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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),

7.69 (d, J = 8.6 Hz, 2H); (f) 4-Acetoxyacetophenone (Table 3, Entry 7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.53 (s, 3H), 7.10 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H); *g)* Ethyl 4-acetoxybenzoate (Table 3, Entry 8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (t, J = 7.2 Hz, 3H), 2.30 (s, 3H), 4.35 (q, J = 7.2 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 8.06 (d, J = 8.6 Hz, 2H); (h) 4-Nitrophenyl acetate (Table 3, Entry 9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 7.29 (d, J = 8.8 Hz, 2H), 8.28 (d, J = 9.2 Hz, 2H); (i) 4-Chlorophenyl acetate (Table 3, Entry 10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 6.62 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 8.9 Hz, 2H); (j) 4-Bromophenyl acetate (Table 3, Entry 11): ^{1}HNMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 6.96 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H); (k) 1,4-Phenylene diacetate (Table 3, Entry 12): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 7.09 (s, 3H); (l) Benzene-1, 2,3-triyl triacetate (Table 3, Entry 13): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 7.10 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 7.0 Hz, 2H); (l) *N*-benzylacetamide (Table 3, Entry 15): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 3H), 4.39 (d, J = 5.6 Hz, 2H), 6.11 (s, 1H), 7.24–7.33 (m, 5H); *m) N*-Phenylacetamide (Table 3, Entry 16): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H), 7.19 (t, J = 6.8 Hz, 1H), 7.43 (t, J = 6.2 Hz, 2H), 7.61 (t, J = 6.0 Hz, 2H); (n) *N, N*-Diphenylacetamide (Table 3, Entry 17): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H), 7.19 (m, 2H), 7.43–7.47 (m, 8H), 10.01 (bs, 1H); (o) *N*-(2-Hydroxyethyl)acetamide (Table 3, Entry 19): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.84 (s, 3H), 3.21 (t, J = 5.8 Hz, 2H), 3.60 (t, J = 7.2 Hz, 2H), 4.78 (bs, 1H), 8.01 (bs, 1H); (p) *S-p*-Tolyl ethanethioate (Table 3, Entry 22): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.37(s, 3H), 7.20 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H); (q) *S*-Phenyl ethanethioate (Table 3, Entry 23): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.4 (s, 3H), 7.40 (m, 4H); (r) *S*-Benzyl ethanethioate (Table 3, Entry 24): ^{1}HNMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 4.08 (s, 2H), 7.20–7.27 (m, 5H); (s) *S*-4-Nitrophenyl ethanethioate (Table 3, Entry 25): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (s, 3H), 7.59 (d, J = 9.2 Hz, 2H), 8.24 (d, J = 9.2 Hz, 2H).

2.3.4. Table 4, Entries 2–4

(a) 2-Phenethyl benzoate (Table 4, Entry 2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.02 (t, J = 6.8 Hz, 2H), 4.49 (t, J = 6.8 Hz, 2H), 7.14–749 (m, 8H), 8.00 (d, J = 6.8 Hz, 2H); (b) Phenethyl pivalate (Table 4, Entry 3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 9H), 2.94 (t, J = 7.0 Hz, 2H), 4.28 (t, J = 7.0 Hz, 2H), 7.3 (m, 5H); (c) Phenethyl isobutyrate (Table 4, Entry 4): ^{1}HNMR (400 MHz, $CDCl_3$) δ 1.13 (s, 3H), 1.16 (s, 3H), 2.50–2.57 (m, 1H), 2.95 (t, J = 13.6 Hz, 2H), 4.30 (t, J = 14.2 Hz, 2H), 7.21–7.25 (m, 5H).

2.4. Procedure for catalyst recovery

To a round-bottom flask was added 2-phenylethanol (2.44 g, 20 mmol) and acetic anhydride (2.04 g, 20 mmol) and a desired amount of catalyst (0.235 g, 1.0 mol% based on alcohol). The mixture was stirred at room temperature for 5 min under TLC analysis until complete consumption of alcohol. Finally the mixture was separated by evaporation in vacuum. The distillates collected before 80 °C/1.0 kPa contained Ac_2O, AcOH, $PhCH_2CH_2OH$, and H_2O and could be used directly for the next cycle; and that collected at 83–85 °C/1.0 kPa was the desired product of 2-phenethyl acetate. The remaining residue in the flask after evaporation was the recovered catalyst and could be recycled for the next cycle of reaction.

3. Results and discussion

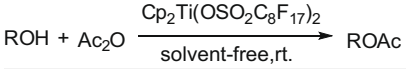
3.1. Characterization of catalyst

To be practically applicable, a catalyst for acylation reactions should be thermally stable and shows strong Lewis acidity and water tolerance. In this study, we used TG-DSC, NMR, and Hammett indicator methods to investigate the physiochemical properties of $Cp_2Ti(OSO_2C_8F_{17})_2$. Notably, the complex exhibited no sign of structure change after exposure to air for more than one year. The solid sample remained in powder form and suffered no change in color. The results indicate that the complex is air-stable. As shown in Fig. 1, the TG curve shows three stages of weight loss. The endothermic step below 100 °C can be assigned to the removal of water molecules. The material is stable up to about 200 °C, after which two overlapping weight losses of exothermic nature appear, plausibly due to the oxidation of organic entities. We observed the removal of pentafluorooctanesulfuryl ligands at 250 °C, and what left behind should be compounds of titanium fluorides. We also employed the ^{1}H and ^{19}F NMR technique to analyze the $Cp_2Ti(OSO_2C_8F_{17})_2$ sample that had undergone thermal treatment at 180 °CC for 2 days, and observed no change. We hence deduce that the $Cp_2Ti(OSO_2C_8F_{17})_2$ complex is thermally stable at 180 °C. The acidity of compounds was determined by Hammett indicators [49,50]. It was found that the complex has relatively strong acidity showing acid strength ($0.8 < H_0 \leqslant 3.3$; H_0 being the Hammett acidity function) stronger than that of the zirconocene and hafnocene perflouroalklysulfonates previously reported by us [44–46]. This result is also consistent with that determined by ESR technique in our former publication [44]. In view of the water tolerance, high thermal stability, and strong acidity of $Cp_2Ti(OSO_2C_8F_{17})_2$, we selected it as a catalyst for the acylation of alcohols, thiols, phenols, and amines.

3.2. Acetylation of alcohols

Using $Cp_2Ti(OSO_2C_8F_{17})_2$ as catalyst, we studied alcohols, phenols, thiols, and amines of structural diversity in acetylation reactions. The results of alcohol acetylation are summarized in Table 1. The acetylation of saturated primary aromatic alcohol appeared to be fast and effective (Table 1, Entries 1–3). The reactions went to completion in 20 min and the acylated products were obtained quantitatively. The acetylation of saturated secondary aromatic alcohols was somewhat slower (Table 1, Entries 4–5); 95% yield of acetate was obtained in 20 min in the acetylation of $PhCH(OH)CH_2CH_3$. (We observed 99% yield after 30 min.) In the case of tertiary aromatic alcohols such as triphenyl methanol (Table 1, Entry 6), only trace amount of the desired ester was obtained at 50 °C but yield at 100 °C was 99%. For the acetylation of the long-

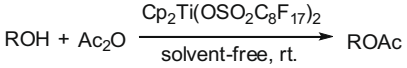
Table 1
Acetylation of saturated aliphatic and aromatic alcohols catalyzed by $Cp_2Ti(OSO_2C_8F_{17})_2$.[a]

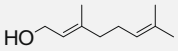
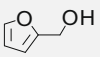
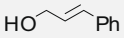
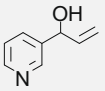
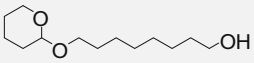
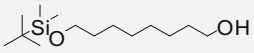


Entry	ROH	Time (min)	Yield (%)[b]
1	$PhCH_2OH$	1	99
2	$PhCH_2CH_2OH$	2	99
3	$PhCH_2CH_2CH_2OH$	20	99
4	$PhCH(OH)CH_2CH_3$	20	95
5	Ph_2CHOH	30	96
6[c]	Ph_3COH	24	Trace
7	$CH_3(CH_2)_8CH_2OH$	20	99
8	$CH_3(CH_2)_6CH_2OH$	15	97
9	$CH_3(CH_2)_2CH_2OH$	10	98
10	$CH_3CH_2CHOHCH_3$	5	99
11	Cyclohexanol	5	99
12[c]	$(CH_3)_3COH$	5	Trace

[a] Reaction conditions: $Cp_2Ti(OSO_2C_8F_{17})_2$, 0.01 mmol; alcohol, 1.0 mmol; Ac_2O, 1.0 mmol; solvent-free; rt.
[b] Isolated yield.
[c] At 50 °C, while at 100 °C the yield was 99%.

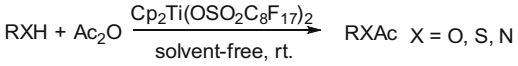
Table 2
Acetylation of functional alcohols catalyzed by $Cp_2Ti(OSO_2C_8F_{17})_2$.[a]



Entry	ROH	Time (min)	Yield (%)[b]
1		5	99
2		5	99
3		5	99
4		5	99
5		15	98
6[c]		20	98
7[c]		20	99

[a] Reaction conditions: $Cp_2Ti(OSO_2C_8F_{17})_2$, 0.02 mmol, alcohol, 1.0 mmol; Ac_2O, 1.0 mmol; rt.
[b] Isolated yield.
[c] At 0 °C; $Cp_2Ti(OSO_2C_8F_{17})_2$, 0.05 mmol.

Table 3
Acetylation of phenols, thiols, and amines catalyzed by $Cp_2Ti(OSO_2C_8F_{17})_2$.[a]



Entry	ROH	Time	Yield (%)[b]
1[c]	PhOH	1 h	84
2	PhOH	1 h	98
3	2-Naphthol	1 h	99
4	1-Naphthol	2 h	94
5	$4\text{-}MeOC_6H_4OH$	1 h	99
6	$4\text{-}NCC_6H_4OH$	1 h	92
7	$4\text{-}MeOCC_6H_4OH$	1 h	99
8	$4\text{-}EtOOCC_6H_4OH$	1.5 h	99
9	$4\text{-}O_2NC_6H_4OH$	3 h	99
10	$4\text{-}ClC_6H_4OH$	1 h	99
11	$4\text{-}BrC_6H_4OH$	1 h	99
12[d]	$4\text{-}HOC_6H_4OH$	3 h	95
13[e]	benzene-1,3,5-triol	6 h	94
14[f]	$PhCH_2CH_2OH$+PhOH	5 min	99 ($PhCH_2CH_2OAc$ / PhOAc = 99/1)
15	$PhCH_2NH_2$	1 min	99
16	$PhNH_2$	10 min	99
17[g]	Ph_2NH	1 h	98
18[h]	Ph_2NH	1 h	28
19[i]	$H_2NCH_2CH_2OH$	1 min	99 ($AcHNCH_2CH_2OH$ / $H_2NCH_2CH_2OAc$ = 99/1)
20[j]	$PhCH_2NH_2$+$PhCH_2CH_2OH$	1 min	98 ($PhCH_2NHAc$ / $PhCH_2CH_2OAc$ = 99/1)
21[j]	$PhCH_2NH_2$+PhOH	1 min	97 ($PhCH_2NH_2$ / PhOH = 100/0)
22	$4\text{-}MeC_6H_4SH$	2 h	96
23	PhSH	2 h	98
24	$PhCH_2SH$	2 h	89
25	$4\text{-}O_2NC_6H_4SH$	2 h	90
26[f]	$PhCH_2CH_2OH$+$PhCH_2SH$	5 min	99 ($PhCH_2CH_2OAc$ / $PhCH_2SAc$ = 99/1)
27[k]	PhOH+PhSH	1 h	99 (PhOAc / PhSAc = 100/0)

[a] $Cp_2Ti(OSO_2C_8F_{17})_2$, 0.02 mmol; Substrate, 1.0 mmol; Ac_2O, 1.0 mmol; rt.
[b] Isolated yield, ratio in parentheses indicate the ratio of major product to minor product determined by ^1H NMR.
[c] $Cp_2Ti(OSO_2C_8F_{17})_2$, 0.01 mmol.
[d] Ac_2O, 2.0 mmol; di-acetate.
[e] Ac_2O, 3.0 mmol; tri-acetate.
[f] Ac_2O, 1.0 mmol; $PhCH_2CH_2OAc$.
[g] At 50 °C.
[h] Without catalyst.
[i] Ac_2O 1.0 mmol; $HOCH_2CH_2NHAc$ as major product, no $AcOCH_2CH_2NHAc$ was observed.
[j] Ac_2O, 1.0 mmol; $PhCH_2NHAc$.
[k] Ac_2O, 1.0 mmol; PhOAc.

Table 4
Acylation of 2-phenylethanol with various acylating reagent catalyzed by $Cp_2Ti(OSO_2C_8F_{17})_2$.[a]

$$PhCH_2CH_2OH + RCO(OCR, Cl \text{ or } OH) \xrightarrow[\text{solvent-free}]{Cp_2Ti(OSO_2C_8F_{17})_2} PhCH_2CH_2OC(O)R$$

Entry	Acylating reagent	Cat. (mol%)	Time (h)	Yield (%)[b]
1	CH_3COCl	0.5	immediately	99
2	PhCOCl	2.0	0.5	95
3	$(t\text{BuCO})_2O$	1.0	10 min	99
4	$(i\text{PrCO})_2O$	1.0	10 min	99
5	$(PhCO)_2O$	2.0	1.0	98
6[c]	CH_3COOH	2.0	2.0	99
7[c]	PhCOOH	2.0	2.0	92

[a] 2-Phenylenthanol, 1.0 mmol; acyl chloride or anhydride, 1.0 mmol; rt.
[b] Isolated yield.
[c] 2-Phenylethanol, 1.0 mmol; acylating acid, 1.5 mmol; 80 °C.

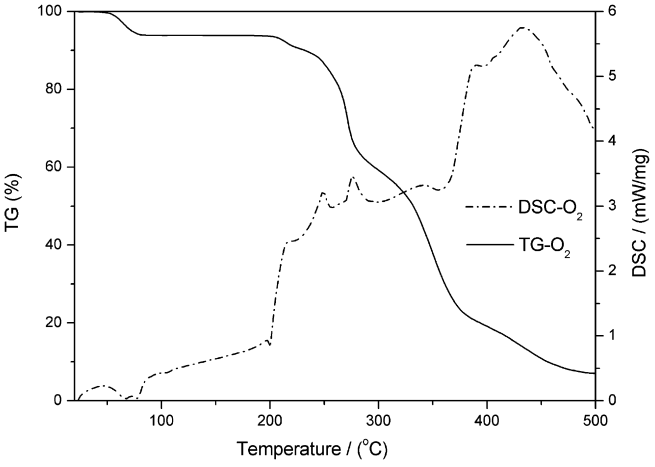


Fig. 1. TG-DSC curves of $Cp_2Ti(OSO_2C_8F_{17})_2$.

er aliphatic alcohols, the outcome was similar to that of aromatic alcohols, and almost quantitative acetylated products were obtained (Table 1, Entries 7–10). When one came to $(CH_3)_3COH$, the yield of desired product was low; to obtain quantitative yield, reaction temperature had to be raised to 100 °C (Table 1, Entry 12). In general, we found that the rate of the acetylation of aliphatic alcohols with long carbon chain was lower than that of aromatic alcohols, indicating that acetylation activity of alcohols with aryl group(s) is higher than that with alkyl group(s).

3.3. Acetylation of alcohols containing different functional groups

Listed in Table 2 are the results of acetylation of alcohols that contain functional groups sensitive to acids or bases. $Cp_2Ti(OSO_2C_8F_{17})_2$ is highly active for acetylation and shows good tolerance to a variety of functional groups. The acetylation of geraniol, furfural alcohol and prop-2-yn-ol occurs under mild conditions (Table 2, Entries 1–3). The reactions are fast and selective, and the double bond and triple bond are not affected by $Cp_2Ti(OSO_2C_8F_{17})_2$. We observed no rearrangement of allylic alcohols in the acetylation reactions (Table 2, Entries 4,5). In the case of functionalized and acid-liable alcohols such as THP (THP = 2-tetrahydropyranyl) and TBS (TBS = tert-butyldimethyl silyl) protected 1,8-octandiol, the reaction temperature was lowered to 0 °C to allow subtle tuning of acylation reaction rate under solvent-free condition (Table 2, Entries 6, 7). However, it should be noted that the catalyst doses not work with substrates like menthol, iso-menthol, 2-methyl-1-phenyl-2-propanol, linalool and 2-phenyl-2-propanol, etc., which are more rearrangement prone.

3.4. Acetylation of phenol, thiols, and amine

With the good results of alkyl alcohols, we applied the method to the acetylation of phenols (1.0 equivalent) (Table 3). When the acetylation of phenol was carried out in the presence of 1.0 mol% catalyst under solvent-free condition at room temperature, only 84% desired ester was formed. When the loading of the catalyst was increased to 2.0 mol%, the desired phenyl acetate was obtained in quantitative yield (Table 3, Entries 1,2). The results illustrate that phenol was lower than aromatic alcohol in reactivity. The electronic and steric factors of the substrates show subtle influence on the rate of acetylation (Table 3, Entries 3,4). When other substitute phenols were used as substrates, we found that the catalyst was compatible with various functional groups, including Br, Cl, COMe, CO_2Et, CN, and NO_2 (Table 3, Entries 5–11). The di- and tri-hydroxy aromatic compounds afforded the formation of di- and triacetates, respectively, in excellent yields (Table 3, Entries 12–13). Excellent results were obtained over phenols that are less nucleophilic due to the presence of electron-withdrawing groups such as Br, Cl, CO_2Et, CN, and NO_2. The competitive acetylation of 2-phenylenthanol and phenol with one equivalent of acetic anhydride in the presence of 1.0 mol% $Cp_2Ti(OSO_2C_8F_{17})_2$ within 5 min were investigated at room temperature under solvent-free condition. After 5 min, only 2-phenylethyl acetate was obtained (Table 3, Entry 14), and phenol was almost unaffected.

The potential application of $Cp_2Ti(OSO_2C_8F_{17})_2$ as a catalyst for acetylation of various amines (Table 4, Entries 15–21) and thiols (Table 3, Entries 20–27) was also investigated. Excellent results were obtained at room temperature with one equivalent of acetic anhydride in the presence of 2.0 mol% $Cp_2Ti(OSO_2C_8F_{17})_2$. It is obvious that the acetylation rate was influenced by the steric and electronic factors associated with the substrates. The acetylation of primary amines was significantly faster than that of secondary amines (Table 3, Entries 15,16). The acetylation of *N,N*-diphenylamine at 50 °C proceeded slowly without $Cp_2Ti(OSO_2C_8F_{17})_2$ while the use of $Cp_2Ti(OSO_2C_8F_{17})_2$ as a catalyst accelerated the reaction remarkably (Table 3, Entries 17,18). It is interesting to note that in competitive acetylation of one equimolar mixture of 2-phenylethanol and benzyl amine, the amine is selectively acetylated while the alcohol is almost unaffected (Table 3, Entries 19–21). In other words, acetylation of amino alcohols would selectively produce the corresponding acetamides. Such selective acetylation of a primary NH_2 over a primary OH is of considerable synthetic importance.

In contrast, the rate of acetylation of thiols was lower than that of phenols and amines. The acetylation of benzenethiol proceeded faster than that of benzylthiol, and the acetylation of benzenethiol with electron-donating group in the *para*-position was faster than

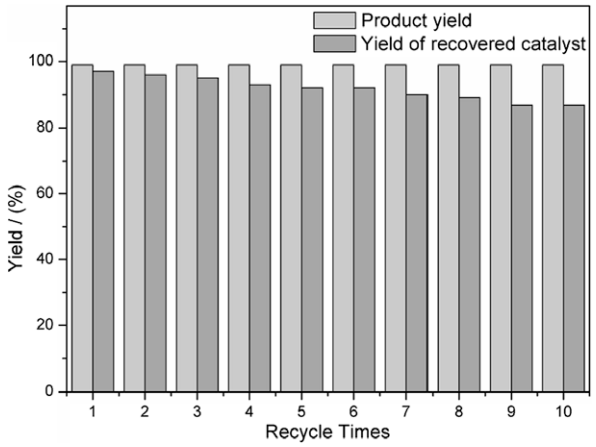


Fig. 2. Acetylation of 2-phenylethanol catalyzed by recovered $Cp_2Ti(OSO_2C_8F_{17})_2$.

that of benzenthiol with electron-withdrawing groups. In the competitive reactions of Table 3, Entries 26 and 27, only phenyl acetate and 2-phenylethyl acetate were obtained, giving another example of high chemoselectivity.

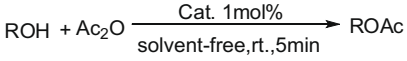
3.5. Catalyst recovery investigation

To test the reusability of the catalyst and reproducibility of catalytic performance, $Cp_2Ti(OSO_2C_8F_{17})_2$ was subject to cycles of acetylation reaction of 2-phenylethanol with acetic anhydride (Fig. 2). It was found that the change in product yield was minimal in a test of 10 cycles, indicating that the catalyst is stable and suitable for reuse.

3.6. Acylation of 2-pheylethanol with various acylation reagents

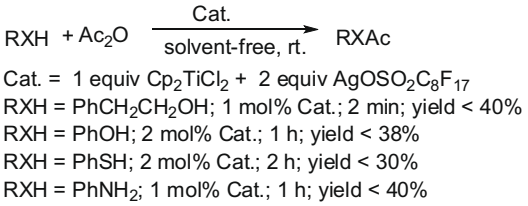
To evaluate $Cp_2Ti(OSO_2C_8F_{17})_2$ as a general acylation catalyst, the complex was tested with various acylating reagents (Table 4). Good to excellent yields were obtained at room temperature with isobutyric, pivalic and benzoyl anhydrides as well as acetic, and benzoyl chloride. For acylation with benzoic anhydride, heating at 80 °C is required. Compared with acyl anhydride and acyl chloride, carboxylic acid could be a better choice because water is liberated as side product. Due to the weak acylating activity of carboxylic acid, the direct acylation in the presence of 2 mol% of $Cp_2Ti(OSO_2C_8F_{17})_2$ with acetic and benzoic acid required heating at 80 °C for one hour, giving yields up to 99%.

Table 5
Acetylation of 2-phenylethanol with acetic anhydride catalyzed by different catalysts.[a]



Entry	Cat. (0.01 equiv)	Yield (%) [b]
1	TiO_2	0
2	Cp_2TiCl_2	0
3	$Cp_2Ti(OTf)_2$	95
4	TMSOTf	88
5	$Sc(OTf)_3$	81
6	$Bi(OTf)_3$	75
7	$Mg(NTf)_2$	35
8	I_2	25
9	DMAP	85
10	$AgOSO_2C_8F_{17}$	35
11	$Cp_2Zr(OSO_2C_8F_{17})_2$	99
12[c]	$Cp_2Ti(OSO_2C_8F_{17})_2$	99
13[d]	$Cp_2Ti(OSO_2C_8F_{17})_2$	95

[a] Reaction conditions: 2-phenylenthanol, 1.0 mmol; Cat. 0.01 mmol; Ac_2O, 1.0 mmol, solvent-free, rt., 5 min.
[b] Isolated yield.
[c] Two minutes.
[d] Catalyst kept in open air for one year.



Scheme 1. Catalytic performance of catalyst system combined with Cp_2TiCl_2 (1 equiv) and $AgOSO_2C_8F_{17}$ (2 equiv) in the acetylation of $PhCH_2CH_2OH$, PhOH, PhSH, $PhNH_2$ with Ac_2O.

3.7. Acetylation of 2-phenylethanol with acetic anhydride catalyzed by different catalysts

We used the acetylation of 2-phenylethanol with acetic anhydride in the presence of 1.0 mol% catalyst at room temperature for 5 min as model procedure to demonstrate the advantage of $Cp_2Ti(OSO_2C_8F_{17})_2$ over other catalysts. Some of the results are tabulated in Table 5. No reaction was observed when TiO_2 and Cp_2TiCl_2 were used as catalysts (Table 5, Entries 1,2). TMSOTf [32] and $Cp_2Ti(OTf)_2$ [40] show high catalytic activity but they are known to be unstable in air (Table 5, Entries 3,4). The reference catalysts of $Sc(OTf)_3$ [30], $Bi(OTf)_3$ [33], $Mg(NTf_2)_2$ [23], I_2 [38] and DMAP [5] (highly toxic; e.g., intravenous LD50 in the rat: 56 mg/kg) [23], and $AgOSO_2C_8F_{17}$ [43], show lower catalytic activity than $Cp_2Ti(OSO_2C_8F_{17})_2$ (Table 5, Entries 5–9). Furthermore, these catalysts are hydrolytic in air and liberate CF_3SO_3H which has been considered as powerful catalyst by Hollis et al. [42]. The freshly prepared catalyst $Cp_2Ti(OSO_2C_8F_{17})_2$ shows higher catalytic activity than our previously reported catalyst $Cp_2Zr(OSO_2C_8F_{17})_2$ (Table 5, Entries 10,11). It is worth pointing out that after being stored in air for one year, $Cp_2Ti(OSO_2C_8F_{17})_2$ exhibits comparable catalytic efficiency to that of a freshly prepared one (Table 5, Entry 12). We also checked the catalytic performance of Cp_2TiCl_2 and $AgOSO_2C_8F_{17}$ for the acetylation of alcohol, phenols, amines and thiols, and found that the yields in all the cases were poor (<40%). The reason is still under investigation (Scheme 1).

4. Conclusions

In summary, we have demonstrated a versatile method for the acylation of alcohols, phenols, thiols, and amines using titanocene bis(perfluorooctanesulfonate) as catalyst. The approach has merits such as high selectivity and yield, operational simplicity, mild solvent-free reaction conditions, and good recyclability of the catalyst, and is very attractive from the standpoint of industrial application.

Acknowledgements

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