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Bulky Metallocavitands with a Chiral Cavity Constructed by Aluminum and Magnesium Atrane-likes, Enantioselective Recognition and Separation of Racemic Alcohols

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ABSTRACT. Seven new type metallocavitand complexes **1**-**7** were synthesized via the self-assembly of aluminum and magnesium atrane-likes. The recognition of *R*-2-butanol from racemic 2-butanol can be achieved in the chiral cavity of metallocavitand complex **5**. The crystal structure of complex **5** showed that the enantioselectivity of the center cavity for the inclusion of two 2-butanol molecules is higher than that of the groups at the outer rim, which indicates that the size-limited cavity is more sensitive to the chirality of 2-butanol. Furthermore, desorption of *R*-2-butanol is successful through vacuumization which afforded complex **6** and gives *R*-2-butanol with an enantiomeric excess (*ee*) value of 53(±1)%. The reaction of enantiopure H_3L^2, Mg^nBu_2, and racemic 1-phenylethanol afforded complex **7**. The

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structure of complex **7** showed that the center cavity was occupied by three H_2O molecules and one molecular *R*-1-phenylethanol suspended in the outer rim of the metallocavitand via a hydrogen bond, which indicated that 1-phenylethanol is too bulky for the size-limited cavity. Because a certain amount of racemic 1-phenylethanol is also co-crystallized in the unit cell, the final separated 1-phenylethanol has an *ee* value of 33(±1)%. The host-guest mechanism for the separation is clearly determined through X-ray crystal structural analysis.

INTRODUCTION

The cavitand molecules with enforced cavities have attracted considerable interest over the last four decades due to their performance advantage of molecular encapsulation. These types of compounds have been widely used to catalyze[1] and promote chemical reactions,[2] stabilize reactive intermediates,[3] detect important chemicals,[4] etc. As a new branch, metallocavitands differ from traditional organic cavitands because they are multimetallic complexes in which metal coordination is required for cavity formation. Compared with organic cavitands, the difficult synthesis work can be avoided for metallocavitands, and the steric and electronic modulation of these complexes can be easily induced by varying the substituents on the simple ligands. To date, many types of metallocavitands, such as Pd(II),[5] Pt(II),[6] Rh(II),[7] Ta(V),[8] Cu(II),[9] Zn(II),[10] Cd(II),[11] Re,[12] and multidentate ligands have been synthesized through self-assembly or macrocycle templates. Recently, excellent work on metallocavitands has been reviewed by Pecoraro[13] and MacLachlan.[14] Among these metallocavitands, chiral metallocavitands have not yet been extensively explored, possibly because of the difficulty in their construction. Excellent enantioselectivities of chiral organic cavitands[15] and some chiral metal caged complexes with nano-sized cavities have been demonstrated in catalytic reactions[16] and separations;[17] however, very few examples of chiral metallocavitands have been tested for their enantioselectivity in host-guest chemistry. For example, Pecoraro has reported that the chiral metallocavitand Gd^{3+}[15-Metallacrown-5] exhibits modest enantioselectivity for mandelate with K_S/K_R values of up to 2.2 ± 0.6.[18] However,

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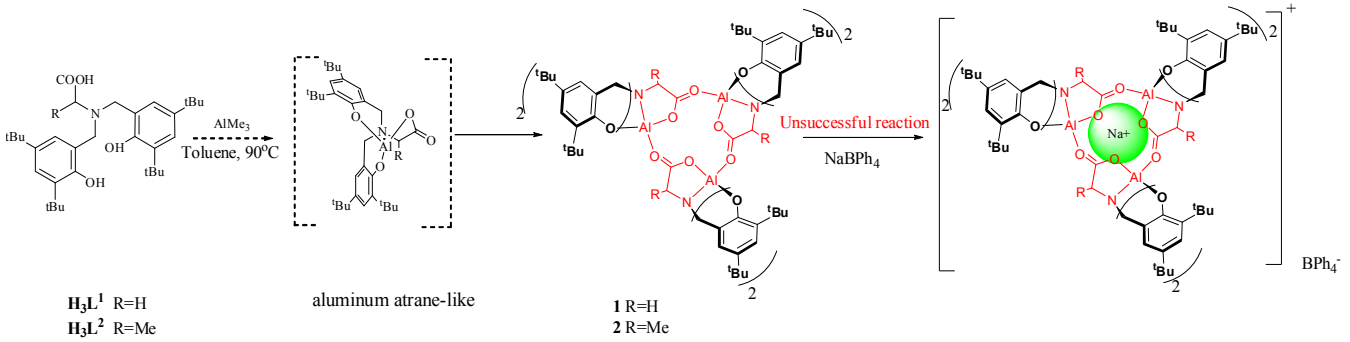
further research is required to explore the construction of new types of chiral metallocavitands and to extend their applications.

In this study, new aluminum and magnesium metallocavitands constructed by tripdol bis(phenol)amino acid ligands and magnesium/aluminum salts were synthesized in an attempt to create an open chiral cavity surrounded by sterically hindering groups. For a potential application, one metal ion as a Lewis acidic site was designed to be embedded in the center of the cavity, which is expected to cooperate with the chiral groups in the rim of the metallocavitands for highly enantioselective separation through multi-pronged effects including coordination, hydrogen bonding, and bulky steric hindrance (Chart 1).

Chart 1 Chiral metallocavitand with one metal ion in the center.



Scheme 1 Synthesis of aluminum metallocavitands **1** and **2**.

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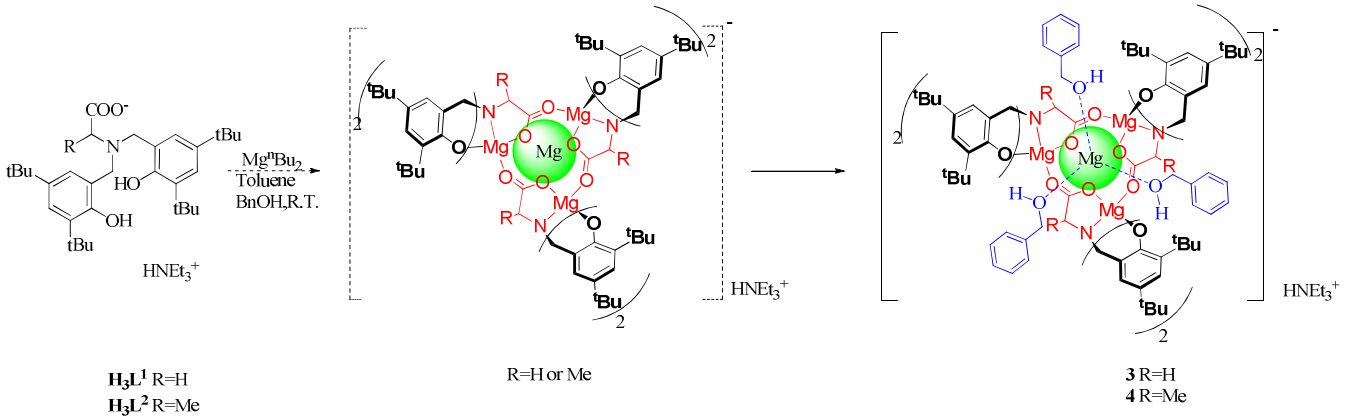

Scheme 2 Synthesis of magnesium metallocavitands **3** and **4**.

RESULTS AND DISCUSSION

Synthesis and structures

As literatures[19] reported the two tripodal bis(phenol)amino acid ligands of 2-(bis(3,5-di-tert-butyl-2-hydroxybenzyl)amino) acetic acid (H_3L^1) and enantiopure 2-(bis(3,5-di-tert-butyl-2-hydroxybenzyl)amino) propanoic acid (H_3L^2) can construct monomeric metal complexes like tricyclic molecules of atrane[20] which are featured by a three-bladed turbine structures and give rise to a chiral environment around the metal. In this study, these types of monomeric metal complexes are denoted atrane-likes. The reaction of H_3L^1 and trimethylaluminum in toluene at 90 °C afforded complex **1** with a 79% yield with an aluminum atrane-like trimer structure, which was verified by X-ray single crystal graphic analysis (Scheme 1). A single set of ^{1}H NMR peaks in $CDCl_3$ (Figure S1) and the existence of the peak at 1629.97 assigned to the trialuminumatrane-like + Na^+ in the mass spectrum (Figure S2) confirm the stability of the metallocavitand structure in a non-coordinated solvent. Because complex **1** is a racemic species as the following structure analysis, enantiopure complex **2** was designed and synthesized by changing the amino acid from glycine to *L*-alanine. The clear one single set of ^{1}H NMR peaks of complex **2** in $CDCl_3$ (Figure S3) and the peak at 1671.800 assigned to the trialuminumatrane-like + Na^+ in the mass spectrum (Figure S4) also prove that this metallocavitand structure is stable in a non-coordinated solution.

Single crystals of analogous complexes **1** and **2** which are crystallized in $P_{21/c}$ and P_1 space groups respectively, were obtained by slowly cooling the saturated hexane solution. The ORTEP drawing of

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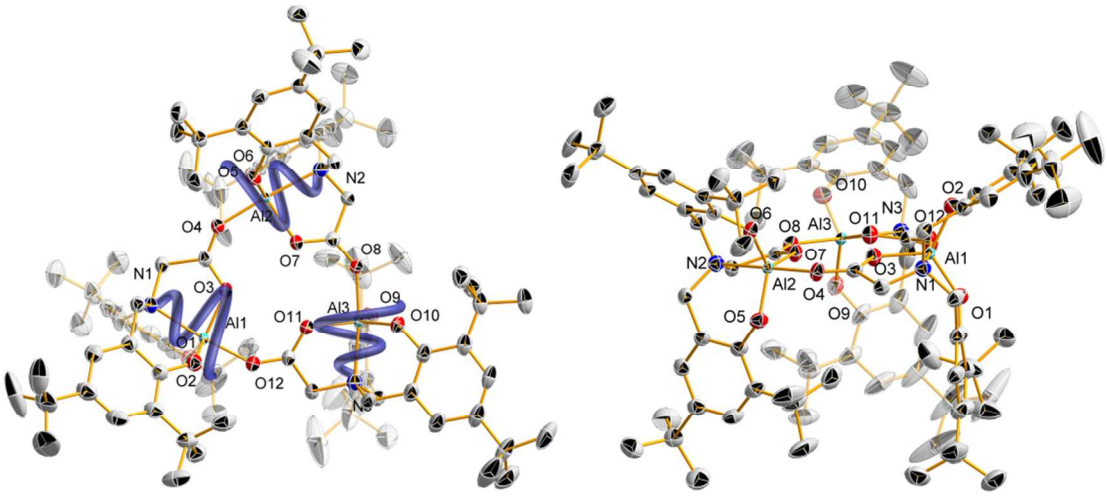
complex **1** is shown in Figure 1. Each aluminum atom, as a characteristic feature of an atrane, is five-coordinated by one nitrogen atom and four oxygen atoms, of which one oxygen atom comes from a neighboring ligand. The surroundings of Al1, Al2, and Al3 atoms are trigonal bipyramid with τ values of 0.88 (Al1), 0.90 (Al2), and 0.83(Al3). τ is a geometric parameter of a five-coordinated metal ion that distinguishes square pyramid (SP) from trigonal bipyramid (TBP) ($\tau = 0$ for SP and $\tau = 1$ for TBP).[21] It is evident that aluminum centers are chiral with the P or M configurations, and the chiralities of the three aluminum atoms are same in one trimer. Complex **1** is a racemic compound with two enantiomers in one unit cell due to the presence of (P, P, P) and (M, M, M) configurations, as shown in Figure 1. The ORTEP drawing of complex **2** is depicted in Figure 2, showing that its structure is similar to complex **1**. As expected, there is only one chiral configuration (S, S, S, M, M, M) for complex **2** in which three S chiralities are derived from three *L*-alanine. Notably, complex **2** has two isomers with similar bond distances in the solid state, as shown in Figure S5b, for the twisted rotation of the phenyl groups, which give rise to slightly different torsion angles between each benzene ring and the plane of the three aluminum atoms. There is a rapid equilibrium between the two isomers in solution, and they give the same NMR signals in a $CDCl_3$ solution. The clear ^1H NMR and ESI mass spectra of complex **2** indicate the nonexistence of other aggregates in the final product after recrystallization. The mass spectra also show that the two metallocavitands can each absorb one sodium ion, but it is difficult to prepare a coordination complex with sodium as the central ion, possibly because of the weak coordinating ability of the center crown constructed by three inner oxygen atoms in the two metallocavitands.



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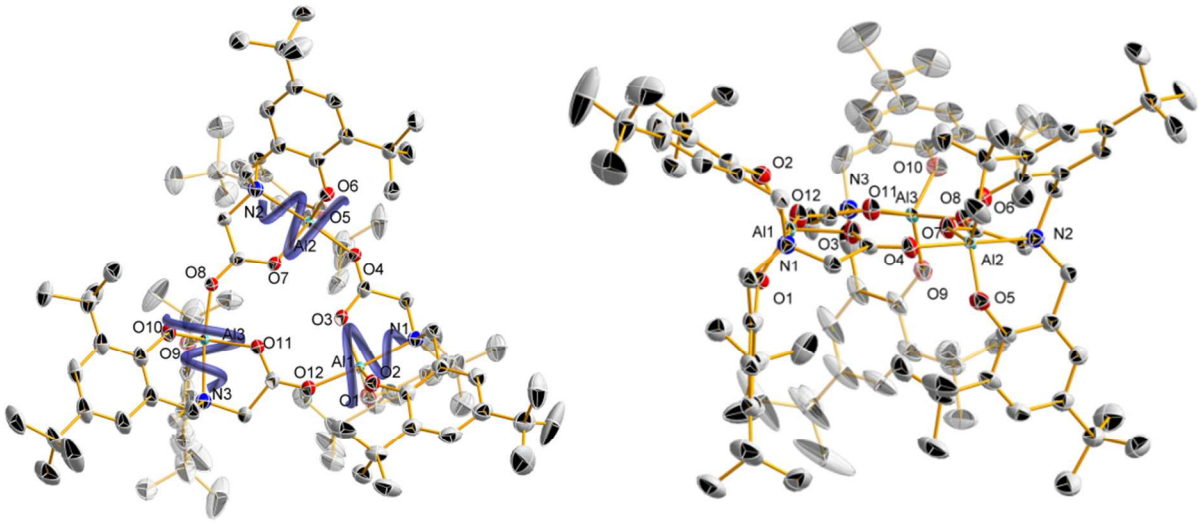
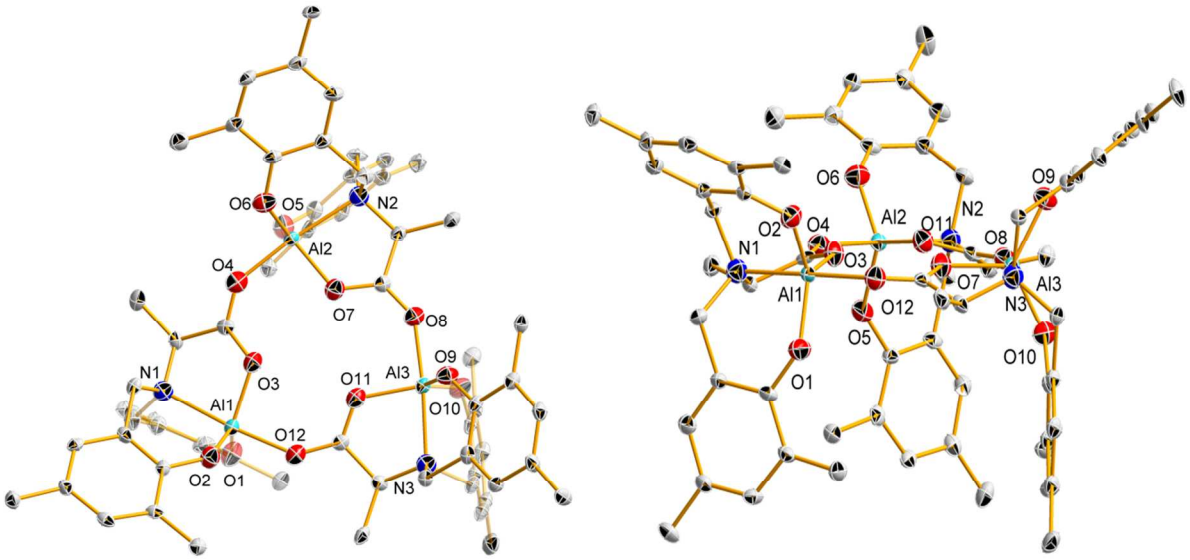
Top view (P, P, P) Side view (P, P, P)



Top view (M, M, M) Side view (M, M, M)

Figure 1 Molecular structure of **1** as 30% ellipsoids. (The hydrogen atoms were omitted for clarity. The upper configuration is (P, P, P), and the lower configuration is (M, M, M)). Selected bond lengths (Å) and angles (°): Al1 N1 2.147(3), Al1 O1 1.735(2), Al1 O2 1.734(2), Al1 O3 1.822(2), Al1 O12 1.881(2), Al2 N2 2.105(3), Al2 O4 1.881(2), Al2 O5 1.747(2), Al2 O6 1.736(2), Al2 O7 1.850(2), Al3 N3 2.106(3), Al3 O8 1.881(2), Al3 O9 1.731(2), Al3 O10 1.742(2), Al3 O11 1.852(2), O12 Al1 N1 174.30(10), O4 Al2 N2 175.87(10), O8 Al3 N3 172.99(10).



Top view Side view

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Figure 2 Molecular structure of **2** as 30% ellipsoids (The hydrogen atoms and the methyl groups on the t-butyl groups were omitted for clarity). Selected bond lengths (Å) and angles (°): Al1 N1 2.115(7), Al1 O1 1.728(5), Al1 O2 1.729(5), Al1 O3 1.827(5), Al1 O12 1.879(5), Al2 N2 2.115(6), Al2 O4 1.868(5), Al2 O5 1.725(5), Al2 O6 1.723(5), Al2 O7 1.832(6), Al3 N3 2.125(7), Al3 O8 1.882(6), Al3 O9 1.727(5), Al3 O10 1.734(5), Al3 O11 1.822(5), O12 Al1 N1 175.3(2), O4 Al2 N2 174.4(3), O8 Al3 N3 174.9(2).

In order to introduce one metal ion as a potential functional point in the center of the metallocavitand, we changed aluminum to magnesium. The tetranuclear complexes **3** and **4** were readily synthesized by the reactions of mixtures of $Mg^{n}Bu_2$, BnOH, and the ligand in toluene at room temperature (Scheme 2). A comparison of the above trinuclear aluminum metallocavitands shows that three negatively charged magnesium atrane-likes create a cavity with a more negative environment; therefore, the fourth magnesium ion can be more firmly fixed into the cavity through covalent bonds to the three magnesium atrane-likes and through electrostatic interactions. These complexes were purified by crystallization, and the yields were up to 57 and 70% for **3** and **4,** respectively. These two complexes are also single-component in $CDCl_3$, toluene, CH_3CN, and even coordination solvent of THF, which was evaluated by the clear single set of NMR peaks (Figures S6, S7). The stability of these two complexes was confirmed by the peaks at 1642.8698 and 1684.8853 in the mass spectra (Figures S8, S9) for complexes **3** and **4**, respectively, which can be ascribed to $Mg_4L_3^{-}+H_3O^{+}$.

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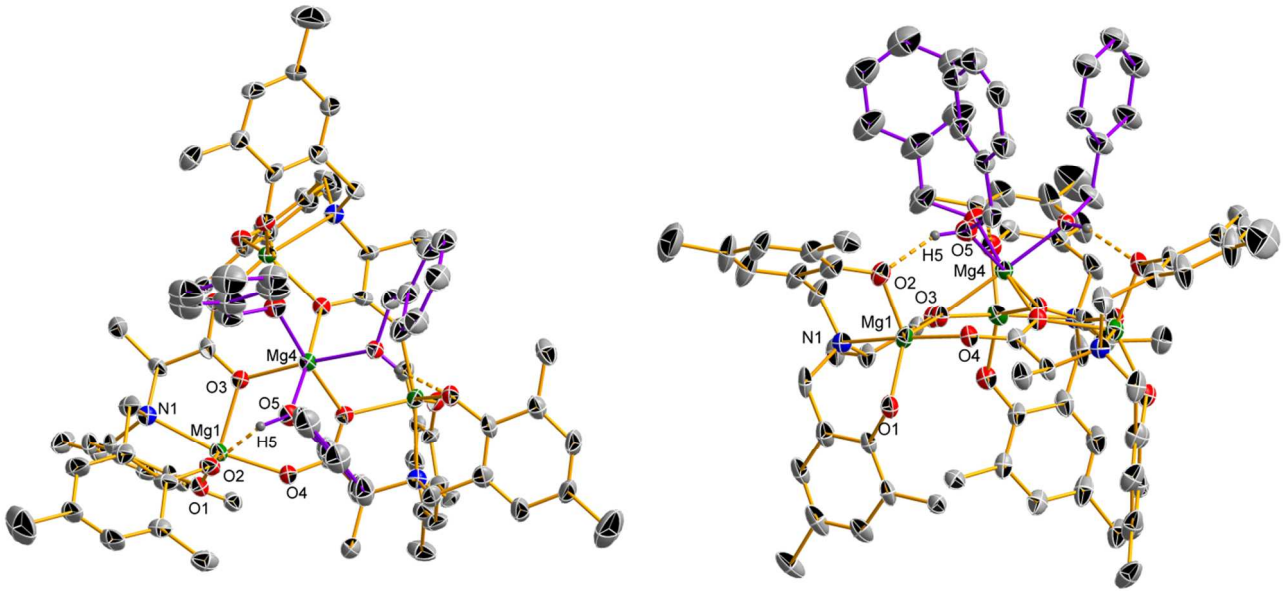

Top View Side View

Figure 3 Molecular structure of the anion portion of **4** as 30% ellipsoids (The hydrogen atoms were omitted for clarity and the bonds in the benzyl alcohols are labeled with the violet color). Selected bond lengths (Å) and angles (°): Mg1 N1 2.219(3), Mg1 O1 1.916(2)， Mg1 O2 1.946(2), Mg1 O3 2.0836(19), Mg1 O4 1.999(2)$^{\#}$, Mg4 O3 2.114(2), Mg4 O5 2.094(2)，O4 Mg1 N1$^{\#}$ 168.36(9), O1 Mg1 O2 133.22(9), O1 Mg1 O3 124.09(9), O1 Mg1 N1 87.26(10). Symmetric operation: # = 1-y, x-y, z.

The single crystals of complex **3** and complex **4** were obtained by slowly cooling the saturated CH_3CN/toluene (1:1, v:v) solution. The solvent molecules in the unit cell of complex **3** are disordered seriously; the crude structure of complex **3** is shown in Figure S10. Fortunately, an accurate structure of complex **4** was obtained after applying the PLATON/SQUEEZE program to suppress the disordered protonated triethyl amine cation. The ORTEP drawing of the anion of complex **4** is depicted in Figure 3, revealing that there are four magnesium atoms in the metallocavitand complexes. Similar to the aluminum analogues, the three atrane-likes of magnesium form a metallocavitand, and the trigonal bipyramidal configuration around Mg1 is more distorted than complex **1**, with τ values of 0.59 (Mg1). Mg4 is centered in the metallocavitand and is six-coordinated by three oxygen atoms from three

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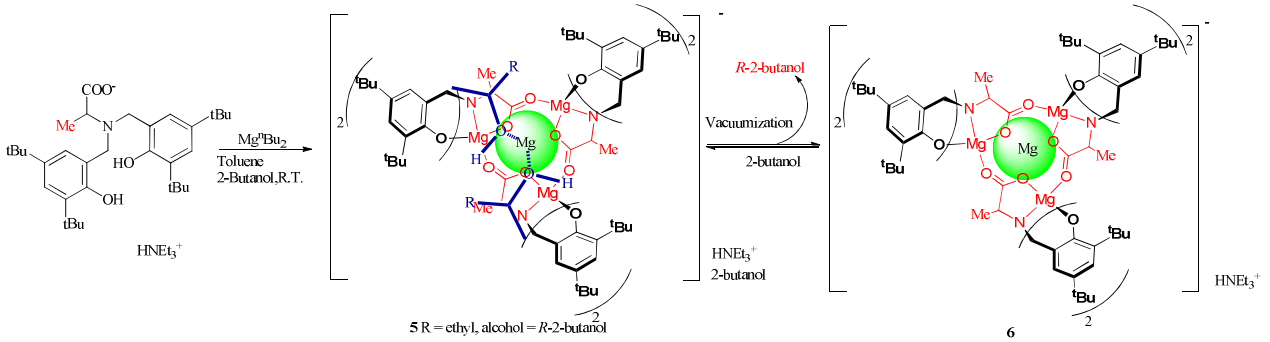
magnesium atrane-likes and three benzyl alcohols; the three benzyl alcohols are further fixed by hydrogen bonds with the oxygen of the phenoxy group. The environment of Mg4 is a nearly perfect octahedron. The chiralities of this tetranuclear complex are (S, S, S, M, M, M) in which the S chiralities are derived from *L*-alanine, which is similar to chiral complex **2**, possibly due to the higher stability of (S, S, S, M, M, M) compared with (S, S, S, P, P, P).

Resolution of a racemic alcohol



Scheme 3 Resolution of racemic 2-butanol.

From the previous analysis, the tetranuclear magnesium metallocavitands can trap three alcohols in the center of the chiral cavity; therefore, the reaction of a mixture of Mg^{n}Bu$_2$, 2-butanol, and the chiral ligand H_3L^2 in toluene was performed in an attempt to trap only the enantiopure alcohol isomers (Scheme 3). After recrystallization of the reaction mixture, pure complex **5** was obtained. The single crystal structure of complex **5** is shown in Figure 4, revealing that the main skeleton structure is the same as complex **4**. It is interesting that only two molecules of 2-butanol can be included in the cavity through the coordinate bonds of O14-Mg4 and O13-Mg4 and hydrogen bonds of O14-H—O6 and O13-H—O2. This phenomena can be attributed to the secondary alcohol of 2-butanol which is bulkier than the primary alcohol for this size-sensitive cavity. Due to the size-limited cavity and chirality of the tetranuclear metallocavitand, both of 2-butanol molecules have *R* chiral configurations. Another interesting feature of this complex is that the included 2-butanol can be easily removed under vacuum at room temperature, and the skeleton complex **6** was obtained. Therefore, the skeleton complex **6** can be recycled to separate enantiomers of 2-butanol under mild condition. Note that another molecular 2-

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butanol is co-crystallized at the outer rim of the metallocavitand in the solid via two hydrogen bonds of N4-H—O15 and O15-H—O5 (Figure 4). The 2-butanol trapped at this location is racemic, because the four atoms of C108, C109, C110, and O15 are nearly planar due to the disorder of chirality at C109. This phenomenon proves that the enantioselectivity in the enforced-cavity is higher than in the peripheral groups. The enantiomeric excess value (*ee*) of the separated 2-butanol is 53(±1)% (Figure S12), which was analyzed by high-performance liquid chromatography (HPLC) after derivation. The *ee* value is slightly lower than that of the crystal structure (67%), which can be attributed to the residual racemic 2-butanol on the surface of the crystalline solid. Complex **6** is sensitive to moisture for the coordination of water to the empty center; thus, only freshly prepared complex **6** can be recycled to separate enantiomers of 2-butanol, giving similar *ee* values. A partial 2-butanol in complex **5** can be replaced by the trace amount of water in the system, which can also lead to the lower *ee* value of the separated 2-butanol compared with the theoretical value calculated from the crystal structure. To gain insight into the interaction between complex **6** and 2-butanol in solution, the related NMR experiments in $CDCl_3$ were also performed (Figure 5, Figure S13, Figure S14). After addition of 3 equivalents of S or R 2-butanol to the solution of enantiopure skeleton complex **6**, the proton signals of the methene of the ligand at 3.19 and 3.02 ppm shifted to 3.20 and 2.94 ppm and to 3.22 and 2.91 ppm, respectively, which indicated that both of S and R 2-butanol can interact with complex **6** in solution. The different chemical shifts partially reflect the different interaction strengths for complex **6** + (S)-2-butanol and complex **6** + (R)-2-butanol. In fact, (R)-2-butanol can cause a more sudden drift upon 1 equivalent guest addition in ^{1}HNMR host signals than (S)-2-butanol which can prove (R)-butanol is the better guest for complex **6** (Figure S13, Figure S14). But the chemical shifts kept changing even after the addition 20 equivalents 2-butanol following the addition of 10 equivalents 2-butanol, we think this may attribute to the low binding constant between complex **6** and 2-butanol. Both the NMR titration and the crystallization results suggest that the interaction for (R)-2-butanol is stronger.

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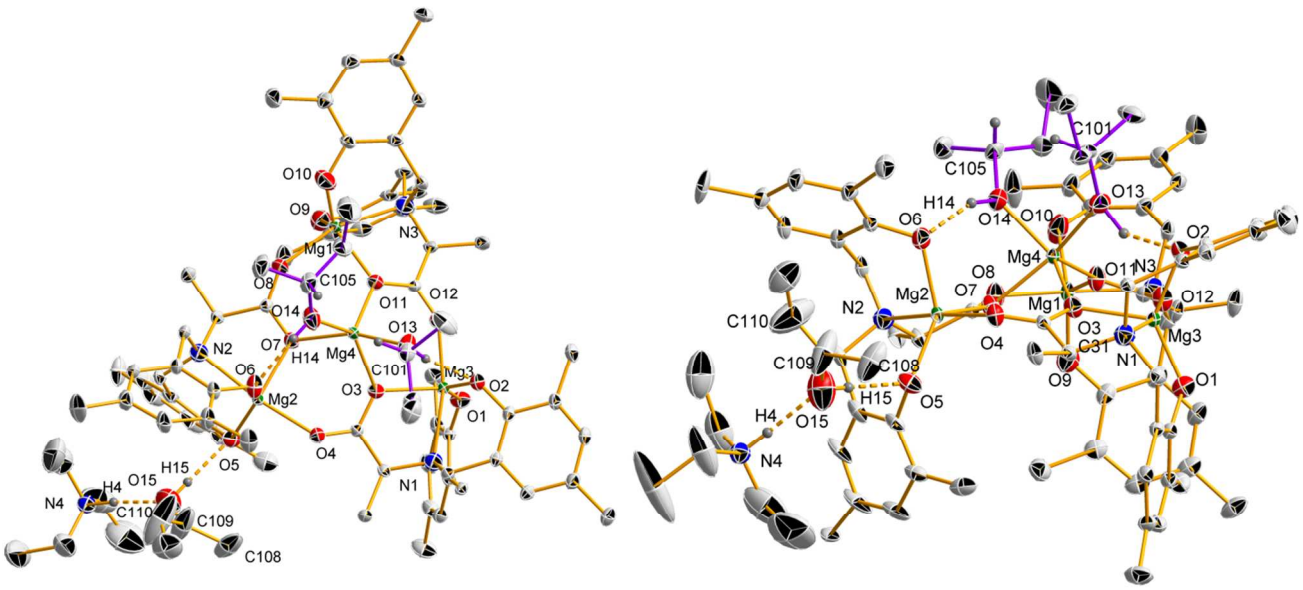

Top View Side View

Figure 4 Molecular structure of complex **5** as 30% ellipsoids. (The hydrogen atoms and the methyl groups on the t-butyl groups were omitted for clarity, and the bonds in in the *R*-2-butanols are labeled with the violet color). Selected bond lengths (Å) and angles (°): Mg1 O8 2.0277(3), Mg1 O9 1.9146(3), Mg1 O10 1.9071(4), Mg1 O11 2.1207(3), Mg4 O3 2.0516(3), Mg4 O7 2.1035(2), Mg4 O11 2.0132(3), Mg4 O13 2.0805(3), Mg4 H13 2.3084, Mg4 O14 2.0226(3), Mg4 C98 2.8597(4), O9 Mg1 N3 89.026(12), O9 Mg1 O8 97.184(12), O9 Mg1 O11 121.820(13), O10 Mg1 N3 92.025(13), O10 Mg1 O8 98.666(14), O10 Mg1 O9 122.709(15), O10 Mg1 O11 113.845(13), O11 Mg4 O3 104.175(11), O11 Mg4 O7 93.243(10), O11 Mg4 O13 104.926(11), O11 Mg4 O14 119.104(13), O13 Mg4 O7 161.586(12), O3 Mg4 O7 88.301(10), O3 Mg4 O13 84.427(10).

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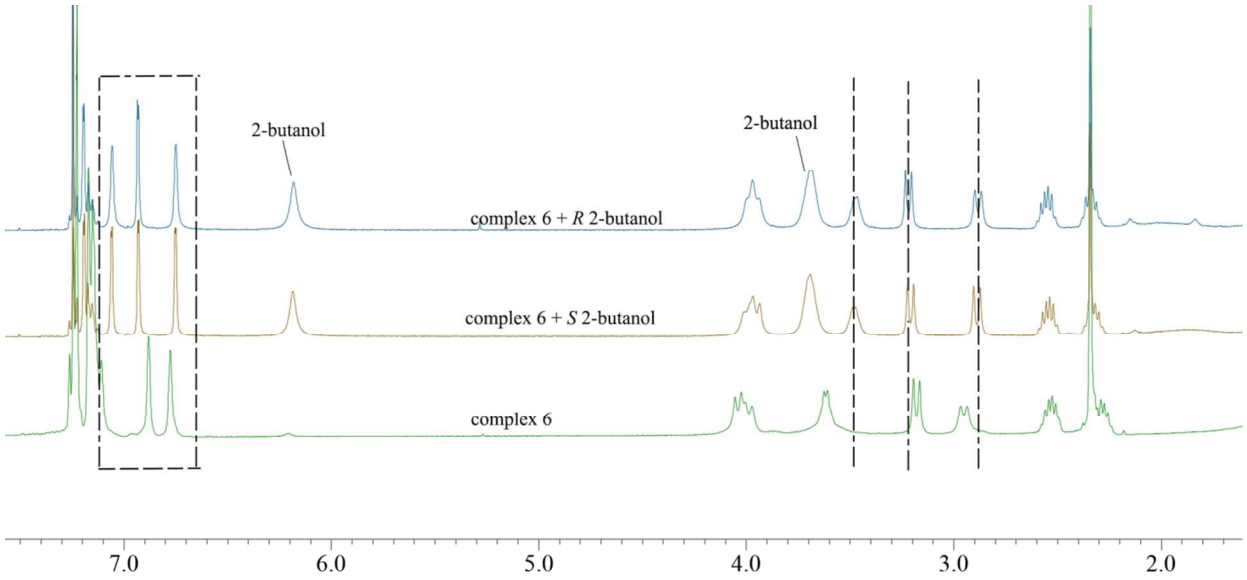

Figure 5 ^{1}H NMR spectra (400 MHz $CDCl_3$) of complex **6** + 2-butanol.

Inspired by the above results, the reaction of mixtures of $Mg^{n}Bu_2$, 1-phenylethanol (PEA), and the chiral ligand H_3L^2 in toluene was also performed in an attempt to separate racemic 1-phenylethanol (Scheme 4). The *ee* value of the final desorbed 1-phenylethanol is 33(±1)% (Figure S15). To understand the lower *ee* value compared with 2-butanol, we obtained the single crystal of complex **7**. Because some disordered solvent molecules are difficult to solve, the PLATON/SQUEEZE routine was applied, and a credible structure was obtained.[21] The structure of complex **7** is shown in Figure 6, revealing that the center cavity included three H_2O molecules rather than the expected 1-phenylethanol, which differs from complex **5** because 1-phenylethanol is too bulky for the size-limited cavity. Based on the solid structure, the co-crystallized 1-phenylethanol attached to the metallocavitand via the hydrogen bond of O16-H—O9 on the outer rim has an absolute *R* configuration. Because there are three molecules of 1-phenylethanol co-crystalized in the crystal, as evidenced by the ^{1}H NMR spectrum (Figure S16), the disorder solvents should include another two molecules of racemic 1-phenylethanol in the unit cell which gives rise to the low *ee* value of the separated 1-phenylethanol and agrees well with the experimental *ee* value.

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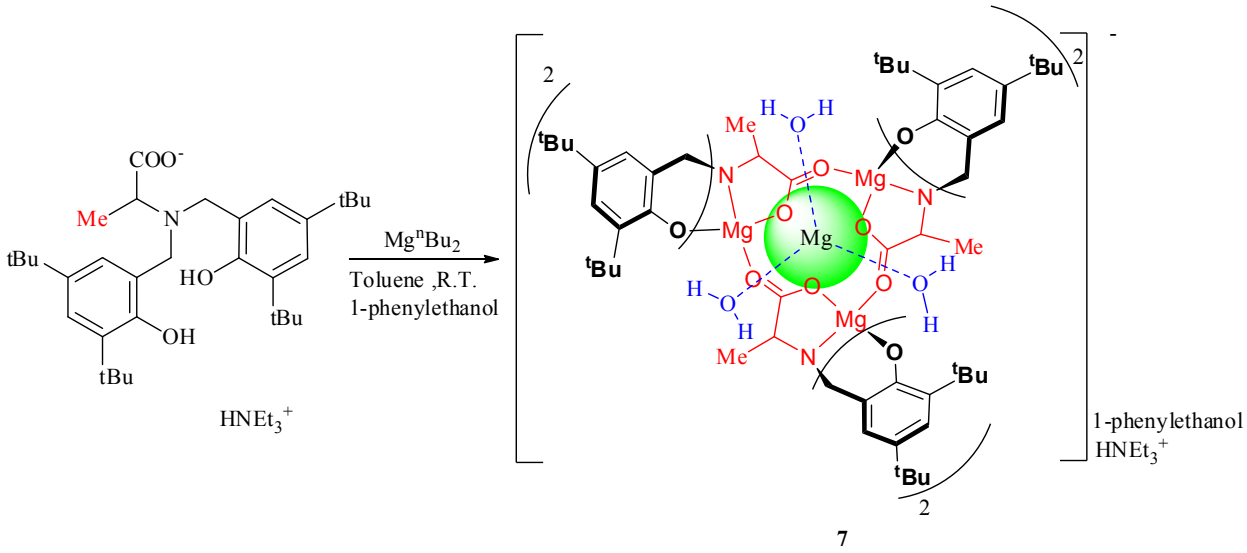

Scheme 4 Resolution of racemic 1-phenylethanol.

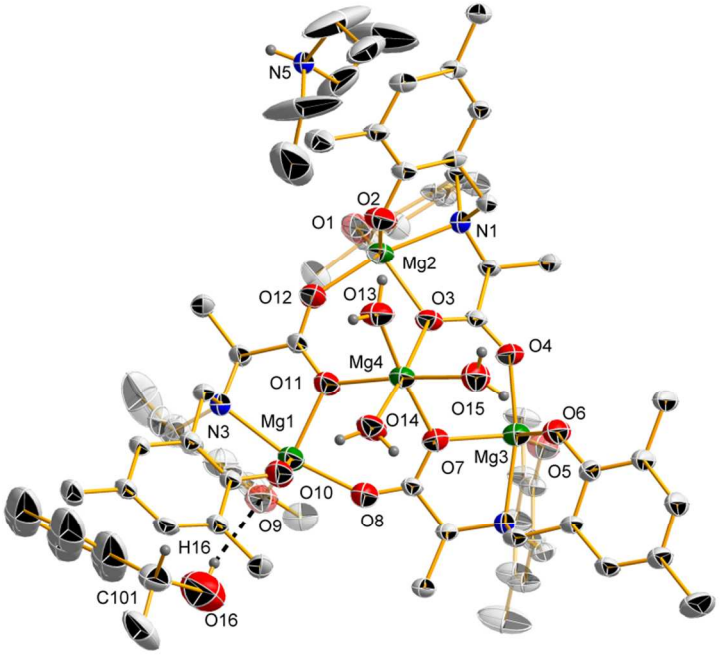

Figure 6 Molecular structure of complex **7** as 30% ellipsoids. (The hydrogen atoms and the methyl groups on the t-butyl groups were omitted for clarity). Selected bond lengths (Å) and angles (°): Mg1 O8 2.0203(8), Mg1 O9 1.9490(9), Mg1 O10 1.9505(9), Mg1 O11 2.0688(7), Mg1 N3 2.2038(9), Mg2 Mg4 3.5609(5), Mg2 O1 1.9454(10), Mg2 O2 1.9436(8), Mg2 O3 2.0775(7), Mg2 O12 2.0074(8), Mg2 N1 2.1994(9), Mg3 O4 2.0158(7), Mg3 O5 1.9099(9), Mg3 O6 1.9539(9), Mg3 O7 2.0840(8), Mg3 N2 2.2204(8), Mg4 O3 2.1102(8), Mg4 O7 2.0852(7), Mg4 O11 2.1344(8), Mg4 O13 2.0493(7), Mg4 O14 2.0656(9), Mg4 O15 2.1078(9).O8 Mg1 O11 90.7(2), O8 Mg1 N3 168.1(3), O11 Mg1 N3 78.0(2), O9 Mg1 O11 129.5(3), O9 Mg1 N3 88.9(3), O9 Mg1 O10 126.5(3), O8 Mg1 O11 90.71(3), O8 Mg1 N3

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168.23(4), O11 Mg1 N3 78.07(3), O9 Mg1 O11 129.39(4), O9 Mg1 O10 126.73(4), O9 Mg1 N3 88.92(4).

Only a few examples of the highly enantioselective inclusion of small alcohols have been reported[17, 22] because enantioselective recognition and inclusion of a small alcohol, such as 2-butanol, is challenging due to the difficult discrimination of the subtle structural difference between the enantiomers. This study suggests that metallocavitand complexes can also be applied to separate small chiral alcohols.

CONCLUSIONS

Seven new metallocavitand complexes **1**-**7** with chiral cavity were synthesized via self-assembly of aluminum and magnesium atrane-likes. The recognition of *R*-2-butanol from racemic 2-butanol can be achieved in the chiral cavity of metallocavitand complex **5**. The crystal structure shows that complex **5** includes two molecules of *R*-2-butanol in the center of the cavity and one racemic 2-butanol is hydrogen bonded on the rim of the metallocavitand, which indicated that the chiral size-limited cavity is more sensitive to the chirality of 2-butanol than the groups at the outer rim. Furthermore, desorption of *R*-2-butanol is successful through simple vacuumization and skeleton complex **6** can be obtained, which can be reused to separate racemic 2-butanol. The metallocavitands are also size-sensitive, as evidenced by the experiment on the chiral resolution of 1-phenylethanol. The host-guest mechanism for the enantioselective separation was clearly revealed through X-ray crystal structural analysis.

EXPERIMENTAL SECTION

General Procedures. In addition to the synthesis of H_3L^1 and H_3L^2, all of the reactions were performed under a dry nitrogen atmosphere using the standard Schlenk techniques or a glovebox. Toluene and hexane were dried by refluxing over sodium benzophenone ketyl. CH_2Cl_2 was dried over P_2O_5. All of the solvents were distilled and stored in solvent reservoirs containing 4 Å molecular sieves and were purged with nitrogen. The ^1H and ^{13}C NMR spectra were recorded using spectrometers of the Varian Mercury Plus family. The mass spectroscopic data were obtained on a Bruker APEX II (FT-

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ICRMS) spectrometer with CD_3Cl and a small amount of ethanol as solvents. BnOH, Et_3N, racemic 2-butanol, and 1-phenylethanol were dried with CaH_2 for 12 at 60 °C and then distilled under nitrogen atmosphere. The other chemicals were purchased and used without further purification. The enantiomeric excess values of the separated alcohols were determined by HPLC with a Chiralcel OB-H column on a Waters 600 Delta instrument. Synthesis of $H_3\mathbf{L^1}$ was achieved using the literature procedure.[19]

Synthesis of $H_3\mathbf{L^2}$. A mixture of 2, 4-di-tert-butylphenol (4.9 g, 24.2 mmol), *L*-alanine (1.1 g, 12.1 mmol), triethyl-amine (1.7 mL, 12.1 mmol), and 36% aqueous formaldehyde (4 mL, 48 mmol) was stirred in 20 mL methanol at room temperature for 12 h and then refluxed for 24 h. The mixture was cooled and filtered, then the residue solid was washed with cold methanol to give a white powder as the triethylamine salt. Further purification was then achieved by washing the precipitate with boiling water and drying the solid in air. Yield：5.4 g，8.6 mmol (72%). Anal. calc for $C_{33}H_{51}N_1O_4(NEt_3)$ (626.4 g/mol): C 74.71, H 10.61, N 4.47. Found: C 75.36, H 10.42, N 4.31. ^{1}H NMR ($CDCl_3$-300 MHz): δ (ppm) 7.15 (s, Ar-*H*, 2H), 6.86 (s, Ar-*H*, 2H), 4.14 (d, CH_2, 2H, J = 14Hz), 3.52 (q, C*H*, 1H), 3.45 (d, CH_2, 2H, J = 13 Hz), 3.11 (q, NCH_2, 6H), 1.26-1.36 (m, -CH_3, t-Bu, 30H), 1.26 (s, t-Bu, 18H). ^{13}C NMR ($CDCl_3$-75 MHz): δ (ppm) 179.5, 154.0, 139.9, 135.4, 123.1, 121.6, 57.3, 53.3, 45.4, 35.0, 34.1, 31.8, 29.6, 8.7, 8.3.

Synthesis of complex **1** ($Al_3\mathbf{L^1}_3$). A mixture of $AlMe_3$ (1.0 M in hexane, 1.1 mL, 1.1 mmol) and 2-(bis(3,5-di-tert-butyl-2-hydroxybenzyl)amino) acetic acid (0.5114 g, 1.0 mmol) in toluene was stirred at 0 °C for 1 h. Next, the solution was heated to 90 °C and stirred for 12 h. Subsequently, the solvent was removed under vacuum, and recrystallization with hexane afforded a white solid. Yield: 0.43 g, 0.26 mmol (79%). A single crystal suitable for structural characterization was obtained from slowing cooling of a warm acetonitrile/toluene (1:1,v:v) solution. Anal. calcd for $C_{96}H_{138}Al_3N_3O_{12}$ (1607.08 g/mol): C 71.75, H 8.66, N 2.61. Found: C 71.20, H 8.45, N 2.50. ESI-MS (positive) in CH_3CN: m/z 1629.97 [**1**+Na^+]. ^{1}H NMR ($CDCl_3$-300 MHz): δ (ppm) 7.15 (s, Ar-*H*, 6H), 6.79 (s, Ar-*H*, 6H), 3.72 (s, ArCH_2N,

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12H), 3.48 (s, COCH_2N, 6H), 1.19 (s, t-Bu, 54H), 1.10 (s, t-Bu, 54H). ^{13}C NMR ($CDCl_3$-75 MHz): δ (ppm) 179.0, 154.9, 139.8, 138.4, 129.9, 124.5, 124.0, 120.2, 59.3, 56.7, 34.7, 34.1, 31.7, 29.3.

Synthesis of complex **2** ($Al_3\mathbf{L^2}_3$). A mixture of $AlMe_3$ (1.0 M in hexane, 1.1 mL, 1.1 mmol) and 2-(bis(3,5-di-tert-butyl-2-hydroxybenzyl) amino) propanoic acid (0.6264 g, 1.0 mmol) in toluene was stirred at 0 °C for 1 h. Next, the solution was heated to 90 °C and stirred for 12 h. Subsequently, the solvent was removed under vacuum, and recrystallization with hexane afforded a white solid. Yield: 0.48 g, 0.29 mmol (88%). A single crystal suitable for structural characterization was obtained from slowing cooling of a warm acetonitrile/toluene (1:1,v:v) solution. Anal. calcd for $C_{99}H_{144}Al_3N_3O_{12}$ (1649.16 g/mol): C 72.10, H 8.80, N 2.55. Found: C 71.80, H 8.65, N 2.35. ESI-MS (positive) in CH_3CN: m/z 1671.8 [**2**+Na^+]. ^{1}H NMR ($CDCl_3$-300 MHz): δ (ppm) 7.18 (s, Ar-*H*, 3H), 7.07 (s, Ar-*H*, 3H), 6.86 (s, Ar-*H*, 3H), 6.73 (s, Ar-*H*, 3H), 4.07 (d, ArCH_2N, 6H, J = 12 Hz), 3.91 (q, COC*H*N, 3H, J = 6.9 Hz), 3.38 (d, ArCH"*H*"N, 3H, J = 12 Hz), 3.07 (d, ArCH"*H*"N, 3H, J = 12 Hz), 1.47 (d, CH_3, 9H, J = 6.9 Hz), 1.34 (s, t-Bu, 27H), 1.22 (s, t-Bu, 27H), 1.18 (s, t-Bu, 27H), 0.81 (s, t-Bu, 27H). ^{13}C NMR ($CDCl_3$-75 MHz): δ (ppm) 181.5， 155.1, 139.9, 138.1, 124.5, 124.0, 120.1, 57.7, 54.5, 34.9, 34.1, 31.7, 29.4, 6.62.

Synthesis of complex **3** ($Mg_4\mathbf{L^1}_3$·3BnOH·$HNEt_3$). A mixture of anhydrous triethylamine (0.17 mL, 1.2 mmol) and 2-(bis(3,5-di-tert-butyl-2-hydroxybenzyl)amino) acetic acid (0.5114 g, 1.0 mmol) in toluene was stirred at room temperature for 3 h. Then, this solution was added dropwise to a mixture of Mg^nBu_2 (1.0 M in hexane, 1.4 mL, 1.4 mmol) and BnOH (1.0 M in toluene, 1.4 mL, 1.4 mmol) in toluene (10 mL) at room temperature. After stirring for 12 h, the solvent was removed under vacuum to afford a white solid, and recrystallization with hexane afforded a white solid. Yield: 0.40 g, 0.19 mmol (57%). A single crystal suitable for structural characterization was obtained from slowing cooling of a warm acetonitrile/toluene (1:1, v:v) solution, but some solvent molecules are very disordered and just crude structure was provide in the supporting information. Anal. calcd for $C_{123}H_{181}Mg_4N_4O_{15}$·$2H_2O$ (**3** + $2H_2O$, 2052.99 + 36.02 g/mol): C 70.72, H 8.93, N 2.68. Found: C 70.63, H 8.46, N 2.40. ^{1}H NMR ($CDCl_3$-300 MHz): δ (ppm) 7.22 (s, Ar-*H*, 18H), 7.07 (s, Ar-*H*, 3H), 6.96 (s, Ar-*H*, 3H), 6.71 (s, Ar-*H*,

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3H), 4.65 (b, PhCH_2, 6H), 4.20 (b, COCH"H"N , 3H), 4.09 (d, COCH"H"N, 3H, J = 12 Hz), 3.48 (d, ArCH"H"N, 3H, J = 12 Hz), 3.03 (d, ArCH"H"N, 3H, J = 12 Hz), 2.77 (d, ArCH"H"N, 6H, J = 12 Hz), 2.33 (q, NCH_2Me (Et_3NH^+), 6H, J = 6.9Hz), 1.37 (s, t-Bu, 27H), 1.28 (s, t-Bu, 27H), 1.24 (s, t-Bu, 27H), 0.95 (s, t-Bu, 27H), 0.74 (t, -CH_3, 9H, J = 6.9Hz). ^{13}C NMR ($CDCl_3$-75 MHz): δ (ppm) 160.6, 140.6, 138.4, 137.2, 129.1, 128.6, 127.7, 127.1, 125.6, 124.2, 123.8, 62.3, 57.4, 56.4, 45.6, 35.0, 33.4, 30.3, 29.2, 8.3.

Synthesis of complex **4** ($Mg_4\mathbf{L^2}_3$·3BnOH·$HNEt_3$). Mg^nBu_2 (1.0 M in hexane, 1.4 mL, 1.4 mmol) was added dropwise to a stirred solution of BnOH (1.0 M in toluene, 1.4 mL, 1.4 mmol) in toluene (10 mL) at room temperature. After stirring for 2 h, the solution was added dropwise to 10 mL toluene solution of 2-(bis(3,5-di-tert-butyl-2-hydroxybenzyl)amino) propanoic acid (0.6264 g, 1.0 mmol). The reaction mixture was stirred for 12 h at room temperature, then the solvent was removed under vacuum to afford a white solid, and the residue was recrystallized with hexane to give a white solid. Yield: 0.49 g, 0.23 mmol (70%). A single crystal suitable for structural characterization was obtained from slowing cooling of a warm acetonitrile/toluene (1:1, v:v) solution. Anal. calcd for $C_{126}H_{187}Mg_4N_4O_{15}$ (2095.07 g/mol): C 72.23, H 9.00, N 2.67. Found: C 71.83, H 9.10, N 2.50. ^{1}H NMR ($CDCl_3$-300 MHz): δ (ppm) 7.21 (s, Ar-H, 18H), 7.05 (s, Ar-H, 3H), 6.96 (s, Ar-H, 3H), 6.75 (s, Ar-H, 3H), 4.64 (m, PhCH_2, ArCH_2N, COCHN, 11H), 3.95 (m, ArCH_2N, 4H), 3.45 (s, ArCH_2N, 2H), 3.24 (d, ArCH"H"N, 2H, J = 12 Hz), 2.87 (d, ArCH"H"N, 2H, J = 12 Hz), 2.30 (m, NCHHMe (Et_3NH^+), 3H), 2.15 (m, NCHHMe (Et_3NH^+), 3H), 1.35 (s, t-Bu, 27H), 1.29 (s, t-Bu, 27H), 1.24 (s, t-Bu, 27H), 0.94 (s, t-Bu, 27H), 0.69 (t, -CH_3, 9H, J = 6.3 Hz). ^{13}C NMR ($CDCl_3$-75 MHz): δ (ppm) 160.6, 128.3, 127.4, 124.8, 123.9, 54.8, 45.6, 35.0, 34.7, 33.9, 33.7, 31.9, 31.8, 30.2, 28.9, 8.0, 5.8.

Synthesis of complex **5** ($Mg_4\mathbf{L^2}_3$·3(butan-2-ol)·$HNEt_3$). Mg^nBu_2 (1.0 M in hexane, 1.4 mL, 1.4 mmol) was added dropwise to a stirred solution of 2-butanol (0.55 mL, 6 mmol) in toluene (10 mL) at room temperature. After stirring for 2 h, the solution was added dropwise to a 10 mL toluene solution of 2-(bis(3,5-di-tert-butyl-2-hydroxybenzyl)amino) propanoic acid (0.6264 g, 1.0 mmol). The reaction mixture was stirred for 12 h at room temperature, then the solvent was removed under vacuum to afford

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a yellow solid, and recrystallization with hexane afforded a yellow solid. Due to the volatilization of 2-butanol, a clear NMR spectrum containing 2-butanol could not be obtained. However the NMR spectrum of a single crystal including the solvent showed that the major peaks are similar to skeleton complex **6,** which indicates that 2-butanol is weakly trapped in the metallocavitand center. A single crystal suitable for structural characterization was obtained from slowing cooling of a warm acetonitrile/toluene (1:1, v:v) solution.

Synthesis of complex **6** ($Mg_4\mathbf{L^2}_3\cdot HNEt_3$). 2-butanol in complex **5** (0.1 g, 0.050 mmol) was removed under vacuum to afford a yellow solid (0.084 g), Yield: 0.084 g, 0.048 mmol (95%). Anal. calcd for $C_{105}H_{163}Mg_4N_4O_{12}$ (1768.17 g/mol): C 71.22, H 9.28, N 3.16. Found: C 71.63, H 9.18, N 3.40. ^{1}H NMR ($CDCl_3$-400 MHz): δ (ppm) 7.22 (s, Ar-*H*, 3H), 7.08 (s, Ar-*H*, 3H), 6.96 (s, Ar-*H*, 3H), 6.78 (s, Ar-*H*, 3H), 4.03 (m, ArC*H*$_2$N, COC*H*N, 6H), 3.63 (d, ArC*H*$_2$N, 3H, J = 6 Hz), 3.19 (d, ArC"*H*"HN , 3H, J = 12 Hz), 2.95 (d, ArCH"*H*"N , 3H, J = 12 Hz), 2.54 (m, NC*H*HMe (Et_3NH^+), 3H), 2.33 (m, NC*H*HMe (Et_3NH^+), 3H), 1.41 (s, t-Bu, 27H), 1.31 (d, C*H*$_3$, 9H), 1.26 (s, t-Bu, 27H), 1.24 (s, t-Bu, 27H), 1.30 (s, t-Bu, 27H), 0.77 (t, -C*H*$_3$, 9H, J = 6.3 Hz). ^{13}C NMR ($CDCl_3$-100 MHz): δ (ppm) 160.5, 138.0, 129.1, 128.3, 126.2, 125.3, 124.0, 56.5, 55.0, 46.0, 35.0, 34.0, 32.0, 30.6, 8.4, 6.0.

Synthesis of complex **7** ($Mg_4\mathbf{L^2}_3\cdot$(1-PEA)$\cdot 3H_2O\cdot HNEt_3$). Mg^nBu_2 (1.0 M in hexane, 1.4 mL, 1.4 mmol) was added dropwise to a stirred solution of 1-phenylethanol (PEA) (0.72 mL, 6 mmol) in toluene (10 mL) at room temperature. After stirring for 2 h, the solution was added dropwise to 2-(bis(3,5-di-tert-butyl-2-hydroxybenzyl)amino) propanoic acid (0.6264 g, 1.0 mmol) in toluene (10 mL). The reaction mixture was stirred for 12 h at room temperature, then the solvent was removed under vacuum to afford a yellow solid, and recrystallization with hexane afforded a yellow solid. A single crystal suitable for structural characterization was obtained from slowing cooling of a warm acetonitrile/toluene (1:1, v:v) solution. Yield: 0.15 mmol, 0.33 g (45%). Anal. calcd for $C_{105}H_{160}Mg_4N_4O_{12}\bullet 3(C_8H_{10}O)\bullet 4(H_2O)$ (2206.19 g/mol): C 70.23, H 9.05, N 2.54. Found: C 69.96, H 9.01, N 2.10. ^{1}H NMR ($CDCl_3$-400 MHz): δ (ppm) 7.36 (m, Ar-*H*, 15H), 7.21 (s, Ar-*H*, 3H), 7.07 (s, Ar-*H*, 3H), 6.96 (s, Ar-*H*, 3H), 6.77 (s, Ar-*H*, 3H), 4.90 (m, PhC*H*, 3H), 3.98 (m, ArC*H*$_2$N, COC*H*N, 6H),

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3.47 (s, ArC*H*$_2$N, 3H), 3.24 (d, ArCH"*H*"N, 3H, J = 12 Hz), 2.91 (d, ArCH"*H*"N, 3H, J = 12 Hz), 2.55 (m, NC*H*HMe (Et_3NH^+), 3H), 2.32 (m, NC*H*HMe (Et_3NH^+), 3H), 1.51 (m, -C*H*$_3$, 9H), 1.40 (s, t-Bu, 27H), 1.28 (s, t-Bu, -C*H*$_3$, 36H), 1.24 (s, t-Bu, 27H), 0.96 (s, t-Bu, 27H), 0.79 (t, -C*H*$_3$, 9H, J = 6.4 Hz).

Separation experiment for 2-butanol. The 2-butanol included in complex **5** was transferred to a flask under vacuum and frozen with liquid nitrogen. The separated 2-butanol was derivatized with 4-methoxybenzoyl chloride in the presence of Et_3N and 4-dimethylaminopyridine (DMAP, used as a catalyst) under continuous stirring at room temperature for 24 h before being subjected to HPLC separation (on a Chiralcel OB-H column with a flow rate of 0.5 mL/min and an eluent of 99:1 of hexane/isopropanol). According to the single crystal structure of complex **5**, the absolute configuration of the major enantiomer was assigned as *R*. The experimental data along with the HPLC graphs with the retention times (t_R) and area percentages for the major and minor enantiomers are provided in the Supporting Information.

Separation experiment for 1-phenylethanol. Complex **7** was dissolved into a mixture of dry isopropanol and CH_2Cl_2 at room temperature. After 4 h, the liquid containing isopropanol and desorbed 1-phenylethanol was filtered, and the enantiomeric excess of the released 1-phenylethanol was determined by chiral HPLC analysis on a Chiralcel OB-H column with an eluent of 95:5 of hexane/isopropanol at a flow rate of 0.5 mL/min.

Crystallographic studies.

The data were collected at temperatures ranging from 100 to 293 K on SuperNova (Dual) X-ray diffraction diffractometer with graphite-monochromated Cu/Mo Kα radiation (λ = 1.54184/0.71073 Å). The structures were solved and refined by the direct methods of the SHELX-97 program.[23] The non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All of the hydrogen atoms were placed by geometrical considerations and were added to the structure factor calculation. In the case of complex **7**, the PLATON/SQUEEZE routine[24] was applied because certain disordered solvents are difficult to solve. The crystal data and refinement results are summarized in Table 1.

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Table 1. Details of the X-ray structure Determinations of Complexes **1**, **2**, **4**, **5**, and **7**.

	1	**2**	**4**	**5**	**7**
formula	$2(C_{96}H_{138}Al_3N_3O_{12})\cdot 5(C_7H_8)\cdot 3(C_2H_3N)$	$2(C_{99}H_{144}Al_3N_3O_{12})\cdot 5.55(C_7H_8)\cdot 0.6(C_2H_3N)$	$(C_{120}H_{165}Mg_4N_3O_{15})\cdot(C_6H_{16}N)$	$(C_{113}H_{179}Mg_4N_4O_{14})\cdot 4(C_7H_8)\cdot(C_4H_9O)$	$(C_{99}H_{150}Mg_4N_3O_{15})\cdot(C_8H_{10}O)\cdot(C_6H_{16}N)\cdot(C_2H_3N)$
fw	3797.92	3834.20	2248.0	2357.50	1984.87
temp	150.00(10)	100.01(10)	99.99(10)	293(2)	150.00(10)
crystal system	monoclinic	triclinic	trigonal	monoclinic	monoclinic
space group	$P2_1/c$	P1	$P3_2$	$P2_1$	$P2_1$
a, Å	18.9563(4)	17.0608(6)	21.817(3)	15.8715(5)	15.9337(7)
b, Å	16.2903(4)	18.6696(6)	21.817(3)	26.8064(8)	26.4951(10)
c, Å	38.5631(9)	19.2836(8)	16.960(3)	17.2847(5)	16.9088(5)
α,°	90.00	80.388(3)	90.00	90.00	90.00
β,°	101.677(3)	75.485(3)	90.00	103.577(3)	99.435(4)
γ,°	90.00	88.132(3	120.00	90.00	90.00
V, Å^3	11662.0(5)	5862.4(4)	6991.1(18)	7148.4(4)	7041.7(5))
Z	2	1	2	2	2
density(calcd) g·cm$^-$	1.082	1.086	1.074	1.095	0.936

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absorb.coeff. mm^{-1}	0.089	0.089	0.084	0.696	0.643
F(000)	4112	2079	2148	2574	2160
Radiation	Mo Kα	Mo Kα	Mo Kα	Cu Kα	Cu Kα
θ range	1.66-25.00	3.03-25.00	3.23-25.00	4.179-70.319	3.12-69.99
index ranges	-22<h<21 -19<k<19 -35<l<45	-20<h<20 -20<k<22 -19<l<22	-25<h<11 -21<k<25 -20<l<10	-19<h<12 -30<k<32 -20<l<21	-19<h<19 -32<k<32 -19<l<20
data/restr./param	19495/55/1273	28538/273/2485	10342/3/443	21494/109/1582	26974/207/1293
GOF	0.984	1.011	0.900	1.039	1.019
final *R* indexes	R_1=0.0795	R_1=0.0865	R_1= 0.0897	R_1=0.0746	R_1= 0.0891
[$I > 2\sigma(I)$]	wR_2=0.1975	wR_2=0.2061	wR_2= 0.2114	wR_2= 0.1917	wR_2= 0.2384
peak and hole e.$Å^{-3}$	0.715,-0.824	0.869, -0.526	0.344,-0.244	0.866,-0.529	0.57,-0.41
CCDC number	988259	988260	988262	988263	988264

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Supporting Information. X-ray crystallographic data of **1**, **2**, **3**, **4**, **5,** and **7** with CCDC numbers of 988259-988264. The NMR and mass spectra, and the HPLC graphs.

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References

1 (a) A. Hamilton, M. Gicquel, P. Ballester and Bo C., *Curr. Org. Chem.*, 2013, **17**, 1499-1506; (b) O. B. Berryman, A. C. Sather, A. Lledo and J. Rebek, *Angew. Chem., Int. Ed.,* 2011, **50**, 9400-9403. (c) M. A. Sarmentero, H. Fernandez-Perez, E. Zuidema, C. Bo, A. Vidal-Ferran and P. Ballester, *Angew. Chem., Int. Ed.*, 2010, **49**, 7489-7492. (d) V. N. G. Lindsay, W. Lin and A. B. Charette, *J. Am. Chem. Soc*,. 2009, **131**, 16383-16385. (e) F. R. P. Crisostomo, A. Lledo, S. R. Shenoy, T. Iwasawa and J. Rebek, *J. Am. Chem. Soc.*, 2009, **131**, 7402-7410. (f) R. J. Hooley, J. Rebek and Jr., *Chem. Biol.*, 2009, **16**, 255-264. (g) R. J. Hooley, S. M. Biros and J. Rebek, *Angew. Chem., Int. Ed.*, 2006, **45**, 3517-3519. (h) A. Gissot and J. Rebek, *J. Am. Chem. Soc.*, 2004, **126**, 7424-7425.

2 (a) Z. J. Wang, K. N. Clary, R. G. Bergman, K. N. Raymond and F. D. Toste, *Nat. Chem.,* 2013, **5**, 100-103. (b) X. Y. Lu and E. Masson, *Org. Lett.*, 2010, 12, 2310-2313.

3 (a) L. Xu, S. G. Hua and S. H. Li, *Chem. Commun.*, 2013, **49**, 1542-1544. (b) Z. Lin, J. Sun, B. Efremovska and R. Warmuth, *Chem. Eur. J.*, 2012, **18**, 12864-12872.

4 (a) Y. J. Ghang, M. P. Schramm, F. Zhang, R. A. Acey, C. N. David, E. H. Wilson, Y. S. Wang, Q. Cheng and R. J. Hooley, *J. Am. Chem. Soc.*, 2013, **135**, 7090-7093. (b) C. Schouwey, R. Scopelliti and K. Severin, *Chem. Eur. J.* 2013, **19**, 6274-6281. (c) E. Busseron, J. Lux, M. Degardin and J. Rebek, *Chem. Commun.*, 2013, **49**, 4842-4844. (d) D. A. Ryan and J. Rebek, *Analyst*, 2013, **138**,

Dalton Transactions Accepted Manuscript

1008. (d) R. Pinalli and E. Dalcanale, *Acc. Chem. Res*,. 2013, **46**, 399-411. (e) R. Pinalli and E.Dalcanale, *Acc. Chem. Res.* 2013**, 46**, 399-411. (f) Z. Csok, T. Kegl, Y. Li, R. Skoda-Foldes, L. Kiss, S. Kunsagi-Mate, M. H. Todd and L. Kollar, *Tetrahedron*, 2013, **69**, 8186-8190. (g) M. Florea and W. M. Nau, *Angew. Chem., Int. Ed.*, 2011, **50**, 9338-9342. h) S. Mirtschin, A. Slabon-Turski, R. Scopelliti, A. H. Velders and Severin, K., *J. Am. Chem. Soc.* 2010, **132**, 14004-14005. (i) S. Mirtschin, E. Krasniqi, R. Scopelliti, and K. Severin, *Inorg. Chem.* 2008, **47**, 6375-6381. (g) R. J. Hooley, T. Iwasawa and J. Rebek, *J. Am. Chem. Soc.*, 2007, **129**, 15330-15339.

5 (a) M. A. Galindo, A. Houlton, W. Clegg, R. W. Harrington, J. Dobado, F. Santoyo-Gonzalez, F. Linares, M. A. Romero and J. A. R. Navarro, *Chem. Commun.*, 2008, 3735-3737. (b) Z. Q. Qin, M. C. Jennings, R. J. Puddephatt, *Inorg. Chem.*, 2002, **41**, 3967-3974. (c) R. F. Carina, A. F. Williams and G. Bernardinelli, *Inorg. Chem.*, 2001, **40**, 1826-1832. (d) J. A. R. Navarro and J. M. Salas, *Chem. Commun.*, 2000, 235-236.

6 (a) C. Dolain, Y. Hatakeyama, T. Sawada, S. Tashiro and M. Fujita, *J. Am. Chem. Soc.*, 2010, **132**, 5564-5565. (b) X. Zhu, E. Rusanov, R. Kluge, H. Schmidt and D. Steinborn, *Inorg. Chem.*, 2002, **41**, 2667-2671. (c) R. D. Schnebeck, E. Freisinger, F. Glahe and B. Lippert, *J. Am. Chem. Soc.*, 2000, **122**, 1381-1390.

7 (a) R. H. Fish, *Coord. Chem. Rev.*, 1999, **185-6**, 569-584. (b) H. Chen, S. Ogo and R. H. Fish, *J. Am. Chem. Soc.*, 1996, **118**, 4993-5001. (c) D. P. Smith, E. Baralt, B. Morales, M. M. Olmstead, M. F. Maestre and R. H. Fish, *J. Am. Chem. Soc.*, 1992, **114**, 10647-10649.

8 O. Sigouin, C. N. Garon, G. Delaunais, X. Yin, T. K. Woo, A. Decken and F.-G. Fontaine, *Angew. Chem., Int. Ed.*, 2007, **46**, 4979-4982.

9 (a) J. Jankolovits, A. D. C. Van-Noord, J. W. Kampf and V. L. Pecoraro, *Dalton Trans.*, 2013, **42**, 9803-9808. (b) M. Tegoni and M. Remelli, *Coord. Chem. Rev.*, 2012, **256**, 289-315. (c) S. S. Tandon, S. D. Bunge and L. K. Thompson, *Chem. Commun.*, 2007, 798-800.

10 (a) M. Yamamura, H. Miyazaki, M. Iida, S. Akine and T. Nabeshima, *Inorg. Chem.*, 2011, **50**, 5315-5317. (b) P. D. Frischmann, A. J. Gallant, J. H. Chong and M. J. MacLachlan, *Inorg. Chem.*, 2008, **47**, 101-112. (c) B. Jacques, C. Dro, S. Bellemin-Laponnaz, H. Wadepohl and L. H. Gade, *Angew. Chem.,*

Dalton Transactions Accepted Manuscript

Int. Ed., 2008, **47**, 4546-4550. (d) B. Dutta, P. Bag, U. Florke and K. Nag, *Inorg. Chem.*, 2005, **44**, 147-157.

11 (a) P. D. Frischmann, G. A. Facey, P. Y. Ghi, A. J. Gallant, D. L. Bryce, F. Lelj and M. J. MacLachlan, *J. Am. Chem. Soc.*, 2010, **132**, 3893-3908. (b) P. D. Frischmann and M. J. MacLachlan, *Chem. Commun.*, 2007, 4480-4482.

12 M. Sathiyendiran, C.-C. Tsai, P. Thanasekaran, T.-T. Luo, C.-I. Yang, G.-H. Lee, S.-M. Peng and K.-L. Lu, *Chem. Eur. J.*, 2011, **17**, 3343-3346.

13 G. Mezei, C. M. Zaleski and V. L. Pecoraro, *Chem. Rev.*, 2007, **107**, 4933-5003.

14 P. D. Frischmann and M. J. MacLachlan, *Chem. Soc. Rev.*, 2013, **42**, 871-890.

15 (a) A. Pappalardo, M. E. Amato, F. P. Ballistreri, G. A. Tomaselli, R. M. Toscano and G. T. Sfrazzetto, *J. Org. Chem.*, 2012, **77**, 7684-7687. (b) M. E. Amato, F. P. Ballistreri, S. D'Agata, A. Pappalardo, G. A. Tomaselli, R. M. Toscano and G. T. Sfrazzetto, *Eur. Org. Chem.*, 2011, **28**, 5674-5680. (c) J. Vachon, S. Harthong, E. Jeanneau, C. Aronica, N. Vanthuyne, C. Roussel and J. P. Dutasta, *Org. Biomol.Chem.*, 2011, **9**, 5086-5091. (d) J. Vachon, S. Harthong, B. Dubessy, J. P. Dutasta, N. Vanthuyne, C. Roussel and J. V. Naubron, *Tetrahedron: Asymmetry*, 2010, **21**, 1534-1541. (e) E. Mann and J. Rebek, *Tetrahedron*, 2008, **64**, 8484-8487.

16 (a) Q. X. Han, C. He, M. Zhao, B. Qi, J. Y. Niu and C. Y. Duan, *J. Am. Chem. Soc.*, 2013, **135**, 10186-10189. (b) B. Jacques, C. Dro, S. Bellemin-Laponnaz, H. Wadepohl and L. H. Gade, *Angew. Chem., Int. Ed.*, 2008, **47**, 4546-4550. (c) D. H. Leung, R. G. Bergman and K. N. Raymond, *J. Am. Chem. Soc.*, 2006, **128**, 9781-9797. (d) D. Fiedler, R. G. Bergman and K. N. Raymond, *Angew. Chem., Int. Ed.*, 2004, **43**, 6748-6751.

17 (a) C. Zhao, Q. F. Sun, W. M. Hart-Cooper, A. G. Dipasquale, F. D. Toste, R. G. Bergman and K. N. Raymond, *J. Am. Chem. Soc.*, 2013, **135**, 18802-18805. (b) T. Liu, Y. Liu, W. Xuan and Y. Cui, *Angew. Chem., Int. Ed.*, 2010, **49**, 4121-4124. (c) R.-G. Xiong, X.-Z. You, B. F. Abrahams, Z. Xue and C-M. Che, *Angew. Chem., Int. Ed.*, 2001, **40**, 4422-4425.

18 J. T. Grant, J. Jankolovits and V. L. Pecoraro, *Inorg. Chem.*, 2012, **51**, 8034-8041.

Dalton Transactions Accepted Manuscript

19 E. Safaei, H. Sheykhi, A. Wojtczak, Z. Jaglic˘ic´ and A. Kozakiewicz, *Polyhedron*, 2011, **30**, 1219-1224.

20 (a) A. Martinez, L. Guy and J.-P. Dutasta, *J. Am. Chem. Soc.*, 2010, **132**, 16733-16734. (b) J.F. Zhang, A. Liu, X. B. Pan, L. H. Yao, L. Wang, J. Fang and J. C. Wu, *Inorg. Chem*., 2011, **50**, 9564-9570. (c) J. G. Verkade, *Coord. Chem. Rev.*, 1994, **137**, 233-295

21 A. W. Addison, T. N. Rao, J. Reedijk, J. V. Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349-1356.

22 (a) P. Li, Y. He, J. Guang, L. Weng, J. C.-G. Zhao, S. Xiang and B. Chen, *J. Am. Chem. Soc.*, 2014, **136**, 547-549. (b) Z. J. Li, J. Yao, Q. Tao, L. Jiang and T. B. Lu, *Inorg. Chem.*, 2013, **52**, 11694-11696. (c) M. C. Das, Q. Guo, Y. He, J. Kim, C. G. Zhao, K. Hong, S. Xiang, Z. Zhang, K. M. Thomas, R. Krishna and B. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 8703-8710. (d) G. Yuan, C. Zhu, W. Xuan and Y. Cui, *Chem. Eur. J.*, 2009, **15**, 6428-6434. (e) G. Li, W. Yu, J. Ni, T. Liu, Y. Liu, E. Sheng and Y. Cui, *Angew. Chem., Int. Ed.*, 2008, **47**, 1245-1249. (f) M. Periasamy, N. S. Kumar, S. Sivakumar, V. D. Rao, C. R. Ram-anathan and L. Venkatraman, *J. Org. Chem.*, 2001, **66**, 3828-3833.

23 G. M. Sheldrick, SHELXL-97 Programm; University of Göttingen: Göttingen, Germany, 1996.

24 A. L. Spek, , *J. Appl. Crystallogr.*, 2003, **36**, 7-13.

Dalton Transactions Accepted Manuscript