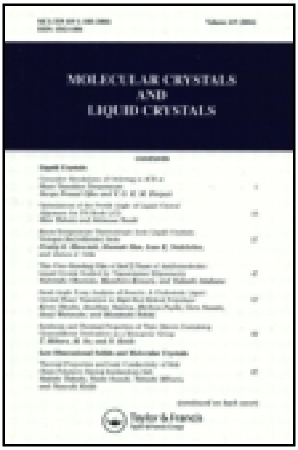

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A Hydrogen-Bonded Organic Network with Appended Chiral Metal Complexes

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Version of record first published: 24 Sep 2006

To cite this article: Toshiyuki Saiki, Takehisa Dewa & Yasuhiro Aoyama (2000): A Hydrogen-Bonded Organic Network with Appended Chiral Metal Complexes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 342:1, 241-248

To link to this article: http://dx.doi.org/10.1080/10587250008038272

Mol. Cryst. Liq. Cryst., 2000, Vol. 342, pp. 241-248
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A Hydrogen-Bonded Organic Network with Appended Chiral Metal Complexes

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Treatment of anthracenebisresorcinol (**1**•4H) with La(O^{i}Pr)$_3$ and binaphthol (BN•2H) as a chiral ligand affords an amorphous and insoluble 1:2:2 adduct (chiral La host) formulated as (**1**•2H)$^{2-}$•2(LaBN)$^+$. This formulation suggests that chiral La^{3+}-binaphthoxide moieties are attached to the half-deprotonated hydrogen-bonded network of the host. The chiral La host catalyzes the Michael reaction of dimethyl malonate with cyclohexenone with ee ≅ 70%. The analogous chiral Al host (**1**•2H)$^{2-}$•2(AlBN)$^+$ obtained from Al(CH$_3$)$_3$ catalyzes the Diels-Alder reaction between *N*-crotonoyl-1,3-oxazolidin-2-one and cyclopentadiene with an ee of ~75% for the minor exo product.

Keywords: chiral metal catalyst; solid catalyst; hydrogen-bonded network; Michael addition; Diels-Alder reaction; La^{3+} and Al^{3+}

INTRODUCTION

We have recently uncovered a simple route to catalytically active metal-organic solid materials [1-4]. This is based on immobilization of metal ions in the hydrogen-bonded network (**2**, ●•••● = O-H•••O-H) of anthracenebisresorcinol **1**•4H, an X-shaped tetraol (Chart 1), in the scheme **1**•4H + 2MX$_n$ → **1**$^{4-}$•2(MX$_{n-2}$)$^{2+}$ + 4HX (**1**$^{4-}$ is the deprotonated tetraanionic species of **1**•4H). The resulting amorphous and insoluble adducts with a suggested metal-coordination network (**2**, ●•••● = O$^-$-(MX$_{n-2}$)$^{2+}$-O$^-$) exhibit remarkable catalytic activities in the acid- and base-

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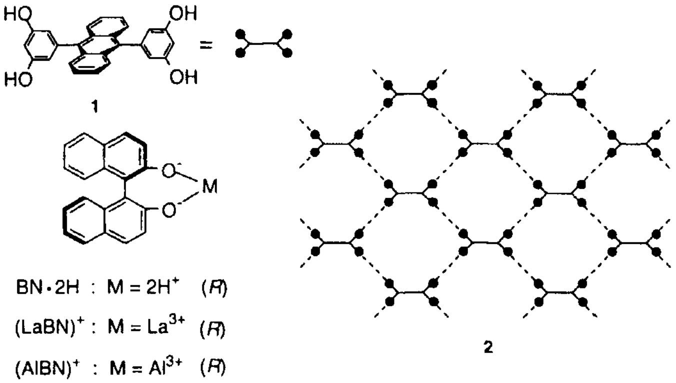
catalyzed reactions such as Diels-Alder (M = Ti^{4+}, Al^{3+}, or Zr^{4+}) [1-3] and Michael (M = La^{3+}) [4], respectively. The present work is concerned about chiral modification of such catalysts. We report here that admixture of host **1**•4H, metal (La^{3+} or Al^{3+}) complex, and binaphthol as a chiral ligand gives a stoichiometric three-component adduct, which exhibits a moderate enantioselectivity in an attempted Michael or Diels-Alder reaction.

Chart 1



Chiral La Host $[(1\cdot 2H)^{2-}\cdot 2(LaBN)^{+}]$: ●----● = $O{-}H\cdots O^{-}{-}(LaBN)^{+}$

Chiral Al Host $[(1\cdot 2H)^{2-}\cdot 2(AlBN)^{+}]$: ●----● = $O{-}H\cdots O^{-}{-}(AlBN)^{+}$

La Host : $[1^{4-}\cdot 2(LaOH)^{2+}]$: ●----● = $O^{-}{-}(LaOH)^{2+}{-}O^{-}$

Al Host : $[1^{4-}\cdot 2(AlCH_3)^{2+}]$: ●----● = $O^{-}{-}(AlCH_3)^{2+}{-}O^{-}$

RESULTS AND DISCUSSION

The polycondensation of host **1**•4H, $La(O^iPr)_3$, and (*R*)- or (*S*)-2,2'-binaphthol (BN•2H, Chart 1) in a homogeneous THF solution proceeds slowly and gives rise to an amorphous three-component adduct (hereafter called the chiral La host) having a stoichiometry of **1**:La:BN = 1:2:2, as confirmed by ^1H NMR and ICP (inductively coupled plasma) analyses after decomposition of the adduct into soluble components upon acid treatment. The chiral La host can be formulated as $(1\cdot 2H)^{2-}\cdot 2(LaBN)^{+}$;

the overall scheme being **1**•4H + 2La(O^{i}Pr)$_3$ + 2(BN•2H) → (**1**•2H)$^{2-}$ •2(LaBN)$^+$ + 6^{i}PrOH, where (**1**•2H)$^{2-}$ is the half-deprotonated dianionic species of **1**•4H and (LaBN)$^+$ is the cationic La^{3+}-binaphthoxide complex (Chart 1). The IR spectrum exhibits a broad absorption at 3355 cm^{-1} assignable to hydrogen-bonded O-H groups. The ^{13}C MAS (magic angle spinning) NMR spectrum shows the characteristic resonances for the oxygen-carrying carbon atoms of the host at δ_C = 157 and 162 for C-OH and C-OLa, respectively [5-7]. These observations, coupled with the above formulation, suggest that the network in the chiral La host is maintained by O-H•••O$^-$ hydrogen bonds between host molecules and a cationic chiral metal complex (LaBN)$^+$ is attached to the anionic oxygen in each hydrogen bond (Chart 1), although the amorphous nature of the adduct precludes any confirmation of the structure.

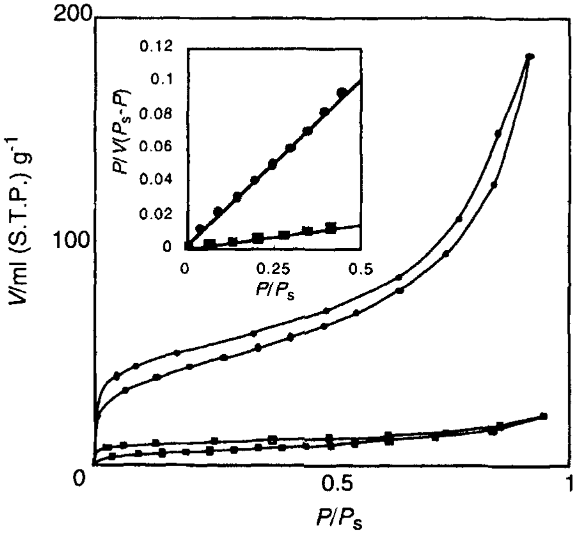
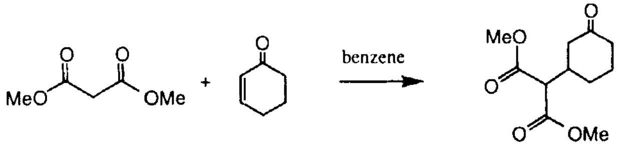
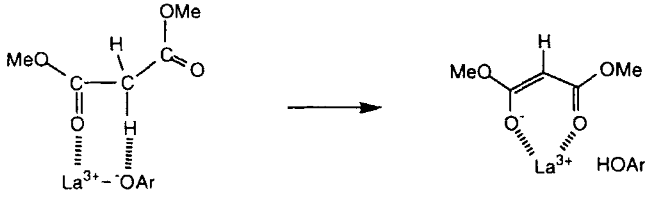


FIGURE 1 Binding isotherms for N_2 and BET analyses thereof (inset) with the La host (adsorption (●) and desorption (○)) and the chiral La host (adsorption (■) and desorption (□)) at 77 K. V (mL) refers to the standard state (S.T.P.) and P_s = 760 torr.

In the absence of binaphthol, the reaction of host **1**•4H and La(O^{i}Pr)$_3$ is very rapid, resulting in exhaustive deprotonation of the host OH groups to give a metal-insertion adduct (La host) $\mathbf{1}^{4-}$•2(LaOH)$^{2+}$ (Chart 1) [4]. The change in network from metal coordination to hydrogen bonding in going from the achiral La host $\mathbf{1}^{4-}$•2(LaOH)$^{4+}$ to the chiral La host (**1**•2H)$^{2-}$•2(LaBN)$^+$ may be steric in origin to accommodate bulky binaphthoxide moieties. This is also reflected on the porosity or specific surface area of the two adducts. In Figure 1 are shown the binding isotherms of N_2 with the La host and the chiral La host at 77 K. Both systems exhibit a Langmuir-type adsorption curve consistent with N_2 monolayer formation in micropores at lower N_2 pressures, followed by an exponential buildup plausibly due to multilayer formation in mesopores at higher guest pressures. BET analysis of the monolayer coverage gives the specific surface area of A_{BET} = 152 m^2/g and 22 m^2/g for the La host and the chiral La host, respectively.



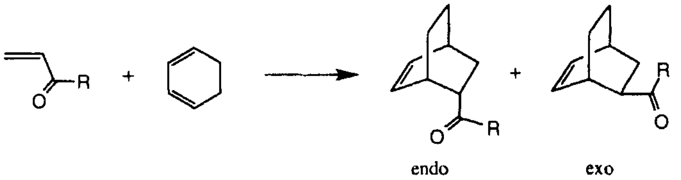
(1)



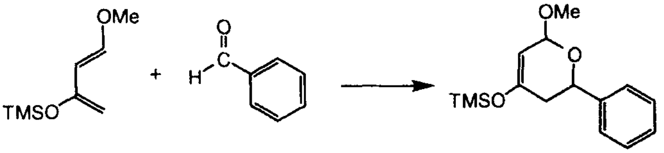
(2)

In a similar manner as the La host [4], the chiral La host catalyzes the Michael reaction of dimethyl malonate with cyclohexenone (eq 1 [8]) in benzene. The reaction proceeds smoothly with a half-life of ~1 h at room temperature under the conditions of catalyst:diester:enone = 1:10:10. When the solid catalyst is removed, no further reaction takes place in the supernatant liquid left, thus confirming that no soluble chiral species, if any, is responsible for the catalysis. After the reaction is complete, catalyst (**1**•2H)$^{2-}$•2(LaBN)$^+$ can be easily recovered as such and used repeatedly, while the liquid organic phase affords, upon removal of the solvent, the Michael product free from La^{3+} contamination essentially in a quantitative yield with a moderate enantioselectivity of ee ≅ 70 %, favoring (*R*)-enantiomer with catalyst derived from (*R*)-binaphthol.

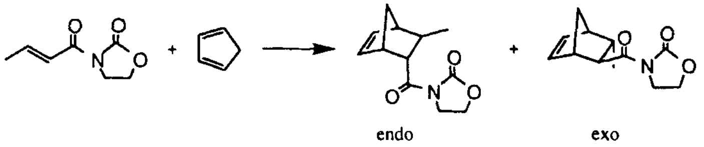
Independent measurements indicate that (1) nonenolizable ketones such as (^{t}Bu)$_2$C=O are bound to the metal when treated with the solid catalyst, as revealed by a significant (~31 cm^{-1}) shift to lower wavenumber in $\nu_{C=O}$, (2) dimethyl malonate is converted to metal-bound enolate upon similar treatment, as shown by the characteristic ^{13}C MAS NMR signal [9] for the enolate carbon (*C*=C–O$^-$) at δ_C = 174 ppm, and (3) the resulting metal-enolate trapped in the solid catalyst reacts readily with cyclohexenone to give the Michael adduct. These observations suggest a mechanism for the present reaction, involving a cooperation of La^{3+} as a Lewis acid and coordinated aryloxy anions as Brønsted bases to promote enolization of dimethyl malonate (eq 2), followed by enantioface-selective reaction of the chelated metal enolate formed with the enone.



(3)



(4)



(5)

An analogous chiral Al host (1•2H)$^{2-}$•2(AlBN)$^+$ (Chart 1) is accessible by the use of Al(CH$_3$)$_3$ in place of La(O^{i}Pr)$_3$ and can be assigned on similar grounds as above. The specific surface area of A_{BET} = 10 m^2/g is again significantly smaller than that (240 m^2/g) of metal-inserted Al host 1^{4-}•2(AlCH$_3$)$^{2+}$ (Chart 1) obtained in the absence of binaphthol [1]. As reported [1,2], the Diels-Alder reactions of acrolein (and acrylic esters as well) with 1,3-cyclohexadiene (eq 3) are catalyzed by the Al host. It turns out here that the Al host also catalyzes the (hetero) Diels-Alder reactions between Danishefsky's diene [10] with benzaldehyde (eq 4 [11,12]) and between a chelating dienophile and cyclopentadiene (eq 5 [13,14]).

All of the three types of Diels-Alder reactions (eqs 3-5) are also catalyzed by the chiral Al host $(\mathbf{1}\bullet 2H)^{2-}\bullet 2(AlBN)^{+}$ as a recoverable/reusable solid catalyst, giving rise to stereoisomer ratios of endo:exo = 99:1 and 55:45 for eqs 3 or 5, respectively, where only one enantiomeric form is shown. The enantioselectivities (ee, %) are 17 (endo) and 38 (exo) for eq 3 (R = H), 10 for eq 4, and 19 (endo) and 75 (exo) for eq 5. Thus, the selectivities are low except for one notable case of the minor exo product derived from a chelating dienophile (eq 5). Conformational fixation of the dienophile via chelation in the more sterically demanding exo transition state may be responsible for the relatively high enantioselectivity observed. The selectivity to a similar extent (ee ≅ 70 %) observed in the chiral La host catalyzed Michael reaction (eq 1) of chelating dimethyl malonate (eq 2) may also be understood along this line.

CONCLUSIONS

The hydrogen-bonding host **1**•4H, metal (La or Al) complex having labile ligands, and a chiral chelating agent BN•2H self-assemble in a stoichiometric manner. The resulting chiral adducts in the solid states catalyze the respective metal-characteristic reactions with moderate enantioselectivities when chelating reagents are involved.

EXPERIMENTAL SECTION

Chiral La and Al Hosts. A 1:2:2 mixture of host **1**•4H (394 mg, 1 mmol), $La(O^{i}Pr)_3$ (632 mg, 2 mmol), and (*R*)- or (*S*)-2,2'-binaphthol BN•2H (572 mg, 2 mmol) in degassed dry THF (35 mL) was stirred at room temperature under nitrogen for 2 h. Precipitates which resulted upon addition of hexane (35 mL) were collected by centrifugation and dried in vacuo at 25 °C for 24 h to give the chiral La host (1200 mg, 83 %) containing one molecule of THF. On standing, it readily adsorbed water and was analyzed as a heptahydrate. Anal. Calcd for

$C_{70}H_{62}O_{16}La_2$ [$(1{\cdot}2H)^{2-}{\cdot}2(LaBN)^{+}{\cdot}THF{\cdot}7H_2O$]: C, 58.51; H, 4.35; La, 19.33. Found: C, 58.48; H, 4.12; La (ICP) 20.3. A similar reaction with $Al(CH_3)_3$ in place of $La(O^iPr)_3$ in the presence of three equivalents (with respect to Al) of phenol under otherwise identical conditions afforded (62 %) the chiral Al host. Anal. Calcd for $C_{66}H_{52}O_{14}Al_2$ [$(1{\cdot}2H)^{2-}{\cdot}2(AlBN)^{+}{\cdot}6H_2O$]: C, 70.58; H, 4.67; Al, 4.80. Found: C, 70.81; H, 5.03; Al (ICP) 5.8.

General Analysis. Spectroscopic and ICP analyses, binding assays for N_2 at 77 K, and stoichiometry determinations were performed as reported [3]. Catalytic reactions were carried out with highly dried or in-situ prepared samples of solid catalyst [1-4]. An equimolar (2 mmol) mixture of dimethyl malonate and 2-cyclohexen-1-one was added to a suspension of chiral La host (0.1 mmol) in benzene (2 mL) and the reaction mixture was stirred at room temperature for 20 h, being occasionally monitored by ^1H NMR spectroscopy for the aliquots taken at appropriate time intervals. The organic layer was separated from the catalyst by centrifugation and workup involving column chromatography on silica gel gave purified product in 86% yield with ee ≅ 70%. The enantiomeric excess (ee) and absolute configuration of the product was determined by the reported method, i.e., by HPLC on a chiral stationary phase (DAICEL CHIRALPAK AS) with hexane/2-propanol (90:10, v/v) as an eluent [15].

The Diels-Alder reactions of acrolein with 1,3-cyclohexadiene (eq 3) [1] and of *N*-crotonoyl-1,3-oxazolidin-2-one [13,14] with cyclopentadiene (eq 5) were carried out in the presence of a catalytic amount of the chiral Al host (catalyst/dienophile/diene = 0.1/1/35 for the former and 0.2/1/80 for the latter) at -20 °C. The endo/exo ratios were determined by ^1H NMR. The ee for the former reaction was evaluated by capillary GLC analysis on poly(ethylene glycol) as a stationary phase (TC-WAX from GL SCIENCES INC.) after conversion of the enantiomeric products into the corresponding diastereomers upon ketalization with (-)-(2*R*, 4*R*)-pentanediol [16]. The ee of the latter reaction was determined directly by HPLC on a DAICEL CHIRALPAK AD with hexane/2-propanol (19/1, v/v) [17]. The hetero Diels-Alder reaction (eq 4) of benzaldehyde (0.86 mmol) with Danishefsky's diene [1-methoxy-3-(trimethylsililoxy)-1,3-butadiene] [10] (1.3 mmol) was carried out with 0.17 mmol of the chiral Al host suspended in 3 mL of a hexane solution. The ee of this reaction was determined by HPLC (DAICEL CHIRALCEL OD with hexane/2-propanol = 90/10, v/v) after conversion (70%) of the product (eq 4) into 2-phenyl-2,3-dihydro-4*H*-

pyran-4-one upon treatmemt with trifluoroacetic acid [11].

Acknowledgment

This work was supported by CREST from Japan Science, and Technology Corporation (JST) and also by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan, for COE Research "Design and Control of Advanced Molecular Assembly Systems" (no. 08CE2005). The convenience provided by Prof. J. Inanaga and Dr. Furuno (Kyushu University) for the analysis of the hetero Diels-Alder reaction is greatly acknowledged.

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