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Short Communication

Air-stable zirconocene bis(perfluorobutanesulfonate) as a highly efficient catalyst for synthesis of α -aminophosphonates via Kabachnik–Fields reaction under solvent-free condition



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ABSTRACT

Zirconocene bis(perfluorobutanesulfonate) [Cp₂Zr(OSO₂C₄F₉)₂·2H₂O] was successfully synthesized by treatment of Cp₂ZrCl₂ with C₄F₉SO₃Ag, and was found to have the nature of air-stability, water tolerance, high thermal stability and strong Lewis acidity. This complex showed high catalytic efficiency for the synthesis of α aminophosphonates via Kabachnik–Fields reaction of aldehydes/ketones, amines and diethyl phosphite under mild and solvent-free conditions. Furthermore, it can be reused without loss of activity in a test of five cycles. Compared with our previously reported complex of Cp₂Zr(OSO₂C₈F₁₇)₂·3H₂O·THF, this complex showed better catalytic activity.

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1. Introduction

As a kind of natural amino acid analogs, α -aminophosphonates constitute an important class of compounds owing to their biological and physical properties as well as their utility as synthetic intermediates [1–3]. The synthesis of α -aminophosphonates has received increasing attentions over the last 20 years. The Kabachnik-Fields reaction represents one of the most direct and efficient methods for the synthesis of α -aminophosphonates. The process involves a three-component reaction of an aldehvde, an amine, and a dialkyl or trialkyl phosphite catalyzed by Lewis acid catalysts such as ZnCl₂ [4], SnCl₄ [5], FeCl₃ [6], $TaCl_5-SiO_2$ [7], Mg(ClO₄)₂ [8], Cd(ClO₄)₂·xH₂O [9], Yb(OTf)₃ [10], Cu(OTf)₂ [11], Sc(OTf)₃ [12] and Sn(OTf)₂ [13]. Unfortunately, these catalysts have one or more disadvantages such as air or moisture sensitivity (metal chlorides), potential explosivity (perchloride salts) and the use of stoichiometric and/or toxic (heavy metal pollution), relatively expensive metals (Sc, Yb), and most of these catalysts are not recyclable. Furthermore, the organic solvents are needed in most cases, which can't fulfill the requirement of the green chemistry. Thus, developing an air-stable, highly efficient and recyclable catalyst for the synthesis of α-aminophosphonates via solvent-free Kabachnik-Fields reaction is still highly desirable.

In recent years, cationic group metallocene compounds as Lewis acid catalysts have attracted much attention [14,15]. For example, the groups of Bosnich and Collins have adopted anhydrous metallocene

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bis(triflate) complexes of titanium and zirconium Cp₂M(OTf)₂ $(Cp = C_5H_5; M = Ti, Zr)$ as catalysts to accomplish carbon-carbon bond-forming reactions [16,17]. The anhydrous bis(triflate) complexes are hydroscopic and readily form air-stable, aquo complexes [18], analogous to those reported here, and which are also active as Brønsted and/or Lewis acid catalysts [16]; Brønsted acidity is disadvantageous for applications involving asymmetric catalysis [17c]. Later, Otera and co-worker found that the longer perfluorooctanesulfonate groups could be used as effective counter anions to provide air-stable and water-tolerant organometallic species in sharp contrast to the corresponding hygroscopic organometallic triflates [19,20]. With this in mind, we have synthetized a series of air-stable metallocene bis(perfluorooctanesulfonate) complexes $Cp_2M(OPf)_2$ (M = Ti, Zr; $Pf = OSO_2C_8F_{17}$), which showed moderate to high catalytic efficiency in C-C and C-O bond formation reactions [21-23]. However, their relatively low solubility in organic solvents owing to the strongly lipophobic nature of C_8F_{17} group [24] may decline the catalytic efficiency. Besides, perfluorooctanesulfonate (PFOS) compounds have been found to be potentially toxic to animals and human beings [25] and will result in environmental pollution [26]. Hence, we envisioned that perfluorobutyl groups, which are less lipophilic, may increase the solubility as well as the catalytic efficiency. In addition, perfluorobutanesulfonate (PFBS) compounds also exhibited lower toxicity to humans and animals than PFOS [27]. Based on this idea and as part of our ongoing efforts devoted to metallocene complexes, we prepared the complex of zirconocene bis(perfluorobutanesulfonate) $[Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O]$, studied its physiochemical properties (e.g. acidity, thermal stability), and examined its catalytic efficiency



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for the synthesis of α -aminophosphonates via Kabachnik–Fields reaction of aldehydes/ketones, amines, and diethyl phosphite (Scheme 1).

2. Experimental

Preparation of zirconocene bis(perfluorobutanesulfonate) Cp₂Zr(OSO₂C₄F₉)₂·2H₂O [23]: A solution of Cp₂ZrCl₂ (292 mg, 1 mmol) in Et₂O (20 mL) was added with a solution of AgOSO₂C₄F₉ (854 mg, 2.1 mmol) in Et₂O (10 mL), and the resultant mixture was stirred in the dark at room temperature for 1 h. Then the reaction mixture was filtered and evaporated, and the residue was diluted with Et₂O (4 mL) and toluene (10 mL). The solution was kept standing in a refrigerator for 24 h, and the white crystals were precipitated (642 mg, 75%).

Typical procedure for synthesis of α -aminophosphonates (using benzaldehyde, aniline and diethyl phosphate as an example): The complex of Cp₂Zr(OSO₂C₄F₉)₂·2H₂O (41.1 mg, 0.05 mmol), PhCHO (106 mg, 1.0 mmol), PhNH₂ (93 mg, 1.0 mmol), and diethyl phosphite (166 mg, 1.2 mmol) were mixed in a 50 mL round-bottom flask. Then the mixture was stirred at room temperature for 2.5 h under the TLC analysis until the PhCHO and PhNH₂ as well as the intermediate *N*-benzylideneaniline obtained from PhCHO and PhNH₂ were consumed completely. Then the solvents of the resulted mixture were removed by evaporation in a vacuum, followed by adding the petroleum ether (3 × 10 mL), and the recovery catalyst was precipitated and filtered for the next cycle of reaction. The combined organic layer was evaporated to a yellowish solid, then it was subjected to silica gel column chromatography (petroleum ether/ethyl acetate = 5:1), and the pale yellow solid of **4a** was obtained (306 mg, isolated yield = 96%).

3. Results and discussion

3.1. Characterization of $Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$

In this study, we used NMR, TG-DSC, fluorescence spectra and Hammett indicator methods to investigate the physiochemical properties of $Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$ (see Supplementary material). The complex remained as a crystal or powder and suffered no color change after being kept in open air for one year. The thermal behavior of the complex of $Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$ was investigated by TG-DSC in O_2 atmosphere (Figure S1, see Supplementary material). The curves showed that they were thermally stable up to about 250 °C. We estimated the Lewis acidity of $Cp_2Zr(OSO_2C_4F_9)_2$ by the red shift (λ_{em}) of Lewis acid metal ions (Zr^{2+}) with 10-methylacridone on the basis of fluorescence spectra [28], which showed that the fluorescence maximum (λ_{max}) of complex was 475 nm (Figure S2, see Supplementary material). The acidity of the complex was also determined by Hammett indicator method. It has relatively strong acidity with acid strength of $0.8 < Ho \le 3.3$ (*Ho* being the Hammett acidity function). In addition, the complex was highly soluble in methanol and in common polar organic solvents (Table S1, see Supplementary material). In view of the water tolerance, high thermal stability and strong acidity of $Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$, we



Scheme 1. Kabachnik–Fields reaction using $Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$ as catalyst.

adopted it as a catalyst for the Kabachnik–Fields reaction of aldehydes/ketones, amines and diethyl phosphite.

3.2. Screening optimal conditions

To determine the best experimental conditions, the reaction of benzaldehyde, aniline, and diethyl phosphite (DEP) was considered as the model reaction (Table 1). The reaction was tested in various organic solvents in the presence of $Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$. It can be seen that the reaction can occur effectively in MeOH, CH₃CN, THF and Et₂O, but slowly in CH₂Cl₂, *n*-hexane and toluene (Table 1, entries 1-4). Obviously, longer reaction time was required and low yield was obtained when organic solvents were used as reaction media in some cases. While under solvent-free conditions, only 2.5 h is required to get the 96% yield of desired product (Table 1, entry 9). Also, we investigated the loading of catalyst and found that the optimal dosage of $Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$ was 5.0 mol% (Table 1, entries 9-11). Thus, the best results were obtained in the presence of $Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$ (5.0 mol%) affording the desired α -aminophosphonate after 2.5 h at room temperature under solvent-free condition.

3.3. The scope of Kabachnik–Fields reaction catalyzed by $Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$

With the optimal condition in hand, various aldehydes and amines as reactants (Table 2) were screened with $Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$ in direct Kabachnik-Fields reaction, and good-to-excellent yields were obtained. Both of the electron-donating groups and electronwithdrawing groups attached in para-position of phenyl plane in aromatic aldehydes were employed and showed high reactivity (Table 2, entries 2–16). The aldehydes with electron-withdrawing groups (e.g., Cl, Br, CF₃ and NO₂) exhibited higher reactivity in Kabachnik-Fields reaction than those with electron-donating groups in the *para*-position of the phenyl plane (e.g., methyl, methoxyl and hydroxyl) (Table 2, entries 2-16). Tereph-thaldehyde also showed high reactive activity (Table 2, entry 17). The cinnamaldehyde with double bond was tolerant in current catalytic system (Table 2, entry 18). The amines with electron-donating groups were beneficial for catalytic reaction comparing with the amines bearing electronwithdrawing groups (Table 2, entries 19–24). α -Naphthylamine, benzidine and 8-aminoquinoline showed high reactive activity in this catalytic system (Table 2, entry 25-26). Acetophenone and cyclohexanone can be also used in this reaction with satisfactory yields (Table 2, entries 25–26). We also investigated *n*-butylamine, cyclohexylamine, piperidine, 2-aminopyridine and 4-aminopyridine (Table 2, entries 31–34). However, for aliphatic amines, piperidine and 2-aminopyridine, the corresponding α -aminophosphonates were

Table I						
$Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$	catalyzed	synthesis	of	α -aminophosphonates	under	various
conditions ^a .						

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Entry	Solvent	Catalyst (mol%)	Time (h)	Yield (%) ^b
1	MeOH	5	6	82
2	CH ₃ CN	5	7	79
3	THF	5	6	84
4	Et ₂ O	5	8	73
5	CH ₂ Cl ₂	5	10	68
6	n-Hexane	5	10	58
7	Toluene	5	10	48
8	H ₂ O	5	10	64
9	Neat	5	2.5	96
10	Neat	3	5	81
11	Neat	7	2.5	96

^a PhCHO: 1.0 mmol; PhNH₂: 1.0 mmol; diethyl phosphite: 1.2 mmol.
 ^b Isolated yield.

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Table 2

 $Product \ yield \ for \ reaction \ of \ aldehydes/ketones, \ amines \ and \ diethyl \ phosphite \ catalyzed \ by \ Cp_2 Zr(OSO_2 C_4 F_9)_2 \cdot 2 H_2 O^a.$

Entry	R ¹	R ²	R ³	Product	Time (h)	Yield (%) ^b
1	Ph	Н	Ph	4a	2.5	96
2	p-CH ₃ OC ₆ H ₄	Н	Ph	4b	3	90
3	p-CH ₃ C ₆ H ₄	Н	Ph	4c	3	91
4	$p-(CH_3)_2NC_6H_4$	Н	Ph	4d	3	89
5	$m-NO_2C_6H_4$	Н	Ph	4e	2.5	97
6	0-NO ₂ C ₆ H ₄	Н	Ph	4f	2.5	96
7	$p-CF_3C_6H_4$	Н	Ph	4g	2.5	98
8	0-CF ₃ C ₆ H ₄	Н	Ph	4h	2.5	96
9	o-FC ₆ H ₄	Н	Ph	4i	3	92
10	p-ClC ₆ H ₄	Н	Ph	4j	2.5	93
11	p-BrC ₆ H ₄	Н	Ph	4k	2.5	93
12	o-BrC ₆ H ₄	Н	Ph	41	3	91
13	o-HOC ₆ H ₄	Н	Ph	4m	3	89
14	$m-HOC_6H_4$	Н	Ph	4n	3	90
15	p-HOC ₆ H ₄	Н	Ph	40	3	91
16	3-MeO-4-HO-C ₆ H ₃	Н	Ph	4р	3	90
17	Tereph-thaldehyde		Ph	4q	3.5	90 ^c
18	C ₆ H ₅ CH=CH	Н	Ph	4r	3.5	87
19	Ph	Н	PhCH ₂	4s	4	86
20	$p-HOC_6H_4$	Н	PhCH ₂	4t	4	84
21	Ph	Н	p-CH ₃ C ₆ H ₄	4u	2.5	95
22	Ph	Н	$p-ClC_6H_4$	4v	2.5	91
23	Ph	Н	$p-NO_2C_6H_4$	4w	3	89
24	Ph	Н	$p-CF_3OC_6H_4$	4x	3	87
25	Ph	Н	α -Naphthylamine	4y	3	90
26	Ph	Н	Benzidine	4z	3.5	89 ^d
27	Ph	Me	Ph	4aa	4.5	85
28	Cyclohexanone		Ph	4ab	4	84
29	n-C ₃ H ₇	Н	$p-CH_3C_6H_4$	4ac	8	78
30	Ph	Н	8-Aminoquinoline	4ad	5	81
31	Ph	Н	n-C ₄ H ₉	4ae/5a	8	73/19 ^e
32	Ph	Н	Cyclohexyl	4af/5a	10	68/24 ^e
33	Ph	Н	Piperidine	4ag/5a	10	55/35 ^e
34	Ph	Н	2-Aminopyridine	4ah/5a	10	51/38 ^e
35	Ph	Н	4-Aminopyridine	5a	12	49

^a PhCHO: 1.0 mmol; PhNH₂: 1.0 mmol; diethyl phosphite: 1.2 mmol; rt.; neat; Cp₂Zr(OSO₂C₄F₉)₂·2H₂O: 0.05 mmol.

^b Isolated yield.

^c Two equivalents of aniline were used.

^d Two equivalents of benzaldehyde were used.

^e The products are α -aminophosphonate (**4ae–4ah**)/ α -hydroxyphosphonate (**5a**).

obtained, and another solid byproduct was obtained in a very short time, which was characterized as the corresponding α -hydroxyphosphonate **5a**. While, for 4-aminopyridine, the only byproduct α -hydroxyphosphonate was afforded (Table 2, entry 35).

3.4. Catalyst comparison investigation

As shown in Table 3, several catalysts were evaluated by the current reaction. It can be seen that the isolated yields were lowered to 30%

Table 3	
Catalant	

Catalyst comparison	in the	Kabachnik-Fields reaction ^a .
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Entry	Catalyst (mol%)	Yield (%) ^b
1	AlCl ₃	25
2	ZrCl ₄	32
3	InBr ₃	76
4	$Mg(ClO_4)_2$	58
5	Sc(OTf) ₃	82
6	Bi(OTf) ₃	72
7	Cp_2ZrCl_2	19
8	$Cp_2Zr(OSO_2CF_3)_2 \cdot 3H_2O \cdot THF$	84
9	$Cp_2Zr(OSO_2C_8F_{17})_2 \cdot 3H_2O \cdot THF$	88
10	$Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$	96
11	$Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$	93°

^a PhCHO: 1.0 mmol; PhNH₂: 1.0 mmol; diethyl phosphite: 1.2 mmol; rt.; neat; cat.: 0.05 mmol; time: 2.5 h.

^b Isolated yield.

^c Catalyst kept in open air for one year.

using the traditional metal chlorides as catalysts owing to possible hydrolysis (Table 3, entries 1-2). With the catalysts InBr₃ and $Mg(ClO_4)_2$, the yields were 76% and 58%, respectively (Table 3, entries 3-4). We also investigated metal triflates as catalysts, such as Sc(OTf)₃ and Bi(OTf)₃, and the yields were about 80% (Table 3, entries 5-6). These catalysts are hydrolytic in air, and Godeau and coworkers proposed that the presence of water molecules in the vicinity of the bismuth cation could generate a hybrid Lewis/Brønsted acid (LBA) as active catalytic species [29]. When the precursor Cp₂ZrCl₂ was used as catalyst, the yield was only 19% (Table 3, entry 7). It is interesting to note that the complex of $Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$ showed high catalytic efficiency and the yield was 96%, which was higher than those of $Cp_2Zr(OSO_2CF_3)_2 \cdot 3H_2O \cdot THF$ and $Cp_2Zr(OSO_2C_8F_{17})_2 \cdot 3H_2O \cdot THF$ as catalysts (Table 3, entries 8-10), though it should be mentioned that these two complexes feature lower Lewis and Brønsted acidity at the same 5.0 mol% loadings. Furthermore, after being stored in air for one year, the complex of $Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$ also exhibited catalytic efficiency comparable to the freshly prepared sample (Table 3, entry 11).

3.5. Catalyst recovery investigation

To test the reusability of the catalyst and reproducibility of catalytic performance, $Cp_2Zr(OSO_2C_4F_9)_2 \cdot 2H_2O$ was subject to recycling experiments of the Kabachnik–Fields reaction of benzaldehyde, aniline and diethyl phosphite (see Supplementary material). The change in product yield was negligible in a trial of five recycling experiments, demonstrating that the catalyst was stable and suitable for reuse.



Scheme 2. Proposed mechanism on the Kabachnik-Fields reaction.

3.6. A plausible mechanism

The plausible mechanism was shown in Scheme 2. According to the report, the pathway of this one-pot reaction depends on the nature of the amines [30]. *Path A*: Aromatic amines react with the benzaldehyde very quickly. After formation of Schiff base followed by the nucleophilic attack of phosphate on imino carbon, subsequent shifting of hydrogen atom leads to the formation of α -aminophosphonates. *Path B*: for *n*-butylamine, cyclohexylamine and 2-aminopyridine, the imine is not immediately formed and thus there is a competition between the addition of diethyl phosphite on the aldehyde and on the imine. Once α -hydroxyphosphonate is generated, it will not react with amine to form α -aminophosphonate even with long time heating. While 4-aminopyridine was also investigated, the product α -aminophosphonate wasn't afforded, probably because of its low nucleophilicity, and the only byproduct afforded was α -hydroxyphosphonate.

4. Conclusions

In summary, we have demonstrated a versatile method for the synthesis of α -aminophosphonates via Kabachnik–Fields reaction of aldehydes/ketones, amines, and diethyl phosphite using zirconocene bis(perfluorobutanesulfonate) as a catalyst. The approach has merits of high yield, operational simplicity, mild solvent-free reaction conditions and good recyclability of the catalyst. On account of its stability as well as storability, the complex should find a broad range of utility.

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Appendix A. Supplementary data

Experimental procedures, characterization data and copies of ¹H NMR, ¹³C NMR and ³¹P NMR spectra for this article are available online at http://www.sciencedirect.com. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.10.013.

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