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Impact of Na– and K–C π-Interactions on the Structure and Binding of $M_3(sol)_n(BINOLate)_3Ln$ Catalysts

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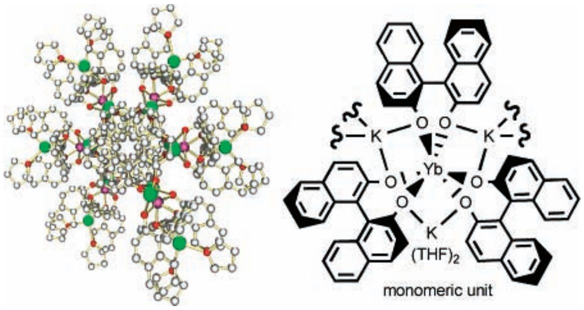
ABSTRACT



Shibasaki's heterobimetallic complexes $M_3(THF)_n(BINOLate)_3Ln$ [M = Li, Na, K; Ln = lanthanide(III)] are among the most successful asymmetric Lewis acid catalysts. Why does $M_3(THF)_n(BINOLate)_3Ln$ readily bind substrates when M = Li but not when M = Na or K? Structural studies herein indicate Na– and K–C cation–π interactions and alkali metal radius may be more important than even lanthanide radius. Also reported is a novel polymeric $[K_3(THF)_2(BINOLate)_3Yb]_n$ structure that provides the first evidence of interactions between $M_3(THF)_n(BINOLate)_3Ln$ complexes.

Shibasaki's $M_3(THF)_n(BINOLate)_3Ln$ complexes (Figure 1) are among the most effective asymmetric Lewis acid catalysts known, exhibiting high enantioselectivities over a broad range of reactions.[1−3] Understanding how these heterobimetallic catalysts work, however, has proven challenging.[4−9] In particular, seemingly subtle alterations in the catalyst composition result in dramatic changes in selectivity. For example, in the nitro aldol reaction with $M_3(THF)_n(BINOLate)_3Ln$, 94% ee was obtained when M = Li and 2% ee was obtained when M = Na. In contrast, the asymmetric Michael reaction gave 92% ee when M = Na and 29% ee for M = Li.[10] The first step in unraveling the factors that are responsible for these striking differences is

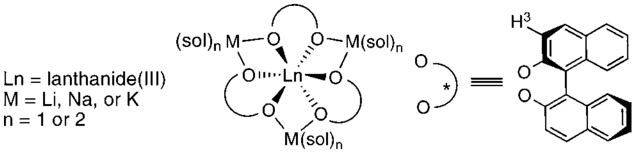


Figure 1. Shibasaki's $M_3(THF)_n(BINOLate)_3Ln$ catalysts.

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understanding the impact of the alkali metal on substrate binding to the lanthanide centers.

Reported herein are solution and solid-state studies of $M_3(sol)_n(BINOLate)_3Ln$ complexes that illuminate dramatic differences in Ln binding ability when M = Li vs Na and K. Also disclosed is an unprecedented helical polymer, $[K_3(THF)_2(BINOLate)_3Yb]_n$.

We recently demonstrated that DMF reversibly binds to paramagnetic lanthanides in $Li_3(THF)_n(BINOLate)_3Ln$ (Ln = Eu, Pr), exhibiting a >2 ppm lanthanide induced shift (LIS) in the formyl C−H resonance in the ^{1}H NMR spectrum.[8] Salvadori, on the other hand, reported[7] that $Na_3(THF)_6(BINOLate)_3Yb$ does not bind water in solution or in the solid state, which was attributed to the small ionic radius of Yb (La = 1.17, Eu = 1.09, Yb = 1.01). This dichotomy prompted us to examine binding of the lithium analogue, $Li_3(THF)_n(BINOLate)_3Yb$, with DMF. In the presence of $Li_3(THF)_n(BINOLate)_3Yb$, the formyl C−H shifted *over 4 ppm*, consistent with binding to Yb. Furthermore, crystallization of $Li_3(THF)_n(BINOLate)_3Yb$ from pyridine yielded seven-coordinate $Li_3(py)_5(BINOLate)_3Yb{\cdot}py$, the ORTEP of which is shown in Figure 2. We next examined binding of DMF to $Na_3(THF)_6(BINOLate)_3Ln$ [Ln = Yb, Eu][11−13] and $K_3(THF)_6(BINOLate)_3Yb$[7,14] under the same conditions. Surprisingly, no LISs (>0.1 ppm) were observed, indicating that binding to the lanthanide in the Na and K analogues is much less favorable than in the Li series.

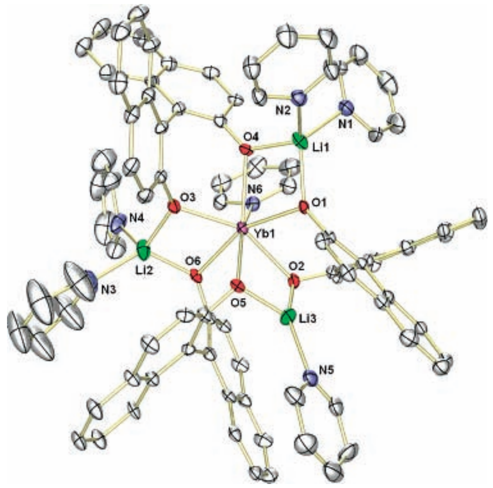

Figure 2. Structure of $Li_3(py)_5(BINOLate)_3Yb(py)$.

To probe the influence of Li vs Na on substrate binding at the lanthanide, $Na_3(THF)_6(BINOLate)_3La$ (Figure 3) and isostructural $Na_3(THF)_6(BINOLate)_3Eu$ (Supporting Information, Figure S1) were crystallographically characterized. In contrast to seven- and eight-coordinate $Li_3(THF)_4(BINOLate)_3Ln{\cdot}THF$ (Ln = Eu, La) and $Li_3(py)_5(BINOLate)_3La{\cdot}py_2$,[8] $Na_3(THF)_6(BINOLate)_3Ln$ is only six-coordinate.

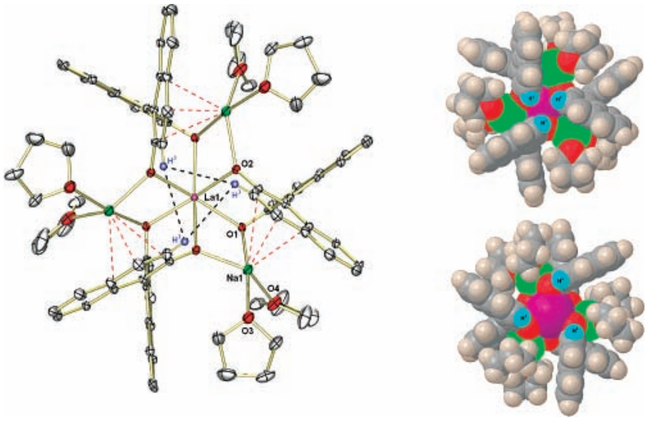

Figure 3. Structure of $Na_3(THF)_6(BINOLate)_3La$ illustrating the Na−C π-interactions. The triangular face is drawn in black. Two views down the C_3-axes with the 3-H protons in blue are shown on the right.

When comparing $M_3(THF)_6(BINOLate)_3Ln$ structures, we found three interdependent factors to be important. The first and most informative aspect of these structures is the presence of Na−C cation−π interactions.[15,16] Positioned directly above the sodium atoms are BINOLate naphthyl rings, three carbons of which are well within the expected range for Na−C cation−π interactions (Table 1, entries 1 and 2).[17] Our analysis of the Yb homologue[7,12] reveals similar interactions (entry 3). Particularly noteworthy is that the

Table 1. Structural Data for $M_3(THF)_6(BINOLate)_3Ln$ Complexes

entry	M	Ln	M_3−Ln (Å)	M−C π-dist (Å)	triangular face (Å)	
1	Na_3	La	1.111(7)	2.94−3.23	2.84	5.02
2	Na_3	Eu	0.950(1)	2.91−3.20	2.78	4.76
3	Na_3	Yb	0.762(7)	2.92−3.20	2.78	4.42
4	Na_3	$La{\cdot}OH_2$	1.130(2)	2.96−3.24	2.83	5.05
5	Li_3	La·THF	0.767(4)	2.71−4.82	3.36[a]	5.35[a]
6	Li_3	Eu·THF	0.737(3)	2.65−4.77	3.28[a]	5.30[a]
7	Li_3	Yb·py	0.479(2)	2.73−4.93	3.58[a]	5.10[a]
8	Li_3	$La{\cdot}py_2$	0.042(2)	2.79−5.10	5.02[a]	4.93[a]
9	K_3	Yb	0.354(6)	3.22−3.62	3.29[a]	3.69[a]

[a] Average value.

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Na−C interactions (2.91−3.23 Å) in the La, Eu, and Yb complexes *are identical and are independent of the lanthanide radius*.

The second factor is the Ln displacement from the Na_3 plane (Table 1) of 1.111(7) Å (La) and 0.950(1) Å (Eu). We calculated a similar displacement for known $Na_3(THF)_6(BINOLate)_3Yb$ [0.762(7) Å].[12] Although the displacement had been noted, its origin was unknown.[12,7] The displacement distances parallel the Ln radii (La > Eu > Yb). Salvadori observed that $Na_3(THF)_6(BINOLate)_3Yb$ exhibits D_3 symmetry by NMR down to −100 °C[7] suggesting that in solution the Yb sits in the Na_3 plane. On binding the substrate to form a seven-coordinate adduct, however, the lanthanide must be displaced from the M_3 plane (Table 1, entries 4−7).

The Na−C cation−π interactions cause the Ln−Na_3 displacement and result in the inequivalent C_3-symmetric faces in $Na_3(THF)_6(BINOLate)_3Ln$ in the solid state (Figure 3, right). To quantify this inequivalency, we define the third structural factor, the triangular faces, as the distances between the three 3-H protons of the BINOLate ligands (Figure 3, blue hydrogens). The 3-H protons interact most directly with incoming or Ln-bound substrates. The equilateral triangular faces of $Na_3(THF)_6(BINOLate)_3Ln$ highlight these differences (La: 2.84 vs 5.02 Å and Eu: 2.78 vs 4.76 Å, Table 1). It is also telling that the triangular faces of $Na_3(THF)_6(BINOLate)_3La$ and $Na_3(THF)_6(BINOLate)_3La{\cdot}OH_2$ are almost identical,[12] as are the La−Na_3 displacements and Na−C distances (Table 1, entry 1 vs 4). Thus, almost no structural change is observed in the solid state between $Na_3(THF)_6(BINOLate)_3La$ and $Na_3(THF)_6(BINOLate)_3La{\cdot}OH_2$. It follows that $Na_3(THF)_6(BINOLate)_3Yb$, with the much smaller Yb radius, would require significant structural reorganization to bind water or larger Lewis bases (La = 1.17 vs Yb = 1.01 Å radii).[7]

Comparison of the lanthanide displacements in $Na_3(THF)_6(BINOLate)_3La$ and seven-coordinate $Li_3(THF)_4(BINOLate)_3La{\cdot}THF$ is also informative. Despite the greater displacement of the La in six-coordinate $Na_3(THF)_6(BINOLate)_3La$ than in seven-coordinate $Li_3(THF)_4(BINOLate)_3La{\cdot}THF$, the triangular face (or binding pocket) of the Na analogue is *smaller*. Butting of the sodium atoms with the naphthyl π systems positions the BINOLate 3-H's into the substrate-binding site. In contrast, the smaller lithium does not exhibit Li−C π-interactions[17] in $Li_3(THF)_4(BINOLate)_3Ln$ complexes, allowing greater distortion of the $(BINOLate)_3Ln$ core to accommodate substrates larger than water.

We next desired to explore how the larger potassium would impact the structure of $M_3(THF)_6(BINOLate)_3Ln$ complexes. Thus, $K_3(THF)_6(BINOLate)_3Yb$ was crystallized from pyridine. Like the sodium derivatives, six-coordinate $K_3(py)_6(BINOLate)_3Yb$ contains K−C cation−π interactions in the solid state[17] (3.22−3.62 Å) as well as an unusual η^3-pyridine with only K−C π-interactions (Figure 4). The larger potassium radius results in longer K−C π-distances, a smaller Yb−K_3 displacement [0.354(6) Å, entry 9 in Table 1], and a smaller difference in the triangular faces [3.16, 3.35, 3.38 vs 3.55, 3.56, 3.96 Å]. Potassium π-interactions were also observed in coordinatively saturated $K_3(toluene)_6(BINOLate)_3In$ (K−C 3.35−3.42 Å).[18] Following the logic outlined above for the sodium analogues, we hypothesize that the propensity of $M_3(THF)_n(BINOLate)_3Ln$ complexes to bind Lewis bases at the lanthanide center is Li ≫ Na > K due to the alkali metal ionic radii.

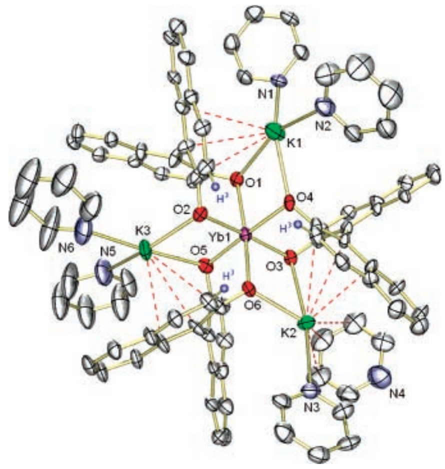

Figure 4. One of six independent molecules of $K_3(py)_6(BINOLate)_3Yb$.

Similarly, crystallization of $K_3(THF)_6(BINOLate)_3Yb$ from THF/pentane initially provided poor quality blocklike crystals, the structure of which was most consistent with six-coordinate $K_3(THF)_6(BINOLate)_3Yb$.[19] On standing, solutions of $K_3(THF)_6(BINOLate)_3Yb$ formed X-ray quality needles. Surprisingly, an unprecedented helical polymer, $[K_3(THF)_2(BINOLate)_3Yb]_n$, was observed (Figure 5).

Polymeric $[K_3(THF)_2(BINOLate)_3Yb]_n$ exhibits intramonomer (3.27−3.66 Å) and intermonomer (3.02−3.37 Å) K−C π-interactions (Figure 6). K1 binds two BINOLate oxygens and two THF's and exhibits intramonomer π-interactions. The other two potassium atoms are disordered over three positions with occupancy of 40.5, 45.5, and 14%, the latter of which is not discussed. K2 (40.5% occupancy) binds two BINOLate oxygens, as usual, and contains both intra- and *intermonomer* cation−π interactions. Interestingly, K2′ (45.5% occupancy) binds one BINOLate oxygen *in two different monomeric units*. The disordered potassiums participate in intra- and intermonomer cation−π interactions. In a comparison of K1, which binds four oxygens, to K2 and K2′, which each bind two oxygens but have more contacts with the naphthyl carbons, it is useful to recall that the cation−π interaction, $K^+{\cdots}$(benzene), and the binding of water, $K^+{\cdot}OH_2$, are 19 and 18 kcal/mol, respectively, in the gas phase.[15] The extensive K−C cation−π interactions in the monomeric and polymeric structures attest to the importance of these interactions.

In summary, this study provides insight into the structures and binding preferences of one of the most successful classes

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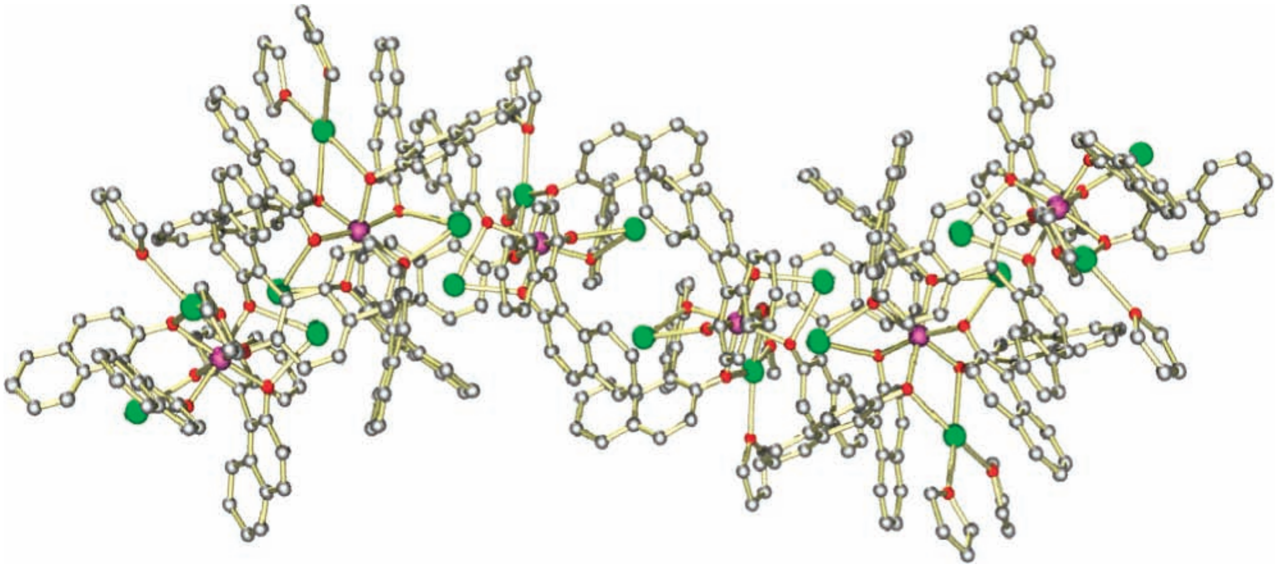

Figure 5. Structure of the $[K_3(THF)_2(BINOLate)_3Yb]_n$ helical polymer.

of asymmetric catalysts, Shibasaki's $M_3(THF)_n(BINOLate)_3Ln$ complexes. The solid-state structure of $Li_3(py)_5(BINOLate)_3$-Yb•py and solution binding of DMF by $Li_3(THF)_n$-$(BINOLate)_3Yb$ stand in sharp contrast to the sodium and potassium analogues, $M_3(THF)_6(BINOLate)_3Yb$, which exhibit little or no binding of DMF or water. These results are the first evidence that lanthanide *size is not the primary determinant for substrate binding to the lanthanide*.

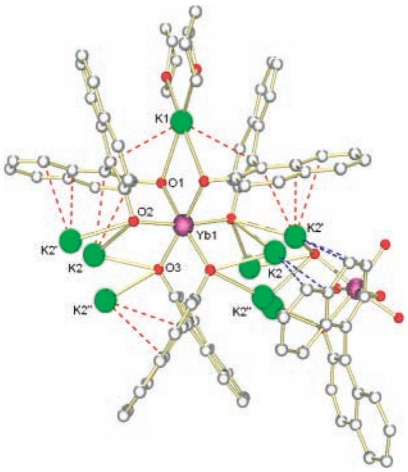

Figure 6. Structure of the monomeric unit in $[K_3(THF)_2$-$(BINOLate)_3Yb]_n$ illustrating the disordered K atoms.

We have also characterized the unique helical polymer $[K_3(THF)_2(BINOLate)_3Yb]_n$ which provides the first evidence of interactions between $M_3(THF)_n(BINOLate)_3Ln$ complexes. The additional cation−π interactions in this species compensate for the reduced number of K−O bonds.

Finally, our data support earlier proposals that reactions promoted by these bifunctional catalysts (M = Na, K) likely involve a BINOLate oxygen first acting as a Brønsted base and accepting a proton from the substrate.[7,10] The protonated BINOLate oxygen likely detaches from the lanthanide to open a coordination site before substrate binding at the Ln center can take place.

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Supporting Information Available: Procedures, full characterization of new compounds, and all CIF data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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