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Characterization of Dimeric and Tetrameric μ-Hydroxide Ytterbium(III) Binaphtholate Complexes

Alfred J. Wooten,[a] Luca Salvi,[a] Patrick J. Carroll,[a] and Patrick J. Walsh[a],*

[a] Vagelos Laboratories, University of Pennsylvania, Department of Chemistry, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323, USA
Fax: (+1)-215-573-6743; e-mail: pwalsh@sas.upenn.edu

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This manuscript is dedicated to Prof. M. Shibasaki, whose creativity and insight has changed the way we think of asymmetric Lewis acid catalysis.

Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: Shibasaki's heterobimetallic Lewis acids, $M_3(THF)_n(BINOLate)_3Ln$ (M = Li, Na, K and Ln = lanthanide), are an exceptionally useful class of asymmetric catalysts that exhibit high levels of enantioselectivity across a wide range of reactions. In many instances, it is necessary to add water (and base) to achieve maximum enantioselectivity. We have investigated the reaction of water with $M_3(THF)_n(BINOLate)_3Yb$ (M = Li, K) complexes and observed formation of a novel hydroxide-bridged dimer (M = Li) and tetramer (M = K). These compounds have been characterized, including X-ray structure analysis. Under anhydrous conditions, only 6-coordinate monomeric $Li_3(THF)_n(BINOLate)_3Yb$ and $K_3(THF)_n(BINOLate)_3Yb$ complexes were isolated and characterized by X-ray crystallography. Isolation of the dimer $Li_4(THF)_7(BINOLate)_4Yb_2(\mu\text{-}OH)_2$ and tetramer $K_4(THF)_9(BINOLate)_6Yb_4(\mu_3\text{-}OH)_4$ indicates that added water can react with this important class of bifunctional catalyst to give new products.

Keywords: additives; asymmetric catalysis; bridging hydroxide; heterobimetallic catalysts; lanthanides; Lewis acids

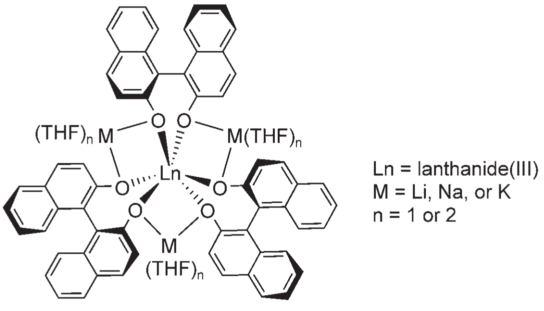

Figure 1. Shibasaki's $M_3(THF)_n(BINOLate)_3Ln$ catalysts without bound H_2O.

In the early 1990s, Shibasaki and co-workers reported the synthesis and applications of a series of heterobimetallic Lewis acid catalysts, $M_3(THF)_n(BINOLate)_3Ln$ [Figure 1, M = Li, Na, K and Ln = lanthanide(III)] and their 7-coordinate hydrates $M_3(THF)_n(BINOLate)_3Ln{\cdot}OH_2$.[1–6] These bifunctional catalysts are exceptional in their ability to catalyze a broad range of asymmetric transformations, such as the Henry reaction,[1,7] conjugate additions,[4,5,7–10] aldol condensations,[6,11] cyanoethoxycarbonylation of aldehydes,[12] and hydrophosphonylation of aldehydes and cyclic imines,[13,14] to name a few.

Despite the widespread successful application of these heterobimetallic catalysts in asymmetric synthesis, their reaction mechanisms are not well understood, because their multifunctional nature complicates mechanistic studies.[12,14–19] Furthermore, many reactions catalyzed by $Li_3(THF)_n(BINOLate)_3Ln$ complexes require additives, such as H_2O, to improve reaction efficiency and enantioselectivity.[3,6,20] For example, water and tris(2,6-dimethoxyphenyl)phosphine oxide were added in the asymmetric cyanoethoxycarbonylation of aldehydes promoted by $Li_3(THF)_n(BINOLate)_3Y$. With these additives, products were isolated in up to 99% yield and 98% *ee*.[12] One possible role of these additives is to allow generation of 7- and 8-coordinate intermediates, which we have recently demonstrated is possible with the isolation of $Li_3(THF)_4(BINOLate)_3Ln{\cdot}THF$ (Ln = Eu, La) and $Li_3(py)_5(BINOLate)_3La{\cdot}py_2$ adducts.[18] Interestingly, in the absence of the additives, the cyanoethoxycarbonylation reaction did not proceed.

Inspired by the impact of additives on these bifunctional catalysts,[3,6,20] we set out to further explore their reactivity with H_2O. We were particularly interested in $M_3(THF)_6(BINOLate)_3Yb$ [M = Na or K] complexes, because these compounds do not bind water.[19] Herein, we report the reactions of **1** and **2** with water, leading to formation of the unique dimeric and tetrameric complexes, $Li_4(THF)_7(BINOLate)_4Yb_2(\mu\text{-}OH)_2$ and $K_4(THF)_9(BINOLate)_6Yb_4(\mu_3\text{-}OH)_4$.

Shibasaki's complexes $Li_3(THF)_n(BINOLate)_3Yb$ (**1**) and $K_3(THF)_6(BINOLate)_3Yb$ (**2**) were prepared by combining 3 equivs. of $Li_2(BINOLate)$ or $K_2(BINOLate)$, respectively, with 1 equiv. of $Yb(O_3SCF_3)_3$ in THF. The crystalline solids were isolated in 73% (**1**) and 68% (**2**) yield [Eq. (1)].[1,4,19]

$$Yb(O_3SCF_3)_3 + 3\ M_2(BINOLate) \xrightarrow{\text{THF, rt}} M_3(THF)_n(BINOLate)_3Yb \qquad (1)$$

1, M=Li (73% yield)
2, M=K (68% yield)

X-ray quality crystals of **1** and **2** were obtained by gas phase diffusion of anhydrous pentane into dry THF solutions containing each compound at room temperature. The structure of **2** is illustrated in Figure 2, with **1** being shown in the Supporting Information.

Both **1** and **2** contain an LnO_6 core that can be described as a distorted octahedron. In addition to the chirality of the BINOLate ligands, the lanthanide centers are stereogenic. As observed with other $M_3(THF)_n(BINOLate)_3Ln$ complexes,[21] use of (*R*)-BINOL led to the Δ configuration at the lanthanide. The BINOLate Yb–O bond distances in **1** range from 2.200(4) to 2.214(4) Å, with Li–O bond distances ranging from 1.929(6) to 2.021(9) Å. The Yb–O bond distances in **1** are similar to those in Aspinall's $[Li(THF)_2]_2[Li(OEt_2)](BINOLate)_3Yb$ complex [Yb–O = 2.193(9) to 2.232(8) Å; Li–O = 1.83(3) to 1.98(3) Å].[22] Complex **2** exhibits similar Yb–O bond distances [2.196(4) to 2.234(4) Å] and K–O bond distances of 2.568(5) to 2.773(4) Å.

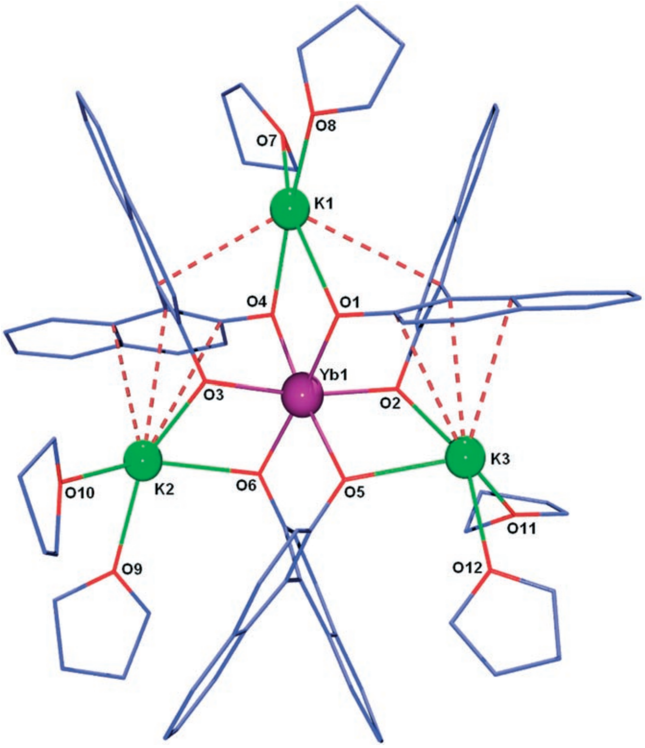

Figure 2. Structure of $K_3(THF)_6(BINOLate)_3Yb$ (**2**) indicating K–C π-interactions with dashed lines.

In addition to longer K–O bonds, the larger potassium atoms exhibit K–C cation-π interactions between three carbons of neighboring BINOLate naphthyl rings (Figure 2). The π-interactions in **2** cause the ytterbium center to be displaced by 0.1522(6) Å out of the K_3-plane. We propose that ytterbium is forced out of the K_3-plane to properly orient the naphthyl groups to maximize the K–C π-interactions. The K–C π-distances in **2** range from 3.17 to 3.36 Å and are well within the expected range for such interactions.[23] For example, the K–C π-distances in coordinatively saturated $K_3(toluene)_6(BINOLate)_3In$ range from 3.35 to 3.42 Å.[24]

After successful isolation of **1** and **2**, they were recrystallized from THF with wet pentane (HPLC grade) at room temperature. Pale, X-ray quality crystals were obtained after several days and their structures were determined at low temperature. To our surprise, X-ray analysis revealed that a bridging hydroxide dimer $Li_4(THF)_7(BINOLate)_4Yb_2(\mu\text{-}OH)_2$ (**3**) and tetramer $K_4(THF)_9(BINOLate)_6Yb_4(\mu_3\text{-}OH)_4$ (**4**) were formed. In addition to the formation of **3** and **4**, X-ray quality crystals of unreacted **1** and **2** were observed, as determined by unit cell analysis. It is noteworthy that the hydrates, $Li_3(THF)_n(BINOLate)_3Yb\cdot OH_2$ and $K_3(THF)_6(BINOLate)_3Yb\cdot OH_2$ were not observed. The structures of **3** and **4** are illustrated in Figure 3 and Figure 4, respectively.

Dimeric $Li_4(THF)_7(BINOLate)_4Yb_2(\mu\text{-}OH)_2$ (**3**) contains hydroxy groups that bridge the two ytterbium centers. Each ytterbium center exhibits a distorted octahedral geometry and is bound by four BINOLate oxygens and the two hydroxide groups. Three of the lithium atoms are coordinatively saturated, binding two THF molecules and two oxygens from neighboring naphthyl rings. The remaining lithium atom binds only one THF and interacts with one bridging hydroxide [Li–OH distance of 2.085(10) Å]. The BINOLate Yb–O bond distances in **3** range from 2.192(3) to 2.224(3) Å, with BINOLate Li–O bond distances falling between 1.898(9) and 1.949(10) Å. The Yb–O distances to the hydroxide range from 2.190(3) Å to 2.303(3) Å. The Yb–O–Yb angles with the hydroxide bridges are 102.55°(11) and 108.97°(13), respectively. The presence of the hydroxide groups in **3** was con-

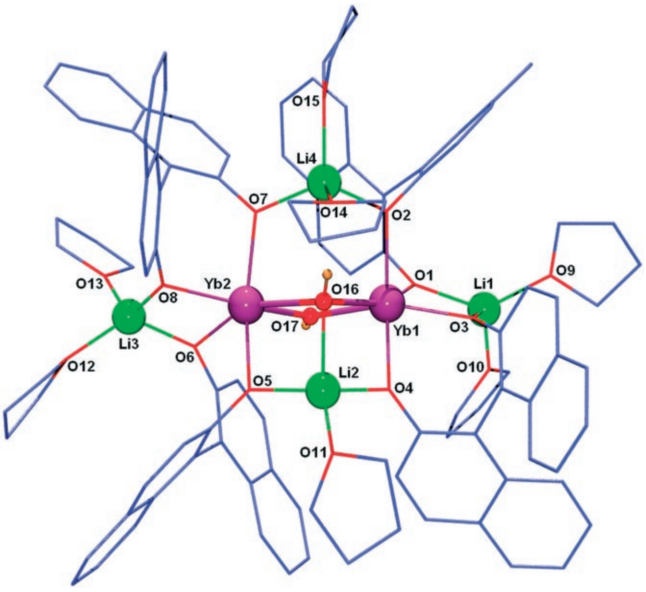

Figure 3. Structure of dimeric Li$_4$(THF)$_7$(BINOLate)$_4$Yb$_2$(μ-OH)$_2$ (**3**).

firmed by a strong ν_{OH} absorption at 3560 cm^{-1} in the IR spectrum.

Dimeric Li$_4$(THF)$_7$(BINOLate)$_4$Yb$_2$(μ-OH)$_2$ (**3**) can be compared to the Li$_4$(THF)$_8$(BINOLate)$_5$La$_2$ dimer that was recently characterized by Shibasaki and co-workers.[16] This compound was prepared by addition of Li(O$_3$SCF$_3$) to a THF solution containing the monomeric Li$_3$(THF)$_6$(BINOLate)$_3$La complex. Unlike **3**, Li$_4$(THF)$_8$(BINOLate)$_5$La$_2$ is stabilized by two bridging BINOLate ligands.

In contrast to dimeric Li$_4$(THF)$_7$(BINOLate)$_4$Yb$_2$(μ-OH)$_2$ (**3**), K$_4$(THF)$_9$(BINOLate)$_6$Yb$_4$(μ$_3$-OH)$_4$ (**4**) contains four bridging hydroxide ligands and a tetrameric distorted cubic core (Figure 4 and Figure 5). Like **3**, each ytterbium center in **4** is 6-coordinate. In contrast, the Yb centers are bound to three BINOLate oxygens and three bridging hydroxide groups. The six BINOLate ligands in this complex bridge neighboring ytterbium centers and span the adjacent vertices of the square faces of the cubic core (Figure 5). The BINOLate Yb–O distances range from 2.087(7) to 2.158(6) Å, with bridging hydroxide Yb–O distances between 2.312(6) and 2.355(6) Å. The bridging hydroxide Yb–O distances in **4** are slightly longer than the Yb–O bridging hydroxide bonds in **3**, as might be expected. The hydroxide Yb–O–Yb angles in **4** range from 102.6°(2) to 105.5°(3), resulting in a distortion of the cubic core. The core structure of **4** is reminiscent of the structures of catalytically active Zr$_4$(BINOLate)$_6$(μ$_3$-OH)$_4$[25] and Ti$_4$(BINOLate)$_6$(μ$_3$-OH)$_4$.[26,27] While we cannot explain the factors that give rise to the structural differences in **3** and **4**, we note that the Brønsted basicities of the binaphtholate moiety are dependent on the alkali metal (ROLi < RONa < ROK).[28,29]

Unlike the potassium atoms in the monomer K$_3$(THF)$_6$(BINOLate)$_3$Yb (**2**), which are four coordinate, one of the potassium atoms (K2) in **4** is five coordinate, binding three THF ligands and two BINOLate oxygens (Figure 4). It was also established that

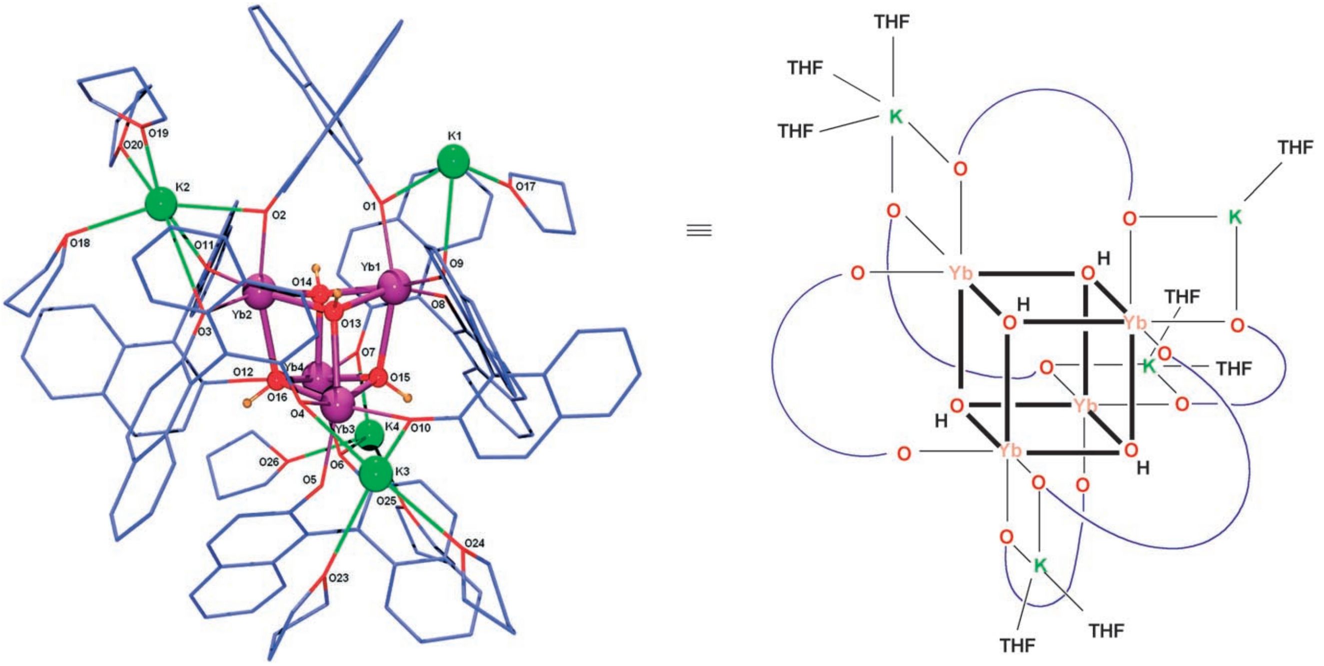

Figure 4. Structure of K$_4$(THF)$_9$(BINOLate)$_6$Yb$_4$(μ$_3$-OH)$_4$ (**4**) with line representation.

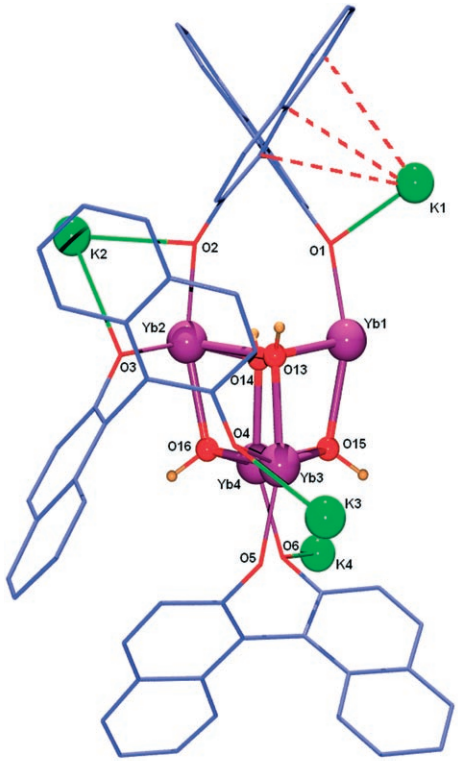

Figure 5. Partial structure of $K_4(THF)_9(BINOLate)_6Yb_4(\mu_3\text{-}OH)_4$, illustrating the cubic core, three of the face bridging BINOLate ligands, and K−C π-interactions to K1.

K3 is four coordinate, binding two BINOLate oxygens and two ligands. The two ligands had rather large thermal parameters so a disorder model was devised in which 60% of the molecules contained one THF and a water ligand coordinated to K3 and 40% of the molecules contain two THF ligands (Supporting Information). The other two potassium atoms (K1 and K4) bind one and two THF ligands, respectively (Figure 4). The potassium K1, which is bound by only one THF, exhibits K−C π-interactions with a neighboring naphthyl ring (Figure 5).[23] The three K−C-π distances in this complex are 3.36, 3.35, and 3.53 Å. The THF ligand is directed away from the naphthyl ring to maximize K−C π-interactions and to relieve unfavorable steric congestion. The K−C-π distances in **4** are similar to those in **2** (3.17 to 3.36 Å) and $K_3(toluene)_6(BINOLate)_3In$ (3.35 to 3.42 Å).[24]

Inspired by the co-crystallization of monomer (**1**) with dimer (**3**) (M = Li) and monomer (**2**) with tetramer (**4**) (M = K), we monitored the reaction of $M_3(THF)_n(BINOLate)_3Yb$ (M = Li and K) with water by NMR. Thus, 30 mg of **1** and **2** were separately combined with 5 equivs. of water and heated to 60 °C for 3 days in THF-d_8. ^1H NMR analysis of the reaction mixtures revealed significant amounts of unreacted monomers, with little product formation. Based on these results, we speculate that dimer and tetramer are formed reversibly from the monomers and water. Furthermore, we believe that their formation can be driven by crystallization resulting from the greater insolubility of the dimer and tetramer in THF than the monomers.

In summary, we have structurally characterized two monomeric $M_3(THF)_n(BINOLate)_3Yb$ (**1**, M = Li; **2**, M = K) and two unique hydroxide-bridged oligomers $Li_4(THF)_7(BINOLate)_4Yb_2(\mu\text{-}OH)_2$ (**3**) and $K_4(THF)_9(BINOLate)_6Yb_4(\mu_3\text{-}OH)_4$ (**4**). Both dimer **3** and tetramer **4** are formed upon reaction of monomers $M_3(THF)_n(BINOLate)_3Yb$ [M = Li (**1**), K (**2**)] with water. The structural difference of the monomers *vs.* the dimer **3** and tetramer **4** provides an additional perspective as to how water, as an additive, can impact the structure of this important class of bifunctional catalyst. Another possible role of additives (H_2O) is to allow generation of 7-coordinate intermediates.[3,18] This observation is curious because several reactions catalyzed by $M_3(THF)_n(BINOLate)_3Ln$ complexes require added water to achieve high enantioselectivity.[3,6,20] At this time, the catalytic activity and/or relevance of the hydroxide-bridged compounds to reactions catalyzed by $M_3(THF)_n(BINOLate)_3Yb$ [M = Li and K] is unclear. On the basis of recent reports using the tetrameric clusters $Zr_4(BINOLate)_6(\mu_3\text{-}OH)_4$[25] and $Ti_4(BINOLate)_6(\mu_3\text{-}OH)_4$[26,27] as stable and effective catalyst in organic reactions, one should remain mindful of the potential formation and influence of hydroxide-bridged oligomers in asymmetric reactions when water is used as an additive with $M_3(THF)_n(BINOLate)_3Ln$ catalyst.

Experimental Section

General Procedure: Synthesis of $M_3(THF)_n$-$(BINOLate)_3Ln$ Complexes

$Li_3(THF)_n(BINOLate)_3Yb$ (1): [(*R*)-BINOLate]Li_2 (0.721 g, 2.42 mmol) was dissolved in 60 mL of THF and $Yb(O_3SCF_3)_3$ (0.50 g, 0.806 mmol) was added as a solid in incremental portions to the clear solution of [(*R*)-BINOLate]Li_2. The reaction mixture was allowed to stir for 3 days at room temperature inside the glove-box. The solution was then filtered through dry Celite and all volatile materials were removed under vacuum. CH_2Cl_2 (60 mL) was added to the remaining solid and the undissolved material was separated by filtering through Celite. After complete drying under vacuum, the solid was placed on a frit and washed once with 2 mL of cold dry diethyl ether and three times with 5 mL of dry hexanes. Compound **1** was obtained as a white powder after drying under reduced pressure; yield: 0.749 g [73% based on $Yb(O_3SCF_3)_3$]. Pale X-ray quality crystals were obtained *via* vapor diffusion of dry pentane into a THF solution of **1**. Elemental analysis were obtained after drying a crystalline sample to a constant weight. ^1H NMR (300 MHz, THF-d_8): $\delta = -13.44$ (br-s, 2H), −1.02 (br-s, 2H), 2.95 (br-s, 2H), 8.31 (d, 2H, $J = 8.1$ Hz), 23.74

(br-s, 2H), 88.59 (br-s, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, THF-d_8): $\delta = 56.6$, 108.0, 110.4, 114.1, 116.5, 122.1, 124.0, 124.7, 140.6 and 178.3; IR (KBr): $\nu = 3048$, 2956, 2873, 1615, 1591, 1558, 1502, 1464, 1425, 1341, 1278, 1249, 1143, 1071, 995, 957, 936, 860, 823, 746, 669, 576, 482 cm^{-1}; anal. calcd. for $C_{72}H_{60}O_9Li_3Yb$: C 68.46, H 4.79; found: C 68.31, H 4.88.

$K_3(THF)_n(BINOLate)_3Yb$ (2): The amount of reagents used are as follows: [(*R*)-BINOLate]K_2 (0.50 g, 1.38 mmol), $Yb(O_3SCF_3)_3$ (0.285 g, 0.460 mmol), and 60 mL of THF. Pale X-ray quality crystalline blocks were obtained *via* vapor diffusion of dry pentane into a THF solution of **2**. Yield: 0.423 g [68% based on $Yb(O_3SCF_3)_3$]. ^1H NMR (300 MHz, THF-d_8): $\delta = 3.02$ (br-s, 2H), 5.47 (br-s, 2H), 5.78 (br-s, 2H), 7.52 (d, 2H, $J = 7.6$ Hz), 10.16 (br-s, 2H), and 20.43 (br-s, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, THF-d_8): $\delta = 116.7$, 119.7, 121.8, 122.1, 126.5, 127.8, 128.9, 132.0, 147.9, and 157.9; IR (KBr): $\nu = 3044$, 2974, 2870, 1610, 1588, 1551, 1499, 1461, 1422, 1341, 1284, 1249, 1141, 1668, 994, 955, 934, 858, 823, 747, 664, 571, 496, 462 cm^{-1}; anal. calcd. for $C_{84}H_{84}O_{12}K_3Yb$: C 64.02, H 5.37; found: C 63.78, H 5.15.

Synthesis of $Li_4(THF)_7(BINOLate)_4Yb_2(\mu\text{-}OH)_2$ (3)

$Li_3(THF)_3(BINOLate)_3Yb$ (**1**) (100 mg) was added to a 20-mL vial and dissolved in THF (2.0 mL). This vial was then placed within a 60-mL screw-capped vial that was half-filled with pentane (HPLC grade). After several days of vapor diffusion, pale crystals suitable for an X-ray diffraction study were formed. IR (KBr): $\nu = 3560$, 3047, 2974, 2874, 1614, 1590, 1557, 1501, 1464, 1424, 1341, 1278, 1248, 1180, 1147, 1071, 1049, 996, 957, 898, 862, 823, 743, 666, 593, 574, 480 cm^{-1}; anal. calcd. for $C_{108}H_{106}O_{17}Li_4Yb_2$: C 63.28, H 5.21; found: C 63.31, H 5.10. The low solubility and paramagnetic nature of **3** made it very difficult to get reasonable and interpretable ^1H and $^{13}C\{^1H\}$ NMR data.

Synthesis of $K_4(THF)_8(BINOLate)_6Yb_4(\mu_3\text{-}OH)_4$ (4)

$K_3(THF)_3(BINOLate)_3Yb$ (**2**) (100 mg) was added to a 20-mL vial and dissolved in THF (2.0 mL). This vial was then placed within a 60-mL screw-capped vial that was half-filled with pentane (HPLC grade). After several days of vapor diffusion, pale crystals suitable for an X-ray diffraction study were formed. The paramagnetic nature of **4** also made it very difficult to get reasonable and interpretable ^1H and $^{13}C\{^1H\}$ NMR data. In addition, it provided to be difficult to separated **4** from unreacted monomer **2**, which in turn lead to inaccurate elemental analysis results.

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