A Novel Bimetallic Tetrahedron Cobalt Complex Promoting the Addition of Diethylzinc to Benzaldehyde

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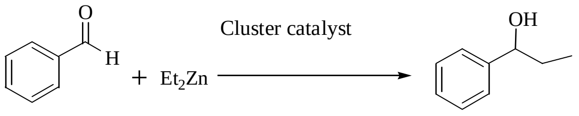
Abstract: Our recent work found a novel bimetallic tetrahedron cobalt complex which can catalyze the addition of diethylzinc to benzaldehyde effectively.

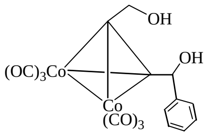
Keywords: Catalyzed addition, cobalt complex, diethylzinc, benzaldehyde.

Asymmetric catalytic addition of dialkyzinc to aldehyde using chiral ligands has become one of the most active areas in asymmetric synthesis. In recent years, various chiral ligands have exhibited good results in promoting this asymmetric addition[1], such as β -amino alcohol and chiral amine which possess chiral carbon centers, chiral (η^6-arene) chromium complexes[2], derivatives of Ferrocene[3], which possess planar chirality, and BINOL and NOBIN[4]. Further development of novel catalysts is still strongly desired. Our initial interest is to realize asymmetric catalysis induced by chiral framework cluster[5], which would be strong evidence for catalysis by an intact cluster. During the investigation, a novel highly functional cobalt complex was found to have significant activity. It catalyzes the addition of diethylzinc to benzaldehyde. We aware that it would be a meaningful and desirable project to develop this kind of polynuclear transition metal clusters to a new family of chiral catalyst. To hope, this kind of catalyst will be a conceptual breakthrough in asymmetric catalysis due to its special electronic environment of transition metal and the tetrahedron cluster structure of the framework. In this paper, we report the catalyst activity of **1** (the precursor of optically pure chiral cluster) in the addition reaction of diethylzinc to benzaldehyde.

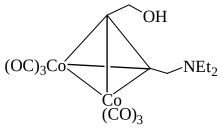
To approach the problem posed in a systematic fashion we desired two catalyst[6]. For catalyst **2**, the cluster should contain both the hydroxyl group and the amino group, which is necessary to enhance the nucleophilicity of dialkyzinc. For catalyst **1**, the cluster bears two hydroxyl groups and has relative sterically congested structure. Both two clusters have been prepared according to **scheme 1** and **2**.

The IR spectra of two clusters exhibited a large number of absorption bands between 1856 and 2087 cm^{-1}, which were assigned to terminal carbonyl vibrations.





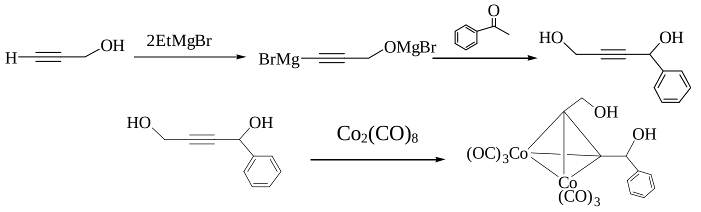
catalyst **1**



catalyst **2**

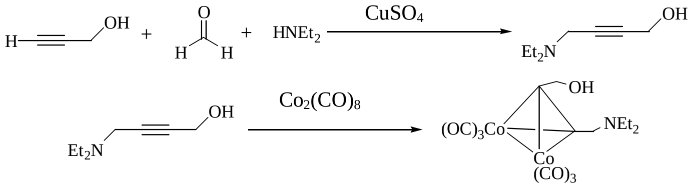
The wide bands around 3400 cm^{-1} are the characteristic absorption of the OH unit. For the ^{1}H NMR spectra, the signals around δ 4.80 can be assigned to the two protons in CH_2OH, and the chemical shifts at δ 6.0 corresponds to the protons of OH groups.

Scheme 1



catalyst **1**

Scheme 2



catalyst **2**

Our initial tetrahedron catalyst **2**, which was designed as the effective amino alcohol catalyst, showed little activity in promoting the addition of diethylzinc to benzaldehyde. However, good results were obtained in this catalyzed addition when using the catalyst **1**, due to its sterically congested structure which may left the cavity complementary to active dialkyzinc in both shape and electron environments.

Solvents play a prominent role in the reaction. The results based on the catalyzed addition using 5 mol% catalyst **1** are listed in **Table 1**. The non-polar solvents, such as hexane, cyclohexane, benzene, toluene, are more effective than the polar solvents. It is worth pointing out that although the catalyst is more soluble in polar solvents, the reaction yield is lower. For example, in ether the yield was 57%, and in THF no corresponding alcohol was obtained. A weak coordination of the solvents with catalyst may be involved.

Table 1 Effect of solvents on the addition of Et_2Zn to benzaldehyde[a]

Entry	Solvent	Yield (%)[b]
1	Benzene	75
2	Toluene	76
3	Hexane	84
4	Cyclohexane	71
5	Ether	57
6	CH_2Cl_2	<15
7	THF	/

a. using 5 mol% catalyst **1**
b. the yield based on benzaldehyde was determined by GC analysis

We also investigated the effect of the amount of catalyst **1**. As **Table 2** listed, 75% chemical yield is obtained with 5 mol% of the catalyst **1**. It is noting that the yields of reaction increase with the increasing amount of the catalyst.

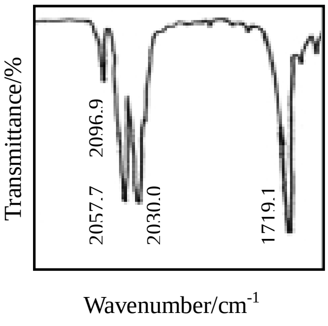
Table 2 Effect of the amount of the catalyst 1 on the addition of Et_2Zn to benzaldehyde[a]

Entry	The amount of catalyst [b] (mol%)	Yield (%)
1	5	75
2	10	84
3	15	88
4	20	90

a. solvent: benzene
b. relative benzaldehyde

Furthermore, our attempt to isolate the catalyst seems to be unsuccessful because it is a tough and time-consuming job to separate the catalyst and product. However, the IR of the separated mixture shows intense terminal carbonyl absorption bands in the range 2100-2023 cm^{-1}(**Figure1**), which indict the integrity of the cluster. Thus, it is reliable that it is the cluster as a unit that promotes the addition of diethylzinc to benzaldehyde. The exact mechanism remains to be elucidated.

Figure 1 The IR spectrum of the separated mixture



Typical procedure

To a solution of catalyst **1** (0.05 mmol) in hexane (15 mL)，diethylzinc (0.25 mL) was added dropwise at room temperature under nitrogen. After stirring for 0.5 h, benzaldehyde (0.107 g, 1 mmol) was added and the reaction mixture was stirred for 12 h at room temperature. The reaction was quenched by the addition of 5% cold aqueous HCl solution and the reaction mixture was extracted with ether. The ether extracts was dried over $MgSO_4$ and filtered. After concentration, the crude mixture was filtered through a silica-gel column to separate from the catalyst. The yield of 1-phenyl propanol was determined by GC analysis.

In summary, the model catalyst **1** has been synthesized and shows good results in the catalyzed addition. It also provides us with some basic structure-reactivity information to guide our work ahead; such as two hydroxyl function groups and sterically congested structure are responsible for the catalysis activity. Our work on the introduction of chiral factor to the model cluster's framework and asymmetric addition induced by this kind of tetrahedron framework chirality is under way, and the results will be reported later.

Acknowledgment

We are grateful to the National Natural Science Foundation of China for the financial support of this work.

Reference and notes

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6. Cluster **1**: red oil; IR (KBr, cm^{-1}) 3446, 2095, 2028, 1018; ^{1}HNMR (CDCl$_3$, δ_{ppm}): 7.36 (m, ArH), 5.91 (s, CH_2), 4.79 (s, OH), 3.58 (m, CH). Cluster **2**: dark red solid; IR (KBr, cm^{-1}) 3429, 2092, 2051, 2023; ^{1}HNMR (CDCl$_3$, δ_{ppm}): 1.77 (s, CH_3), 2.60 (m, CH_2), 4.29 (m, CH_2), 6.05 (m, CH_2), 4.81 (s, OH).

Received 27 June, 2000
Revised 20 February, 2001