0 Hz, 8H, Ar-H), 3.62 (t, J = 6.0 Hz, 12H, overlap of O-CH₂-(THF) and $-CH_2$ - (four hydrogens of C14 and C43)), 3.54 (s, 12H, cryptand), 3.50 (t, J = 6.0 Hz, 12H, cryptand), 2.52 (t, J = 6.0 Hz, 12H, cryptand), 2.32 (s, 6H, Mes-CH₃), 2.10 (s, 12H, Mes-CH₃), 1.78 (t, J = 6.0 Hz, 8H, O-CH₂-CH₂-); ¹³C NMR (THF- d_{8} , 150 MHz): δ 150.5, 142.2, 140.3, 137.7, 136.3, 133.5, 126.8, 129.7, 127.5, 126.7, 126.1, 124.0, 117.6, 112.9, 107.7, 99.6 (C7 and C36), 71.2 ([2,2,2]-cryptand), 68.4 ([2,2,2]-cryptand), 68.0 (THF), 54.7 ([2,2,2]-cryptand), 39.7 (C14 and C43), 26.2 (THF), 22.8 (Ar-CH₃), 21.3 (Ar-CH₃); ¹¹B NMR (128.3 MHz, THF-*d*₈, ppm, 293 K): δ 38.2 ppm. IR (KBr, cm⁻¹): 3408 (br), 3042, 2963, 2883, 2817, 1657 (w), 1603, 1475, 1444, 1356, 1301, 1260, 1132, 1104 (s), 949, 844, 743. Calcd for C₈₀H₉₄B₂K₄N₂O₉·THF: C 68.27, H 6.96, N 1.90%; Found: C 68.19, H 7.01, N 1.78%.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b02157.

¹H NMR, ¹³C NMR, and ¹¹B NMR spectra of the compounds **1-H**, **2**, **3**, and **4**, computational details (PDF)

Accession Codes

CCDC 1849078–1849081 (compounds 1-H, 2, 3, and 4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.ca-m.ac.uk/data_request/cif, or by emailing data_request@ccdc. cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Funding

This work has been supported by the National Natural Science Foundation of China (No. 21771094 and 21671087) and the Fundamental Research Funds for the Central Universities (lzujbky-2017-k07). We also acknowledge the support from the Vice-Chancellor's Postdoctoral Research Fellowship Funding of the University of Wollongong and the computational resources provided by NCI's National Computational Merit Allocation Scheme. Notes

The authors declare no competing financial interest.

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