

Incorporation of La^{3+} in an Organic Network. A Polyphenol-Derived Solid Brønsted-Base Catalyst

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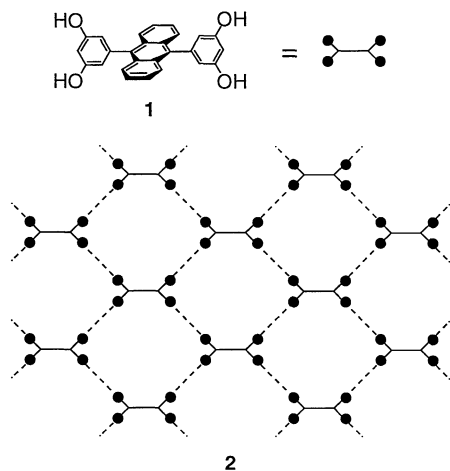
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Treatment of anthracenebisresorcinol **1** (a tetraphenol) with $\text{La}(\text{O}^i\text{Pr})_3$ in THF affords an amorphous 1:2 (1^{4-} to La^{3+}) coordination polymer (La host). It catalyzes typical base-promoted reactions such as Michael, nitroaldol, and, less effectively, aldol reactions, where the insoluble catalyst (La host) can be readily recovered and repeatedly used.

A variety of metal-containing soluble catalysts are used in organic syntheses. Homogeneous catalytic systems require separation of organic product(s) from the metallic species, usually by extraction. This inevitably leaves organic and aqueous wastes, the latter containing deactivated metal species. We are trying to develop efficient metal-organic solid catalysts, which are readily recovered and hence reusable. Our strategy is to immobilize soluble metal complexes in a known hydrogen-bonded network via polycondensation in the scheme $\text{O}-\text{H}\cdots\text{O}-\text{H} + \text{MX}_n \rightarrow \text{O}\cdots[\text{MX}_{n-2}]^{2+}\cdots\text{O} + 2\text{HX}$ ($\text{X} = \text{RO}^-$, etc).¹ Anthracenebisresorcinol **1** forms a network shown in structure **2** ($\bullet\cdots\bullet = \text{O}-\text{H}\cdots\text{O}-\text{H}$),² in which the Lewis-acid centers such as Ti^{4+} , Al^{3+} , and Zr^{4+} have been immobilized. The resulting amorphous solids exhibit a remarkable catalytic performance in the Diels-Alder reactions.¹ The present work is concerned with an extension to incorporate Brønsted bases. Rare-earth metal alkoxides and phenoxides are an interesting class of alkoxide (phenoxide) bases.^{3,4} We report here that lanthanum isopropoxide can be used to incorporate La^{3+} ions in the network to give a catalyst which is effective for typical base-catalyzed reactions.



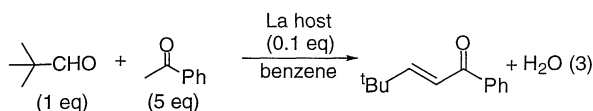
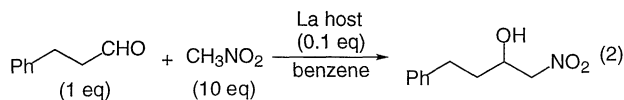
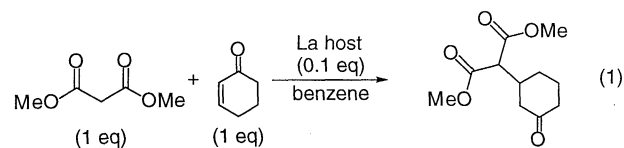
Reaction of apohost **1** and $\text{La}(\text{O}^i\text{Pr})_3$ ⁵ ($1:\text{La} = 1:2$) in THF solution under inert atmosphere results in rapid precipitation of yellow particles (called the La host hereafter), the solution thereby becomes a slurry. The La host is readily recovered in a nearly quantitative yield by centrifugation followed by washing with THF

and drying at room temperature in vacuo. On standing, even when kept in a sealed vessel, it gradually absorbs water. The La host is insoluble in all common solvents. When treated with 1N HCl, however, it decomposes into its components, where the ratio of $1:\text{La} = 1:2$ is confirmed by ^1H NMR and ICP (inductively coupled plasma) analyses of the solubilized organic (**1** in DMSO- d_6) and inorganic (La^{3+} in 1N HNO_3) components, respectively. The NMR solution also shows a variable amount of THF (~ 1.5 mol), while that of $^i\text{PrOH}$ if any is < 0.2 mol.

The La host is amorphous and shows no X-ray powder diffraction pattern. The solid-state ^{13}C CP/MAS spectrum exhibits a ~ 10 ppm downfield shift (from 155 and 157 ppm in apohost **1** to 166 ppm in the La host) in δ_{C} for C-OLa, characteristic of aryloxy metal species (metal = Ti^{4+} , Zr^{4+} , or Y^{4+}).⁶ The IR spectrum (Nujol) shows a broad absorption at ~ 580 cm^{-1} assignable to $\nu_{\text{La}-\text{O}}$.⁷ From the combined evidence, the La host is best described as an amorphous 1:2 coordination polymer composed of tetraanionic polyphenoxide 1^{4-} and hydroxylanthanum dications with $\text{O}\cdots[\text{LaOH}]^{2+}\cdots\text{O}$ bridges, possibly leading to a 2D network (structure **2**, where $\bullet\cdots\bullet = \text{O}\cdots[\text{LaOH}]^{2+}\cdots\text{O}$) with additional THF and water molecules. Found: C, 43.94; H, 3.96; La (ICP) 30.7%. Calcd for $\text{C}_{32}\text{H}_{36}\text{O}_{11.5}\text{La}_2$ ($1^{4-}\cdot 1.5\text{THF}\cdot 2(\text{LaOH})\cdot 4\text{H}_2\text{O}$): C, 43.55; H, 4.11; La 31.5%.

The La host catalyzes various reactions which were reported to be subject to catalysis by a soluble binaphthoxide- La^{3+} complex.⁸ Michael reaction of dimethyl malonate with cyclohexenone (eq 1) is one of such reactions.^{8a} The La host (freshly prepared and well-dried; 0.1 mmol as $1^{4-}\cdot 1.5\text{THF}\cdot 2(\text{LaOH})$) was completely insoluble in a benzene solution (2 ml) of the diester (2 mmol) and the enone (2 mmol). The mixture was stirred at room temperature for 2 days and then centrifuged to be separated into the liquid phase and the solid; the latter was washed with two 2-ml portions of benzene. The solid as the catalyst was analyzed as such and could be repeatedly used for another run of the same reaction. From the liquid phase combined with benzene washings was recovered, upon removal of the solvent, a quantitative amount of practically pure Michael adduct (eq 1) free of the organic (apohost **1**, not detected by ^1H NMR) or inorganic (La^{3+} , $< 0.02\%$ of that used, by ICP) component of the catalyst. The half-life of the reaction was several hours. When the solid catalyst was removed in the course of the reaction, no reaction took place afterwards in the supernatant liquid left. Thus, the catalysis is undoubtedly provided by the solid state of the La host, which can be easily recovered without leaking into the organic product and is reusable.

Nitroaldol reaction (eq 2) is another characteristic reaction catalyzed by a La^{3+} species.^{8b} Under conditions of aldehyde (2 mmol) and nitromethane (20 mmol) in benzene (2 ml) with the La host (0.1 mmol) at room temperature, a rapid reaction with a half-life of ~ 20 min took place to give the adduct (eq 2) again in a nearly quantitative yield. The La host also catalyzes the aldol reaction



between acetophenone and pivalaldehyde (eq 3).^{8c} The major product is enone arising from dehydration of the initial aldol condensate (eq 3). The reaction proceeds smoothly although, as independently confirmed, the water generated (eq 3) retards the catalytic process. This is a general aspect of the present system. In the presence of 10 mmol of water, the Michael reaction (eq 1) is completely inhibited.

It is not easy to establish precise mechanisms for heterogeneous catalytic systems. By analogy to the soluble systems,⁸ essential catalysis may arise from the La³⁺-coordinated anionic ligands as Brønsted bases to promote enolization of the Michael/aldol donors. Independent measurements reveal that the present substrates can be easily bound to the La host (2-6 mol per host, depending on steric sizes). Coabsorption of Michael/aldol donor and acceptor is also confirmed. The bound carbonyl substrates and related guests show a shift to lower wavenumber in $\nu_{\text{C=O}}$ (31 cm⁻¹, from 1685 cm⁻¹ when free to 1654 cm⁻¹ when bound, in the case of nonenolizable (tBu)₂C=O), indicative of a La³⁺...O=C coordination. Thus, the metal center as a Lewis acid may also essentially contribute to the catalytic process.

In summary, the La³⁺ ion, like previously studied Lewis acids, can be immobilized in the network of polyphenol **1**. A typical class of base-promoted reactions proceeding via enolates are catalyzed by the resulting 2:1 lanthanum(III) polyphenoxide complex as a readily recovered, repeatedly used, insoluble catalyst. Further work is now under way to shed light on the mechanism of the reaction, especially on the key metal-bound enolates. Chiral

modification of the catalyst is also a subject of intense attention.

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- The acid-dissociation or hydrolysis constants of hydrated Al³⁺ and La³⁺ complexes in water ($\text{M}^{3+}(\text{H}_2\text{O})_n + \text{H}_2\text{O} \rightleftharpoons \text{M}^{3+}(\text{H}_2\text{O})_{n-1}(\text{OH}^-) + \text{H}_3\text{O}^+$ with K) differ by a factor of $\sim 10^{10}$ ($\text{p}K = 1.14$ and 10.70 for $\text{M} = \text{Al}$ and La , respectively) (J. E. Huheey, "Inorganic Chemistry," 3rd ed, Harper & Row, New York (1983), Chap. 7). Thus, roughly speaking, La³⁺ is $\sim 10^{10}$ -times less acidic than Al³⁺. Accordingly, the La³⁺-coordinated ligands are much stronger as bases than the Al³⁺-coordinated ones.
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