Synthesis and structure of air-stable Lewis acidic binuclear complex of zirconocene pentafluorophenylsulfonate and its catalytic application in the allylation of carbonyl compounds with tetraallyltin†

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Air-stable Lewis acidic µ2-hydroxy bridged binuclear complex of zirconocene pentafluorophenylsulfonate was successfully synthesized and found to show high catalytic efficiency in chemoselective allylation of carbonyl compounds with tetraallyltin in aqueous methanol media.

Cationic zirconocene compounds have attracted much attention in the past decade due to their applications in polymerization, ring opening, and acetylation reactions.1 Of the most interesting is zirconocene dichloride (Cp2ZrCl2) and its derivatives since they have been regarded as stable non-hazardous organometallic compounds and ideal catalysts.1a-d However, Cp2ZrCl2 has rarely been used as Lewis acid in organic synthesis on account of its weak acidity.1a In general, an organometallic Lewis acid should be as strongly acidic as possible for enhancement of activity. The dilemma is that with rise of acidity, it becomes more susceptible to hydrolysis. For example, Thewalt and Lasser reported the incorporation of triflate as counter anion to bis(cyclopentadienyl) zirconium dichloride for the generation of zirconocene bis(triflate) that was employed by Hollis et al. for the formation of carbon–carbon bonds.3 Unfortunately, zirconocene bis(triflate)s were found unstable in air due to facile hydrolysis.4

Recently, Otera and co-workers postulated that incorporation of pentafluorophenyl groups to tin (e.g., (C6F5)2SnBr2) could enhance acidity and stability.5 The findings led us to envision that pentafluorophenyl groups can serve to overcome the hydrolytic instability of cationic organometallic species. Herein we report the synthesis and characterization of air-stable cationic µ2-hydroxy bridged binuclear complex [(CpZr(OH2)3)2(µ2-OH)2[C6F5SO3]4·xH2O (denoted as 1·xH2O hereafter).

Shown in Scheme 1 is the synthesis of 1·xH2O. Treatment of bis(cyclopentadiene)zirconium dichloride (Cp2ZrCl2) with silver pentafluorophenylsulfonate (AgOSO2C6F5) (2 equiv.) in CH3CN yielded 1·xH2O (after recrystallization from THF–hexane). † The origin of water molecules in the complex was air, and the hydration number (x) varied. The results of

1H NMR spectroscopy (in dry CH3CN) and elemental analysis show that the freshly prepared samples obtained after recrystallization contained twelve water molecules. After vacuum treatment at room temperature for a week, 1·6H2O complex became 1 (i.e. x = 0). Nonetheless, the complex 1 returned to 1·6H2O after exposure to air for 2 days. We found that 1·6H2O remained as dry colorless crystals or white powder and suffered no color change in a test of one month in air. Therefore, complex 1·6H2O is air-stable.

The cationic structure of 1·6H2O crystal was confirmed by X-ray analysis. An ORTEP representation of the structure of cation and crystal cell, as well as selected bonds and angles are shown in Fig. 1. The data show that the zirconium atoms have a geometry of distorted octahedral coordination with the Cp group being trans to OH. The Zr–O distance of 1·6H2O are 2.0926(19), 2.152(2), 2.155(2), 2.193(2), 2.178(2) Å. The Zr–O–Zr angle of 1·6H2O is 110.58 degree. The Zr–Zr distance of 1·6H2O is 3.4896(6) Å. The C6F5SO3− anions and the dissociated H2O molecule are packed around the complex cation in such a way that their oxygen atoms point towards the H2O ligands. The C6F5 sides of the anion, on the other hand, are clustered together to produce hydrophobic domains.

Based on the results of conductivity measurements (Table 1, see ESI†), the ionic dissociation of 1·6H2O in the solution is apparent. The large molar conductivity is consistent with the complete ionization of the complex in aqueous solution into an 1:4 electrolyte.6 Notably, it has a relatively strong acidity with acid strength of 0.8 < pKa ≤ 3.3 (H3O being the Hammett acidity function, see ESI†). In addition, it is highly soluble in methanol and in aqueous solutions of common polar organic solvents (Table 2, also see ESI†). These characteristic features stimulated us to evaluate the performance of 1·6H2O as a Lewis acid catalyst for the allylation of aldehyde with tetraallyltin.

The Lewis acid-catalyzed allylation of carbonyl compounds to produce homoallylic alcohols is a useful organic reaction.7 The transformation is analogous to the aldol condensation reaction but it makes allowance for the subsequent introduction of a variety of alternative functional groups by manipulation of the alkene moiety. Compared to trialkylallyltin and

College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, China. E-mail: deliean@sina.com; E-mail: sfyin73@yahoo.com.cn; Fax: +86-731-511-8161; Tel: +86-731-511-8161 † Electronic supplementary information (ESI) available: Details of characterization of complex 1·6H2O, allylation experiments. CCDC 660033. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b821366f
dialkyl diallyl tin, tetraallyltin offers a more attractive combination of configurational stability with relatively higher reactivity, and has been extensively employed in the allylation of aldehydes with all four organic groups being transferred in the course of the reaction. There are successful cases using Lewis acid catalysts in either pure organic solvent or water-organic mixture in the literature. A mesoporous silica-supported Lewis acid catalyst was reported by Sreekanth et al. The allylation of aldehydes was performed in ionic liquids as well. There were also reports of water- or methanol-promoted allylations without the use of a catalyst, but the non-catalytic systems require relatively longer reaction time and larger equivalents of tetraallyltin. Reactions of benzaldehyde and tetraallyltin in water were conducted using a Brønsted acid was used to shorten the reaction period. Although the method gives good yields within a short period of reaction time, its wide application is limited due to the high price of scandium salts. Additionally, the use of Bronsted acids (e.g., HCl) is environmentally unfriendly.

In the present study, the allylation of benzaldehyde with tetraallyltin was tested in various anhydrous solvents in the presence of 1-H$_2$O. One can see that the reaction occurs smoothly in MeOH, CH$_3$CN, THF, CH$_2$Cl$_2$, but slowly in Et$_2$O and hexane (Table 1, entries 1–7). In view that methanol is relatively cheap, and the catalyst shows good air-tolerance, we performed the reaction in aqueous MeOH solution (Table 1, entries 8–12). It is clear that the yield of 1-phenylbut-3-en-1-ol was nearly quantitative (97%) in the presence of a small amount of water. However, when the water content was increased to 50%, there was remarkable decline in yield. It is plausible that tetraallyltin reacts effectively with water rather than with the substrates.

In order to demonstrate the excellent catalytic activity of I-H$_2$O, we report herein the results of allylation of different aldehydes with tetraallyltin. They are aromatic aldehydes with electron-donating and -withdrawing groups as well as aliphatic aldehydes. It is noted that only a yield of 21% was obtained without catalyst under the same conditions.

Table 2 shows the reaction results in good yields of homoallyl alcohols 4a–i in aqueous methanol (entries 1–9). Usually a highly reactive reagent would cause poor chemoselectivity. For example, Grignard, lithium and titanium reagents often fail to make discrimination between aldehydes and ketones. Over I-H$_2$O, however, we observe good chemoselectivity. As shown in eqn (1), the allylation of RCHO (2a-i) with tetraallyltin catalyzed by I-H$_2$O

![Table 2: Chemoselective allylation of RCHO (2a-i) and acetophenone (3) with tetraallyltin catalyzed by I-H$_2$O](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>RCHO</th>
<th>Product</th>
<th>Yield (%)$^b$</th>
<th>Ratio of 4:5$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhCHO (2a)</td>
<td>4a</td>
<td>97</td>
<td>&gt;99.0:1.0</td>
</tr>
<tr>
<td>2</td>
<td>p-CH$_3$C$_6$H$_4$CHO (2b)</td>
<td>4b</td>
<td>91</td>
<td>&gt;98.7:1.3</td>
</tr>
<tr>
<td>3</td>
<td>p-CH$_3$OC$_6$H$_4$CHO (2c)</td>
<td>4c</td>
<td>90</td>
<td>&gt;98.1:1.9</td>
</tr>
<tr>
<td>4</td>
<td>p-CF$_3$C$_6$H$_4$CHO (2d)</td>
<td>4d</td>
<td>94</td>
<td>&gt;99.6:0.4</td>
</tr>
<tr>
<td>5</td>
<td>p-CF$_3$C$_6$H$_4$CHO (2e)</td>
<td>4e</td>
<td>99</td>
<td>&gt;99.8:0.2</td>
</tr>
<tr>
<td>6</td>
<td>C$_6$H$_5$CH(O)CHO (2f)</td>
<td>4f</td>
<td>93</td>
<td>&gt;97.9:2.1</td>
</tr>
<tr>
<td>7</td>
<td>PhCH$_2$C$_6$H$_4$CHO (2g)</td>
<td>4g</td>
<td>89</td>
<td>&gt;99.1:0.9</td>
</tr>
<tr>
<td>8</td>
<td>C$_6$H$_5$CHO (2h)</td>
<td>4h</td>
<td>90</td>
<td>&gt;99.3:0.7</td>
</tr>
<tr>
<td>9</td>
<td>C$_6$H$_5$CHO (2i)</td>
<td>4i</td>
<td>96</td>
<td>&gt;99.8:0.2</td>
</tr>
</tbody>
</table>

$^a$ RCHO, 1 mmol; Ph(O)CH$_3$, 1 mmol; tetraallyltin, 0.3 mmol; Cat., 0.05 mmol; rt.; 1 h; 3 ml solvent (CH$_3$OH:H$_2$O = 4:1). $^b$ Isolated yield. $^c$ Determined by $^1$H NMR.
acetophenone with tetraallyltin does not occur at room temperature but the corresponding homoallyl alcohol was obtained in 85% yield at 65 °C in the presence of 1\text{ H}_2\text{O}.

\[
\text{\begin{array}{c}
\text{Ph} \\
\text{CH}_3\text{OH}\text{OH}\text{H}_2\text{O} + 1/4 \text{Sn}\text{H}_2\text{O} + 5 \text{ mol}\% \\
\text{1H}_2\text{O} \text{ Yield, 85%} \\
\end{array}}
\]

(1)

To test the reusability of the catalyst and reproducibility of catalytic performance, 1\text{ H}_2\text{O} was subject to cycles of allylation reaction of benzaldehyde with tetraallyltin. It was detected that the change in product yield was minimal in a run of 4 cycles, indicating that the catalyst is stable and suitable for reuse (see ESI†). Therefore, compared to the catalysts reported in the literature, the 1\text{ H}_2\text{O} has the advantages of being high in activity, selectivity, stability and reusability.

In summary, for the first time the novel air-stable Lewis acidic complex of [[\text{CpZr(OH)\text{H}_2}]_2(\text{C}_6\text{F}_5\text{SO}_3)]_4\text{H}_2\text{O} has been synthesized, and can be used as an excellent catalyst for the allylation of carbonyl compounds with tetraallyltin.

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Notes and references


