Electronic Supplementary Information

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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Experimental

General: All chemicals were purchased from Aldrich. Co. Ltd and used as received unless otherwise indicated. The preparation of catalyst was carried out under the protection of nitrogen atmosphere using freshly distilled solvents unless specified otherwise. THF, benzene, and hexane were distilled from sodium/benzophenone while CH_3CN was distilled from CaH_2. The allylation reactions were carried out in air. The NMR spectra were recorded at 25 °C over an INOVA-400M (USA) instrument calibrated with tetramethylsilane (TMS) as internal standard. Elemental analyses were performed over VARIO EL III (Germany). Conductivity was measured on a REX conductivity meter (DDS-307, China). X-ray single crystal diffraction analysis was performed in Shanghai Institute Organic Chemistry, China Academy of Sciences over a SMART-APEX instrument. Catalyst acidity was measured by Hammett indicator method.

Typical procedure for conductivity measurement[S1]: Acetonitrile (10 cm^3) was placed in a beaker; the complex $[\{CpZr(OH_2)_3\}_2(OH)_2][C_6F_5SO_3]_4{\cdot}6H_2O$ (**1**$\cdot 6H_2O$) (7.7mg, 0.005mmol) was then added at room temperature. The probe was placed in the solution for the measurement of correlative conductivity. The results obtained in solutions of various V_{CH_3CN}/V_{H_2O} ratios are summarized in Table 1.

Table 1 Conductivities of zirconocene pentafluophenylsulfonate (**1**·$6H_2O$) [a]

Solvent (10 cm^3) V_{CH_3CN}/V_{H_2O}	Conductivity of **1**·$6H_2O$ [μS·cm-1][b]
5/0	84 (84)[c]
4/1	182.3 (182.3)[d]
3/2	221 (221) [d]
2/3	327 (327) [d]
1/4	186.0 (186.0) [c]
0/5	13.78 (13.78)[e]

[a] In a mixture of CH_3CN and water (0.5mmol·L^{-1}) at 15 °C; the complex was freshly prepared and recrystallized in vacuum at room temperature in a period of two hours. [b] The values given in the parentheses are the molar conductivities (Λ) [μS·cm^{-1}·mol^{-1}]. [c] The sample was not completely dissolved. [d] The sample was completely dissolved. [e] The sample was not dissolved.

Acidity measurement: Catalyst acidity was measured by the Hammett indicator method. The employed indicators included dicinnamalacetone (pKa =—3.0), crystal violet (pKa = 0.8), dimethyl yellow (pKa = 3.3), methyl red (pKa = 4.8), and neutral red (pKa = 6.8), as described previously.[S2-S4] Acid strength was expressed by Hammett acidity function (H_0) that was scaled by pKa values of the indicators.

Solubility determination of 1·6H₂O (representative)[S5]**:** Methanol (0.5cm^3) was placed in a test tube; then complex **1**·$6H_2O$ was added gradually at room temperature. When the amount of **1**·$6H_2O$ added exceeds 321.5 mg, insoluble **1**·$6H_2O$ appeared. Based on the observation, the solubility of **1**·$6H_2O$ was determined to be 643 g·dm^{-3}. According to the same procedure, the solubility of **1**·$6H_2O$ in other solvents were determined. The results are depicted in Table **2**.

Table 2 Solubility of **1**·$6H_2O$ in organic solvents at 25 °C [a] (g·dm^{-3}).

Solv.	MeOH	EtOAc	Acetone	THF	Et_2O	CH_3CN	CH_2Cl_2	Toluene	Hexane
Pure.[b]	643	82	0	4	0	3	0	0	0
Mix.[c]	1560	420	503	324	102	1067	5	0	0

[a] **1**·$6H_2O$ was freshly prepared and recrystallized in vacuum at room temperature in a period of 2 hours. [b] Pure organic solvent. [c] Volume ratio of organic and water: V/V=4/1.

Determination of hydration number: Molecular sieves (4Å, 11.0 g, dried at 355 °C in a muffle furnace for 5 h) were added to CD_3CN (25.0 g), and the mixture was kept overnight under the protection of a nitrogen atmosphere. According to the results of ^1H NMR spectroscopic measurements, there is no water in the as-obtained CD_3CN. The dehydrated CD_3CN was added to freshly prepared **1**·$6H_2O$ (10.0 mg, recrystallized from THF/hexane (2:5) followed by treatment under reduced pressure for a week), and the solution was analyzed by ^1H NMR spectroscopy. Then the sample was subject to elemental analysis.

Crystal data and refinement details: Full single crystals structure data and refinement details of **1**·$6H_2O$ are shown in Table **3**. Refinement of F^2 was against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, whereas conventional R-factors R are based on F with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for the calculation of R-factors(gt), etc., and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data should be even larger. Notably, since our X-ray diffraction apparatus can not work at lower temperature, the X-ray analysis was done at room temperature, leading to the higher heat vibration parameter and the large ellipsoids of the Cp ring. Data collection: Bruker SMART; cell refinement: Bruker SMART; data reduction: Bruker SHELXTL; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: Bruker SHELXTL; software used to prepare material for publication: Bruker SHELXTL.

Table 3 Crystal data and structure refinement of **1**·$6H_2O$[a].

Compound	**1**·$6H_2O$
Formula	$C_{34}H_{36}F_{20}O_{26}S_4Zr_2$
Formula weight	1551.31
Crystal system, space group	Orthorhombic, Pbca
a, b, c, Å	15.4274(9), 12.0826(7), 29.1463(17)
α, β, γ, deg	90, 90, 90
V, $Å^3$	5433.0(5)
Z, D_{calcd}, Mg m^{-3}	4, 1.897
μ, mm^{-1}	0.689
F(000)	3088
Crystal size, mm	0.491×0.405×0.227
θ range, deg.	1.92 to 27.50
Limiting indices	$-19 \le h \le 17$, $-15 \le k \le 15$, $-37 \le l \le 23$
Reflections collected/ unique	30851 / 6169, $R_{int} = 0.0586$
Completeness to theta =27.50	98.9%
Goodness-of-fit on F^2	1.038
Final R indices [$I>2\sigma(I)$]	R1 = 0.0440, wR2 = 0.1185
R indices (all data)	R1 = 0.0571, wR2 = 0.1249
Largest diff peak & hole /e. $Å^{-3}$	0.749 and -0.636

[a] Temperature: 293(2) K; Wavelength: Mo/Kα, 0.71073 Å; Refinement method: Full-matrix least-squares on F^2; Absorption correction: Empirical; CCDC register number: **1**·$6H_2O$ (CCDC660033). $w = 1/[\sigma^2(F_o^2) + (0.0743P)^2 + 0.7773P]$ where $P = (F_o^2 + 2F_c^2)/3$, Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Typical procedure for allylation of benzaldehyde and acetophenone with tetraallyltin in aqueous methanol solution: To a solution of **1**•$6H_2O$ (0.05mmol, 77mg) in 3 cm^3 solvent (CH_3OH/H_2O = 4:1), PhCHO (106.1 mg, 1 mmol), acetophenone (120.1mg, 1 mmol) and tetraallylstannane (0.3 mmol, 84.9 mg) were added using a syringe. Then the mixture was stirred at room temperature and subject to TLC analysis for one hour. The resulted solution was subject to evaporation and the residue was dissolved in diethyl ether (20 cm^3). The catalyst precipitated and was filtered out, and could be immediately reused in the next reaction. The organic layer was mixed with methanol and 2N HCl (1 cm^3) and stirred for 15 minutes, and then $NaHCO_3$ (aq) was added for neutralization. After filtration, the aqueous layer was extracted with ethyl acetate (10 cm^3 × 3), and the organic layers were combined and washed with brine, then dried with anhydrous sodium sulfate. The resulted solution was subject to evaporation, whereas the residue was subject to silica gel column chromatograph (ethyl acetate/petroleum ether = 1/8). The collected colorless oil showed an isolated yield of 1440 mg, 97%.

The residue was examined by ^{1}H NMR to determine the product ratio of **4** to **6**; **4a-i** and **6** are known compounds, [S6-S8] and the ^{1}H NMR data are summarized as follows:

1-Phenyl-3-buten-1-ol (4a): δ_H (400MHz; $CDCl_3$; Me_4Si) 2.01 (1H, br, OH), 2.49-2.58 (2H, m, CH_2), 4.75 (1H, t, *J* 5.42, CH), 5.14-5.20 (2H, m, 2 vinyls), 5.82 (1H, m, vinyl), 7.25-7.43 (5H, m, aromatic).

1-(p-Methylphenyl)-3-buten-1-ol (4b): δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.01 (1H, br, OH), 2.33 (3H, s, CH_3), 2.48-2.51 (2H, m, CH_2), 4.69 (1H, t, *J* = 6.6Hz, CH), 5.11-5.17 (2H, m, 2 vinyls), 5.76-5.81 (1H, m, vinyl), 7.14 (2H, d, *J* 7.8, aromatic), 7.24 (2H, d, *J* 7.8, aromatic).

1-(p-Methoxyphenyl)-3-buten-1-ol (4c): δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.94 (1H, br, OH), 2.50 (2H, d, *J* 6.6 Hz, CH_2), 3.81 (3H, s, CH_3), 4.69 (1H, t, *J* 6.3Hz, CH), 5.11-5.18 (2H, m, 2 vinyls), 5.80 (m, 1H, vinyl), 6.89 (2H, d, *J* 8.8, aromatic),7.27 (2H, d, *J* 8.8, aromatic).

1-(p-Chlorophenyl)-3-buten-1-ol (4d): δ_H (400 MHz; $CDC1_3$; Me_4Si) 2.16 (1H, s, OH), 2.41-2.50 (2H, m, CH_2), 4.71(1H, dd, *J* 6.8Hz, 3.2Hz, CH), 5.13-5.17 (2H, m, 2 vinyls), 5.73-5.80 (1H, m, vinyl), 7.26-7.32 (4H, m, aromatic).

1-(p-Trifluoromethylphenyl)-3-buten-1-ol (4e): δ_H (400MHz; $CDC1_3$; Me_4Si) 2.21(1H, s, OH), 2.57-2.43 (2H, m, CH_2), 4.80 (1H, m, CH), 5.18 (2H, m, 2 vinyls), 5.75-5.83 (1H, m, vinyls), 7.47 (2H, d, *J* 8.2, aromatic), 7.61 (2H, d, *J* 8.2, aromatic).

1-Phenyl-1, 5-hexadien-3-ol (4f): δ_H (400 MHz, $CDCl_3$, Me_4Si) 1.78 (1H, br, OH), 2.35-2.48 (2H, m, CH_2), 4.37 (1H, dd, *J* 13.2, 6.8, CH), 5.16-5.22 (2H, m, 2 vinyls), 5.81-5.91 (1H, m, vinyl), 6.27 (1H, dd, *J* 15.6, 6.4 Hz, vinyl), 6.63 (1H, d, *J* 15.6 Hz, vinyl), 7.22-7.26 (1H, m, aromatic), 7.30-7.34 (2H, m, aromatic), 7.38-7.40 (2H, m, aromatic).

1-Phenyl-5-hexen-3-ol (4g): δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.60 (1H, br, OH), 1.80 (2H, m, CH_2), 2.16-2.36 (2H, m, CH_2), 2.64-2.84 (2H, m, CH_2), 3.66 (1H, m, CH), 5.25 (2H, d, *J* 11.8, 2 vinyl), 5.75-5.86 (1H, m, vinyl), 7.16-7.31 (5H, m, aromatic).

Undec-1-en-4-ol (4h): δ_H (400 MHz; $CDC1_3$; Me_4Si) 0 .88 (3H, t, *J* 7.0, CH_3), 1.28 (12H, bs,

$(CH_2)_5$), 1.44-1.48 (2H, m, CH_2), 1.84 (1H, s, OH), 2.11-2.17 (1H, m, one proton of CH_2), 2.27-2.32 (1H, m, one proton of CH_2), 3.62-3.66 (1H, m, CH), 5.11-5.15 (2H, m, 2 vinyls), 5.79-5.87 (1H, m, vinyl).

Oct-1-en-4-ol (4i): δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.89 (3H, t, *J* 7.20 Hz, CH_3), 1.27-1.45 (6H, m, $(CH_2)_3$), 2.13-2.25 (2H, m, CH_2), 2.47 (1H, s, OH), 3.59-3.62 (1H, m, CH), 5.07-5.12 (2H, m, 2 vinyls), 5.77-5.84 (1H, m, vinyl).

2-Phenyl-4-penten-2-ol (6): δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.58 (3H, s, CH_3), 1.89 (1H, s, OH), 2.48-2.52 (1H, m, one proton of CH_2), 2.62-2.72 (1H, m, one proton of CH_2), 5.04 (1H, d, *J* 11.2 Hz, vinyl), 5.08 (1H, d, *J* 5.2Hz, vinyl), 5.62-5.65 (1H, m, vinyl), 7.24 (1H, t, *J* 7.52, aromatic), 7.35 (2H, t, *J* 7.40, aromatic), 7.45 (2H, d, *J* 7.40, aromatic).

Typical procedure for catalyst recovery in allylation of benzaldehyde with tetraallyltin in aqueous methanol solution: To a solution of **1**•$6H_2O$ (0.5mmol, 770mg) in 10 cm^3 solvent (CH_3OH/H_2O = 4:1), PhCHO (1061 mg, 10 mmol and tetraallylstannane (3 mmol, 849 mg) was added using a syringe. The mixture was stirred and subject to TLC analysis at room temperature for one hour. The resulted solution was subject to evaporation in vacuum and the residue was dissolved in diethyl ether (100 cm^3). The catalyst precipitated and was filtered out.

Table 4 Yield of benzaldehyde with tetraallyltin catalyzed by recovered catalyst **1**·$6H_2O$ [a]

Entry of cycle	1	2	3	4
Yield(%)[b]	97	97	96	95
Cat.(%)[c]	97	95	93	89

[a] Reaction conditions: benzaldehyde, 10 mmol, tetraallyltin, 0.3 equiv, catalyst, 5.0 mol%, rt. [b] Isolated yield of 1-phenylbut-3-en-1-ol. [c] Isolated yield of recovered catalyst.

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