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Air-stable titanocene bis(perfluorooctanesulfonate) as a new catalyst for acylation of alcohols, phenols, thiols, and amines under solvent-free condition

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ABSTRACT

Air-stable titanocene bis(perfluorooctanesulfonate) [$Cp_2Ti(OSO_2C_8F_{17})_2$] that shows high Lewis acidity was prepared from Cp_2TiCl_2 and $AgOSO_2C_8F_{17}$. The compound was characterized by different techniques, and examined as a catalyst for acylation reactions. It was found that using equimolar acetic anhydride as acetylating agent and under solvent-free condition, $Cp_2Ti(OSO_2C_8F_{17})_2$ exhibits high activity and selectivity in the acetylation of various alcohols, phenols, thiols, and amines. Also, good catalytic efficiency is observed in the acylation of 2-phenylethanol across various acylating reagents. The catalyst can be reused without loss of activity in a test of ten cycles. The $Cp_2Ti(OSO_2C_8F_{17})_2$ catalyst affords a simple, efficient and general method for the acylation of alcohols, phenols, thiols, and amines.

1. Introduction

The acylation of alcohols, phenols, thiols, and amines is very important in various organic transformations, especially in the synthesis of natural compounds and polyfunctional molecules such as nucleosides, carbohydrates, and steroids [1–6]. A number of Lewis acids such as TMSCl [7], MoO_2Cl_2 [8], $ErCl_3$ [9], $RuCl_3$ [10], $ZrOCl_2$ [11], $Zn(ClO_4)_2$ [12] $TiCl_4 + AgClO_4$ [13], $Cu(OTf)_2$ (Tf = CF_3SO_2) [14], $Er(OTf)_3$ [15], $Al(OTf)_3$ [16], $TiCl_3(OTf)$ [17], $Ce(OTf)_3$ [18], $Sn^{IV}(tpp)(OTf)_2$ (tpp = tetra phenylporphyrin) [19], $Sc(NTf)_3$ [20], have been reported to show catalytic activity towards the acylation of alcohols with acid anhydride. Chakraborti et al. also reported a number of good catalytic systems for the acylation reactions [21–29]. Particularly, $Sc(OTf)_3$ [30,31], a commercially available and moisture-stable Lewis acid, is extremely active for this reaction. Unfortunately, due to the high price of scandium salts and its intolerance towards various functional groups, $Sc(OTf)_3$ is limited in application. TMSOTf is another catalyst for acylation of alcohols and phenols [32]. It is cheaper and catalytically more powerful than $Sc(OTf)_3$, showing high efficiency and selectivity under relatively mild conditions. It was claimed that TMSOTf is tolerant towards functional groups of acetylene, allylic ester, ether, halide, ketal, nitrile, sulfonate, thioester and triene. However, TMSOTf is very sensitive to water, and its utilization is hence limited. According to Orita et al. $Bi(OTf)_3$ is an acylation catalyst that is air-stable and shows tolerance towards alcohols [33,34], but the catalyst is not recyclable. Another disadvantage is that most of these catalysts need organic solvents as media for acylation. Presently, considerable attention has been paid to solvent-free reactions. Besides being environmentally friendly, solvent-free reactions in many cases can offer synthetic advantages in terms of yield, selectivity and simplicity of reaction procedure. The use of solvent-free acetylation procedure is limited [21–29,35–38].

Recently, cationic group four metallocene compounds have attracted much attention [39]. The metallocene bis(triflate) complexes of titanium and zirconium $Cp_2M(OTf)_2$ ($Cp = C_5H_5$; M = Ti, Zr) were initially obtained by reacting Cp_2MCl_2 (M = Ti, Zr) with AgOTf and later by reacting Cp_2MMe_2 (M = Ti, Zr) with TfOH [40]. The complexes were successfully employed to catalyze reactions that involve the formation of carbon-carbon bonds [41]. It is known that the complexes are not stable in air and undergo facile hydrolysis [42]. For practical use of the compounds as catalysts, one has to control the hygroscopic character of the cationic metallocene derivatives. Due to their hydrophobic and electron-withdrawing features, long perfluoroalkanes have been used to produce metal perfluoroalkanesulfonates that show strong Lewis acidity and good water tolerance. Organotin perfluorooctanesulfonate was found to be air-stable and water-tolerant, in sharp contrast to the corresponding organotin triflates that are highly hygroscopic [43]. With such understanding, 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 $[\{CpHf(OH_2)_3\}_2(\mu^2\text{-}OH)_2][OSO_2C_8F_{17}]_4$ [44–46]. Previously, we reported metallocene complex $Cp_2Zr(OSO_2C_8F_{17})_2$ as a catalyst highly efficient for the acylation

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of alcohols, phenols, thiols, and amines under solvent-free conditions, and found that this approach has merits such as operational simplicity, solvent-free condition, mild reaction conditions, and catalyst recyclability [47]. In view that $Cp_2Ti(OSO_2C_8F_{17})_2$ is higher than $Cp_2Zr(OSO_2C_8F_{17})_2$ in Lewis acidity, the former should be catalytically more efficient than the latter in acylation reactions. In this study, we investigated the physiochemical properties (e.g., acidity, solubility, thermal stability) of $Cp_2Ti(OSO_2C_8F_{17})_2$ and examined its catalytic activities in the acylation of alcohols, phenols, thiols, and amines under mild solvent-free conditions.

2. Experimental

2.1. General

The chemicals were purchased from Aldrich Co., Ltd., as well as Acros Co., Ltd., and used as received unless otherwise specified. NMR spectra were recorded at 25 °C on INOVA-400 MHz (USA) calibrated with tetramethysilane (TMS) as internal reference. Elemental analyses were performed using VARIO EL III (Germany). Catalyst acidity was measured by the use of Hammett indicators. The employed indicators included dicinnamalalcetone (pKa = −3.0), crystal violet (pKa = 0.8), dimethyl yellow (pKa = 3.3), and methyl red (pKa = 4.8), as described elsewhere [48–50]. Acid strength was expressed in terms of Hammett acidity function (H_0) that was scaled by pKa value of the indicators. TG-DSC analysis was performed on NETZSCH-STA-449C (Operation condition: O_2, 5 °C/min heating rate).

2.2. Typical procedure for preparation of $Cp_2Ti(OSO_2C_8F_{17})_2$ [44]

To a solution of Cp_2TiCl_2 (249 mg, 0.99 mmol) in THF (20 mL) was added a solution of $AgOSO_2C_8F_{17}$ [39] (1.21 g, 2.0 mmol) in THF (10 mL). The mixture was stirred in darkness at room temperature for 1 h, and then subject to filtration. The filtrate was combined with dry hexane (40 mL), and kept refrigerated for 24 h to furnish yellow needle crystals (693 mg, 54%): M.p. 206–210 °C. ^{1}H NMR (400 MHz CD_3CN) δ = 1.78–1.83 (m, 4H, THF), 3.56 (s, nH, H_2O), 3.62 - 3.67 (m, 4H, THF), 6.95 (s, 10H, Cp). ^{19}F NMR (288 MHz CD_3CN) δ = −79.66–−79.75 (m, 3F, CF)3$^-$), −113.28–−113.38 (t, 2F, –CF_2–), −119.36–−119.43 (t, 2F, –CF_2–), −120.34–−120.54 (m, 6F, –(CF_2)–), −121.36–−121.41 (t, 2F, –CF_2–), −124.72–−124.87 (m, 2F, –CF_2–). Elemental analysis results (%) for $C_{26}H_{10}F_{34}O_6S_2Ti$ (as no hydrate and no THF molecule): C, 26.55; H, 0.86; found: C 26.60; H, 0.86 (After pumping at room temperature for a week or at 80 °C for half an hour).

2.3. Typical procedure for acylation reaction catalyzed by $Cp_2Ti(OSO_2C_8F_{17})_2$ (using acetylation of 2-phenylethanol as an example)

To a round-bottom flask was added 2-phenylethanol (122 mg, 1.0 mmol) and equivalent acetic anhydride (102 mg, 1.0 mmol) and a desired amount of catalyst $Cp_2Ti(OSO_2C_8F_{17})_2$ (12 mg, 0.01 mmol, 1.0 mol% relative to 2-phenylethanol). The mixture was stirred at room temperature for 2 min and monitored by TLC. Then the mixture was diluted with petroleum ether (10 mL × 3). By means of filtration, the catalyst was separated, and the filtrate was washed twice with 10 mL of saturated brine, and extracted by petroleum ether (10 mL × 2). Subsequently the portions of petroleum ether were combined together, dried by sodium sulfate, and evaporated to obtain the crude ester. Finally, the ester was subject to column chromatography on silica gel (petroleum ether: ethyl acetate = 8:1, R_f = 0.7) to afford the colorless liquid, 162 mg, yield, 99%. The following are the ^{1}H NMR data for desired ester.

2.3.1. Table 1, Entries 1–12

(a) Benzylacetae (Table 1, Entry 1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H), 5.06 (s, 2H), 7.20–7.31 (m, 5H); (b) 2-Phenylethyl acetate (Table 1, Entry 2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 3H), 2.90 (t, J = 7.09 Hz, 2H), 4.25 (t, J = 7.2 Hz, 2H), 7.17–7.29 (m, 5H); (c) 3-Phenylpropyl acetate (Table 1, Entry 3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.95 (t, J = 7.2 Hz, 2H), 2.05 (s, 3H), 2.73 (t, J = 6.2 Hz, 2H), 4.12 (t, J = 6.0 Hz, 2H), 7.13–7.31 (m, 5H); (d) 1-Phenylpropyl acetate (Table 1, Entry 4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 7.4 Hz, 3H), 1.73–1.99 (m, 2H), 2.00 (s, 3H), 5.67 (t, J = 6.8 Hz, 1H), 7.28 (m, 5H); (e) Benzhydryl acetate (Table 1, Entry 5): ^{1}HNMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 6.98 (s, 1H), 7.66–7.70 (m, 10H); (f) Trityl acetate (Table 1, Entry 6): ^{1}H NMR (400 MHz, $CDCl_3$) 2.21 (m, 3H), 7.28–7.44 (m, 15H); (g) Undecyl acetate (Table 1, Entry 7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J = 6.0 Hz, 3H), 1.19–1.29 (m, 17H), 1.59 (t, J = 6.8 Hz, 2H), 2.02 (s, 3H), 4.03 (t, J = 8.4 Hz, 2H); (h) Octyl acetate (Table 1, Entry 8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.4 Hz, 3H), 1.36–1.27 (m, 10H), 1.62 (d, J = 7.6 Hz, 2H), 2.04 (s, 3H), 4.05 (t, J = 6.8 Hz, 2H); (i) n-butyl acetate (Table 1, Entry 9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.2 Hz, 3H), 1.36 (m, 2H), 1.60 (m, 2H), 2.05 (s, 3H), 4.08 (t, J = 6.4 Hz, 1H); (j) *Sec*-butyl acetate (Table 1, Entry 10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.36 (d, J = 7.2, 3H), 1.60 (m, 2H), 2.05 (s, 3H), 4.08 (m, 1H); (k) Cyclohexyl aceatate (Table 1, Entry 11): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20–1.60 (m, 8H), 2.00 (s, 3H), 2.05–2.16 (m, 2H), 3.91(m, 1H); (l) *Tert*-butyl aceate (Table 1, Entry 12): ^{1}H NMR (400 MHz, $CDCl_3$) 1.43 (s, 9H), 1.95(s, 3H).

2.3.2. Table 2, Entries 1–7

(a) Geranyl acetate (Table 2, Entry 1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60 (s, 3H), 1.68 (s, 3H), 1.70 (s, 3H), 2.05–2.13 (m, 7H), 4.59 (d, J = 7.2 Hz, 2H), 5.08 (t, J = 7.0 Hz, 1H), 5.35 (t, J = 7.0 Hz, 1H); (b) Furan-2-yl-acetate (Table 2, Entry 2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (s, 3H), 5.06 (s, 2H), 6.37 (m, 1H), 6.40 (d, J = 3.2 Hz, 1H), 7.42 (bs, 1H); (c) Prop-2-ynyl acetate (Table 2, Entry 3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21(s, 3H), 3.32 (t, J = 5.6 Hz, 2H), 4.82 (d, J = 5.8 Hz, 2H); (d) Cinnamyl acetate (Table 2, Entry 4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H), 4.68 (d, J = 6.4 Hz, 2H), 6.19–6.29 (m, 1H), 6.58 (d, J = 16.2 Hz, 1H), 7.21–7.36 (m, 5H); (e) 1-(Pyridin-3-yl)allyl acetate (Table 2, Entry 5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3H), 2.68–2.77 (m, 2H), 5.10–5.03 (m, 2H), 5.70–5.78 (m, 1H), 5.87 (t, J = 6.6 Hz, 1H), 7.20 (t, J = 6.4 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.67 (t, J = 8.5 Hz, 1H), 8.59 (d, J = 4.6 Hz, 1H); (f) 8-(Tetrahydro-2H-pyran-2-yloxy)octyl acetate (Table 2, Entry 6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (bs, 12H), 1.50–1.63 (m, 8H), 1.69–1.73 (m, 1H), 1.81–1.85 (m, 1H), 2.05 (s, 3H), 3.36–3.41 (m, 1H), 3.48–3.50 (m, 1H), 3.70–3.76 (m, 1H), 3.85–3.89 (m, 1H), 4.05 (t, J = 6.8 Hz, 2H), 4.57 (t, J = 3.2 Hz, 1H); (g) 8-(Tert-butyldimethylsilyloxy)octyl acetate (Table 2, Entry 7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.89 (s, 9H), 1.28 (bs, 12H), 1.46–1.53 (m, 2H), 1.57–1.64 (m, 2H), 2.04 (s, 3H), 3.59 (t, J = 6.6 Hz, 2H), 4.05 (t, J = 6.8 Hz, 2H).

2.3.3. Table 3, Entries 1–13

(a) Phenyl acetate (Table 3, Entry 1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 7.07–7.09 (m, 2H), 7.19–7.24 (m, 1H), 7.34–7.40 (m. 2H); *b)* 2-Napthyl acetate (Table 3, Entry 3): ^{1}HNMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.22 (d, J = 8.8 Hz, 1H), 7.45 (m, 2H), 7.54 (s, 1H), 7.76 (m, 3H); (c) 1-Napthyl acetate (Table 3, Entry 4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.23 (d, J = 6.4 Hz, 1H), 7.43–7.45 (m, 3H), 7.72 (d, J = 8.2 Hz, 1H), 7.84–7.88 (m, 2H); (d) 4-Methoxyphenyl acetate (Table 3, Entry 5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 3.79 (s, 3H), 6.88 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H); (e) 4-Cyanophenyl acetate (Table 3, Entry 6): ^{1}HNMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 7.26 (d, J = 8.4 Hz, 2H),