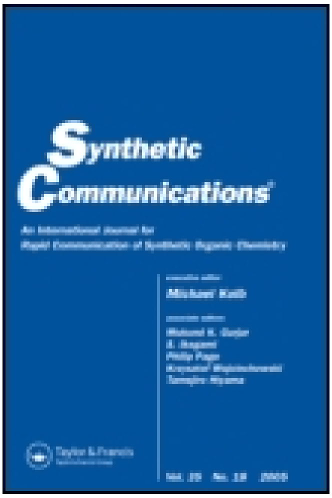

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Zirconocene Bis(perfluorooctanesulfonate)s-Catalyzed Highly Efficient Synthesis of 1,3,5-Triaryl Benzene via Cyclotrimerization of Ketones

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ZIRCONOCENE BIS(PERFLUOROOCTANESULFONATE) S-CATALYZED HIGHLY EFFICIENT SYNTHESIS OF 1,3,5-TRIARYL BENZENE VIA CYCLOTRIMERIZATION OF KETONES

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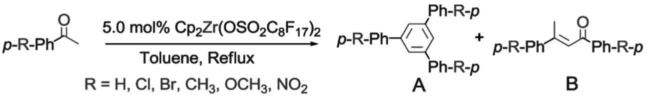
GRAPHICAL ABSTRACT



Yield up to 98%; Selectivity A/B up to 99/1

Abstract *Air-stable zirconocene bis(perfluoroctanesulfonate)s* $[Cp_2Zr]OSO_2C_8F_{17})_2]$ *(**1**) with high Lewis acidity and high thermal stability was prepared by the reaction between* Cp_2ZrCl_2 *and* $AgOSO_2C_8F_{17}$*. The as-prepared complex **1** exhibits good activity and selectivity in the cyclotrimerization of various ketones to the desired 1,3,5-triaylbenzenes. Furthermore, in the cyclic experiments, the complex **1** shows little loss of activity after 10 cycles. The results afford a general and efficient method for the cyclotrimerization of ketones using* $Cp_2Zr(OSO_2C_8F_{17})_2$ *as catalyst.*

Keywords Cyclotrimerization; Lewis acid; perfluorooctanesulfonate; triarylbenzene; zirconocene

INTRODUCTION

The cyclotrimerization reaction is a powerful strategy for the construction of polyaromatic compounds, such as 1,3,5-trisubstitued benzene moiety.[1] Generally, in the process of cyclotrimerization, the reactions of aldolization and dehydration were completed in the presence of Lewis acids in situ to form a central benzene moiety. As far as we know, the Lewis acids used in the cyclotrimerization reaction

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included proton acids (H_2SO_4, HCl, *p*-$MeC_6H_4SO_3H$, $HOOCCH_2SO_3H$) and metallic halides ($InCl_3$, $TiCl_4$, $SnCl_4$, $BeCl_2$, $SiCl_4$, Cp_2ZrCl_2).[2–6] However, because of the harsh reaction conditions, most of these procedures have some disadvantages such as poor yield and poor regioselectivity. Moreover, most of these metallic halides are highly sensitive to air and not recyclable. Therefore, developing an air-stable, highly efficient and recyclable catalyst for the cyclotrimerization of ketones is desirable.

Recently, the cationic group of four metallocene compounds and metal triflate have attracted increasing attention,[7,8] initially obtained by treatment of Cp_2MCl_2 with AgOTf and later from Cp_2MMe_2 and TfOH.[9,10] The complexes were successfully employed as catalysts for various carbon–carbon bond-forming reactions.[11] Unfortunately, these metallocene bis(triflate)s compounds are not stable in open air and suffer from facile hydrolysis.[12] Accordingly, improvement of the hygroscopic character of the cationic metallocene derivatives is in highly demand for practical utilization. Recently, Otera et al. found that organotin perfluorooctanesulfonate was air stable and water tolerant, in sharp contrast to the corresponding organotin triflates, which are highly hygroscopic.[13] With this in mind, we prepared novel metallocene complexes: $Cp_2M(OSO_2C_8F_{17})_2$, [M = Zr, Ti], $[\{CpZr(OH_2)_3\}_2(\mu^2\text{-}OH)_2][OSO_2C_6F_5]_4$, and $[\{CpHf(OH_2)_3\}_2(\mu^2\text{-}OH)_2][OSO_2C_8F_{17}]_4$.[14] In this article, we report the preparation and the physiochemical properties of $Cp_2Zr(OSO_2C_8F_{17})_2$ as well as its application in the catalytic synthesis of 1,3,5-triaylbenzenes.

RESULTS AND DISCUSSION

Zirconocene bis(perfluorooctanesulfonate) (**1**) was prepared conveniently by the reaction between zirconocene dichloride (Cp_2ZrCl_2) and silver perfluorooctanesulfonate ($AgOSO_2C_8F_{17}$) in tetrahydrofuran (THF).[14–17] Notably, the complex remained as a dry crystal or powder and suffered no color change after being kept in open air for 1 year. The Lewis acidity of the metal complexes can be estimated by the binding energies ($\triangle E$ values) of Lewis acid metal ions with $O_2^{\cdot -}$ on the basis of electron spin resonance (ESR) spectra. The $\triangle E$ values of the zirconium complex ($O_2^{\cdot -}$ 1) exhibits relatively large value (Zr^{4+}: $g_{zz} = 2.0331$, $\triangle E = 0.91\,\text{eV}$), which falls between those of $Sc(OTf)_3$ ($g_{zz} = 2.0304$, $\triangle E = 1.00\,\text{eV}$) and $Y(OTf)_3$ ($g_{zz} = 2.0349$, $\triangle E = 0.85\,\text{eV}$). Therefore, the Lewis acidity of **1** was found to fall between those of $Sc(OTf)_3$ and $Y(OTf)_3$.[16,18,19] The thermogravimetry–differential scanning calorimetry (TG-DSC) curves of complex **1** are shown in Fig. 1. It can be seen that the TG curve shows three stages of weight loss. The endothermic step below 220 °C can be assigned to the removal of water molecules. The material is stable up to about 300 °C, after which two overlapping weight losses of exothermic nature appear, plausibly a result of the oxidation of organic entities. We observed the removal of pentafluorooctanesulfuryl ligands at 400 °C, and then compounds of zirconium fluorides were left behind.

To investigate the catalytic activity of the complex $Cp_2Zr(OSO_2C_8F_{17})_2$ (**1**), the cyclotrimerization of acetophenones were employed to prepare 1,3,5-triaylbenzenes. The experiments were carried out in refluxing toluene in the presence of 5 mol% of $Cp_2Zr(OSO_2C_8F_{17})_2$ to give the desired 1,3,5-triaylbenzenes with excellent yields and good stereoselectivity (Scheme 1).

All the results show that the reaction proceeded well for a variety of acetophenones in Table 1. However, the properties of substituting groups present in the

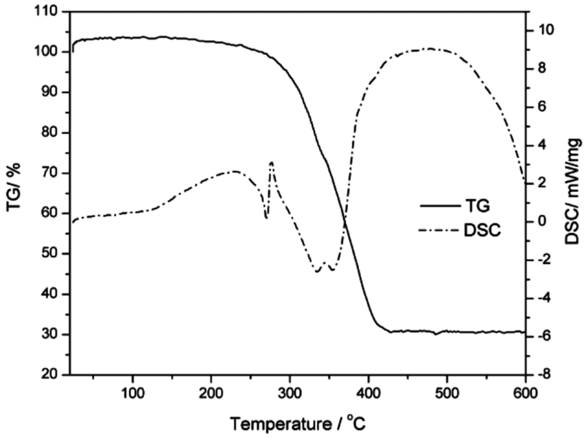
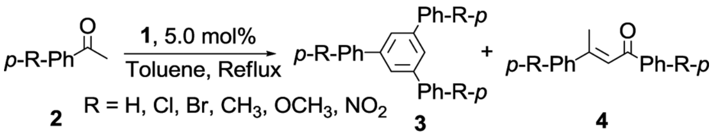


Figure 1. The TG-DSC curves of complex $Cp_2Zr(OSO_2C_8F_{17})_2$.



Scheme 1. Synthesis of 1,3,5-triarylbenzene from ketones catalyzed by **1**.

phenyl influence the reaction speed. The acetophenones with electron-donating groups in the reaction exhibited higher reactivity than those with electron-withdrawing groups. It can be deduced that the electron-donating groups enhanced the density of superconjugated π-electrons in the phenyl plane and C=O bond, leading to stronger interaction of carbonyl group of acetophenones with the zirconium atom of the complex of **1**.

Because of the air stability and thermal stability of complex **1**, the catalyst can be recycled in this reaction. The cyclic experiment was carried out by cyclotrimerization of acetonphone to 1,3,5-triphenylbenzene on a larger scale (10 mmol). After the reaction was finished, methanol was added, and the yellow solid product was

Table 1. Yields of 1,3,5-triarylbenzene synthesized from acetophenones catalyzed by **1** in refluxing toluene

Entry	Substrate	R	Product		Time /h	Yield /%[a]	Select. (**3**/**4**)/%[b]
1	**2a**	H	**3a**	**4a**	3	98	99/1
2	**2b**	Cl	**3b**	**4b**	6	89	92/8
3	**2c**	Br	**3c**	**4c**	6	85	90/10
4	**2d**	CH_3	**3d**	**4d**	3.5	95	95/5
5	**2e**	OCH_3	**3e**	**4e**	3	93	94/6
6	**2f**	NO_2	**3f**	**4f**	24	78	89/11

[a] Isolated yield of **3**.

[b] Selectivity is determined by ^1H NMR.

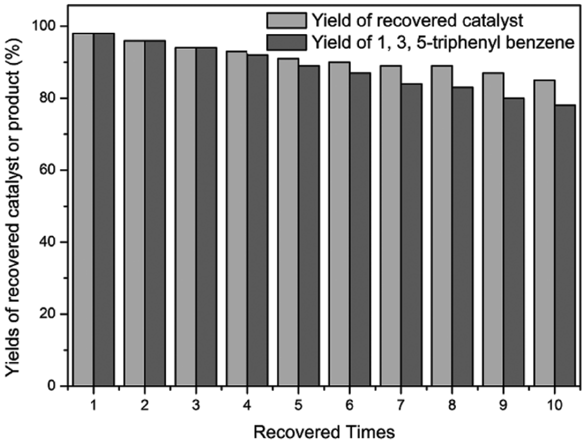


Figure 2. Yield of 1,3,5-triphenyl benzene and recovered catalyst **1** in the catalyst recycle procedure.

precipitated immediately. The superior solubility of the catalyst in methanol can be up to 1222 gL^{-1}. Therefore, the catalyst can be recovered easily from the methanol solvent by the usual workup and used directly for the next catalysis cycle in the same reaction. The yield of the recovered catalyst decreased gradually down to 78% isolated yield in the tenth run relative to the first run, while the yield of 1,3,5-tripenylbenzene was still 85% (Fig. 2).

CONCLUSION

In conclusion, we have demonstrated a versatile method for the cyclotrimerization of ketones using zirconocene bis(perfluorooctanesulfonate) as catalyst. The approach has merits such as high selectivity and yield, operational simplicity, mild reaction conditions, and catalyst recyclability. It is reasonably expected that this method will be useful in organic synthesis.

EXPERIMENTAL

All chemicals were purchased from Aldrich and used as received unless otherwise noted. The catalyst preparation reaction was carried out under nitrogen atmosphere with freshly distilled solvent. Tetrahydrofuran (THF) and *n*-hexane were distilled from sodium/benzophenone. Melting points were measured on a RY-1 melting-point apparatus (Tianjing, China) and were uncorrected. NMR spectra (^{1}H NMR 400 M, ^{19}F NMR 376 M, ^{13}C NMR 100 M) were recorded at 25 °C with $CDCl_3$ as solvent (unless otherwise noted) on an Inova-400 M (USA) instrument calibrated with tetramethysilane (TMS) as an internal reference. Mass (MS) spectra were determined on a HP5989A spectrometer. Elemental analyses were performed on a Vario EL III (Germany). The thermal stability of the samples was investigated with a thermal gravimetric analyzer (TGA, a Netzsch STA 449C) under a nitrogen atmosphere.

Preparation of $Cp_2Zr(OSO_2C_8F_{17})_2$ (1)

A solution of $AgOSO_2C_8F_{17}$ (1.21 g, 2.0 mmol) in THF (10 mL) was added to a solution of Cp_2ZrCl_2 (292 mg, 1.0 mmol) and THF (20 mL). After the mixture was stirred at room temperature for an hour, it was filtered. Dry *n*-hexane (40 mL) was laid over the colorless filtrate, and after keeping it in the refrigerator for 24 h, the colorless crystal was collected (0.794 g, 65%). MP 133–136 °C. ^{1}H NMR (400 MHz, CD_3CN) δ 1.93 to 1.95 (t, 4H, THF), 2.37 (s, n H, H_2O), 3.78 (s, 4H, THF), 6.65 (s, 10H, Cp). ^{19}F NMR (376 MHz CD_3CN) δ −79.96 to −79.00 (t, 3F, CF_3–), −112.79 (s, 2 F, –CF_2–), −118.66 (s, 2 F, –CF_2–), −119.62 to −119.81 [d, 6F, –$(CF_2)_3$–], −120.65 (s, 2 F, –CF_2–), −124.03 to −124.13 (m, 2F, –CF_2–). Elemental analysis calculated (%) for $C_{26}H_{10}F_{34}O_6S_2Zr$ (as no hydrate and no THF): C, 25.60; H, 0.83; found: C, 25.67; H, 0.82 (after pumping for a week at room temperature or heating at 80 °C in the vacuum for 30 min, the catalyst used in this article).

ESR Detection of $O_2^{\cdot -}$1 Complex[16]

A quartz ESR tube (4.5 mm i.d.) containing an oxygen-saturated solution of dimeric 1-benzyl-1,4-dihydronicotinamide $(BNA)_2$ (1.0×10^{-2} M) and **1** (1.0×10^{-3} M) in MeCN was irradiated in the cavity of the ESR spectrometer with the focused light of a 1000 W high-pressure Hg lamp through an aqueous filter. Dimeric $(BNA)_2$, which was used as an electron donor to reduce oxygen, was prepared according to the literature. The ESR spectra of ($O_2^{\cdot -}$ 1) complex in frozen MeCN were measured at 143 K with a Jeol X-band apparatus under nonsaturating microwave power conditions. The *g* values were calibrated precisely with a Mn^{2+} marker, which was used as a reference.

Typical Procedure of Synthesis of 1,3,5-Triphenyl Benzene in Toluene (Representative)

Acetophenone (**2**a) (1.0 mmol, 120 mg), **1** (0.05 mmol, 65 mg), and toluene (3 mL) were added to a 25-mL, round-bottom flask. The mixture was stirred for 3 h at 110 °C, poured into methanol (20 mL), stirred, and filtered. Crude product of **3a** was obtained. Recrystallization of the crude product was completed in ethanol and methylene dichloride (v/v = 1:1) to obtain **3a** (100 mg, mp 170–171 °C, yield 98%). All the analytical data for the compounds (**3a–3f**) are listed.

Selected Data

1,3,5-Triphenyl benzene (3a).[20] Mp 170–171 °C; ^{1}H NMR δ: 7.79 (s, 3H), 7.70 (d, 6H, $J = 8.4$ Hz), 7.49 (t, 6H, $J = 7.6$ Hz), 7.40 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR δ: 142.1, 140.9, 136.2, 129.0, 127.5, 127.4, 125.0; MS (*m*/*z*): 306 (M^+). Elemental analysis calculated (%) for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 94.12; H, 5.91.

1,3,5-Tri(4-chlorophenyl) benzene (3b).[20] Mp 243–245 °C; ^{1}H NMR δ 7.72 (s, 3H), 7.61 (d, 6H, $J = 8.0$ Hz), 7.45 (d, 6H, $J = 8.0$ Hz); ^{13}C NMR δ 141.7, 139.1, 134.0, 129.3, 128.8, 125.1; MS (m/z): 408 (M^+). Elemental analysis calculated (%) for $C_{24}H_{15}Cl_3$: C, 70.35; H, 3.69. Found: C, 70.40; H, 3.70.

1,3,5-Tri(4-bromophenyl) benzene (3c).[20] Mp 263–264 °C; ^{1}H NMR δ 7.69 (s, 3H), 7.45 (d, 6H, $J = 8.4$ Hz), 7.38 (d, 6H, $J = 8.4$ Hz); ^{13}C NMR δ 137.8, 135.9, 132.3,129.4, 125.5, 122.1; MS (m/z): 542 (M^+). Elemental analysis calculated (%) for $C_{24}H_{15}Br_3$: C, 53.08; H, 2.78. Found: C, 59.02; H, 2.80.

1,3,5-Tri(4-methylphenyl) benzene (3d).[20] Mp 176–177 °C; ^{1}H NMR δ 7.61 (s, 3H), 7.27–7.33 (m, 6H), 7.55–7.59 (m, 6H), 2.44 (s, 9H); ^{13}C NMR δ 142.1, 138.5, 137.6, 129.9, 127.1, 124.5, 21.6; MS (*m*/*z*): 348 (M^+). Elemental analysis calculated (%) for $C_{27}H_{24}$: C, 93.06; H, 6.94. Found: C, 93.12; H, 6.95.

1,3,5-Tri(4-methoxylphenyl) benzene (3e).[20] Mp 142–143 °C; ^{1}H NMR δ 7.78 (s, 3H), 7.59 (d, 6H, $J = 7.7$ Hz), 7.29 (d, 6H, $J = 7.7$ Hz), 3.83 (s, 9H); ^{13}C NMR δ 160.8, 137.7, 128.8, 128.5, 125.3,114.3, 56.7; MS (*m*/*z*): 396 (M^+). Elemental analysis calculated (%) for $C_{27}H_{24}O_3$: C, 81.79; H, 6.10. Found: C, 81.78; H, 6.12.

1,3,5-Tri(4-nitrophenyl) benzene (3f).[20] Mp 152–154 °C; ^{1}H NMR δ 8.23–8.25 (d, 6H, $J = 8.3$ Hz), 7.71 (d, 6H, $J = 8.3$ Hz); 7.63 (s, 3H), ^{13}C NMR δ 147.4, 142.8, 137.7, 128.4, 125.2, 124.5; MS (*m*/*z*): 441 (M^+). Elemental analysis calculated (%) for $C_{24}H_{15}N_3O_6$: C, 65.31; H, 3.43; found: C, 65.34; H, 3.44.

Catalyst Recycling Procedure

Acetophenone (**2a**) (10 mmol, 1200 mg) and a catalytic amount of catalyst of 1 (0.5 mmol, 650 mg) were added to a 250-mL, round-bottom flask. After the catalyst was partially dissolved in acetophenone, toluene (30 mL) was added as reaction solvent. The mixture was stirred for 3 h at 110 °C and then poured into methanol (200 mL), stirred, and filtered. Crude product of **3a** was obtained. Recrystallization of the crude product was completed in ethanol and methylene dichloride (v/v = 1:1) to obtain **3a** (1000 mg, mp 170–171 °C, yield 98%). The filtrate of methanol solvent was evaporated. Thus, the crude cyclic catalyst was obtained (98% yield, 635 mg), which can be used for the next reaction immediately. For ^{1}H NMR spectroscopy, it was recrystallized in THF/hexane (v/v = 2:5), and pure catalyst was obtained. ^{1}H NMR (400 M, CD_3CN) δ 1.92 to 1.94 (t, 4H, THF), 2.37 (s, n H, H_2O), 3.77 (s, 4H, THF), 6.66 (s, 10H, Cp). $[Cp_2Zr(OSO_2C_8F_{17}]_2$ was obtained by heating at 80 °C in a vacuum for 30 min.

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