Metallocene bis(perfluoroalkanesulfonate)s as air-stable cationic Lewis acids

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ABSTRACT

Zirconocene and titanocene bis(perfluorooctanesulfonate)s were synthesized. In contrast to the corresponding triflates and perchlorates, these compounds are air- and water-stable. They were proved to be ionic on the basis of conductivity measurements and X-ray analysis, allowing these complexes to be stored for months. The strong Lewis acidity of these cationic metallocene species, which was proved by ESR study, enabled catalytic glycosylation.

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1. Introduction

The Lewis acid chemistry has played a major role in modern organic synthesis [1], yet the conflict between the following issues remains still unsettled. The Lewis acid is desired to be as strongly acidic as possible to acquire higher activity, while it becomes more susceptible to hydrolysis upon increasing the acidity. Cationic group 4 metallocene compounds, which have attracted increasing attention recently [2], represent a typical example. The metallocene bis(triflate) complexes of zirconium and titanium $Cp_2M(OTf)_2$ ($Cp = C_5H_5$, $Tf = CF_3SO_2$) were initially obtained by treatment of Cp_2MCl_2 with AgOTf [3] and later from Cp_2ZrMe_2 and TfOH [4]. These complexes were successfully employed as catalysts for Diels–Alder reaction [5], Mukaiyama–Aldol reaction [6], Hosomi–Sakurai reaction [6a,7], [3+2] nitrone–olefin cycloaddition reaction [8], and glycosylation [9]. Unfortunately, however, these metallocene bis(triflate)s are not stable in open air [10], suffering from facile hydrolysis. Thus, these complexes must be handled under strictly anhydrous conditions. Another notable species are putative metallocene perchlorates $Cp_2M(ClO_4)_2$ (M = Hf and Zr), which have found extremely versatile application to glycosylation technology

[11]. These species also cannot be isolated due to their hydrolytic instability, and so they are usually generated in situ prior to reaction by treating Cp_2MCl_2 with potentially explosive $AgClO_4$. Accordingly, improvement of the hygroscopic character of the cationic metallocene derivatives is highly demanding from the standpoint of practical utilization as catalysts.
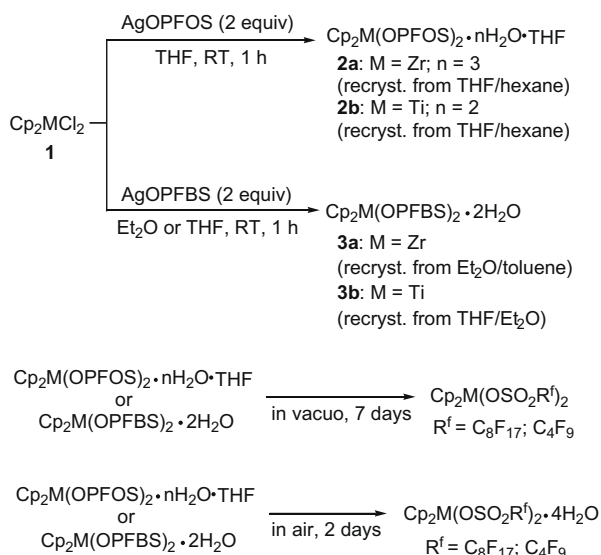
Recently, we disclosed that the perfluorooctanesulfonate group worked as an effective counter-anion to provide cationic organotin species [12], which were found air-stable and water-tolerant in sharp contrast to the corresponding highly hygroscopic organotin triflates [13]. This finding has led us to postulate that longer perfluoroalkanesulfonate groups could serve for overcoming the hydrolytic instability of the cationic organometallic species in a general sense. We report herein successful isolation of air-stable cationic metallocene (M = Zr and Ti) bis(perfluoroalkanesulfonate)s, which enabled facile assessment of Lewis acidity and catalytic activity.

2. Results and discussion

The synthesis of zirconocene and titanocene bis(perfluoroalkanesulfonate)s is straightforward (Scheme 1). Treatment of metallocene dichlorides, Cp_2MCl_2 [M = Zr (**1a**), Ti (**1b**)] with silver perfluorooctanesulfonate ($AgOSO_2C_8F_{17}$ = AgOPFOS) (2 equiv.) in THF or silver perfluorobutanesulfonate ($AgOSO_2C_4F_9$ = AgOPFBS) (2 equiv.) in Et_2O or THF allowed us to isolate the corresponding perfluoroalkanesulfonate derivatives $Cp_2M(OPFOS)_2 \cdot nH_2O \cdot THF$

Previously, we have reported that the Lewis acidity of the metal complexes can be estimated by the binding energies (ΔE values) of Lewis acid metal ions with O_2^{-} on the basis of ESR spectra [16]. Thus, we measured the ESR spectra of O_2^{-}–**2a** and O_2^{-}–**2b** complexes to determine the ΔE values, which are shown in Fig. 2 [16b]. The ΔE value of the titanium complex (O_2^{-}–**2b**) is significantly larger (Ti^{4+}: g_{zz} = 2.0289, ΔE = 1.06 eV) than that of Sc(OTf)$_3$ (g_{zz} = 2.0304, ΔE = 1.00 eV) and is the largest among the ΔE values previously reported by our group [16]. The ΔE of the zirconium complex (O_2^{-}–**2a**) exhibits relatively large value (Zr^{4+}: g_{zz} = 2.0331, ΔE = 0.91 eV), which falls between those of Sc(OTf)$_3$ and Y(OTf)$_3$ (g_{zz} = 2.0349, ΔE = 0.85 eV). Since Lewis acids with the ΔE value larger than 0.88 were presumed to be capable for inducing carbon–carbon bond-forming reactions [16b], it is reasonably expected that the Lewis acidity of **2a** and **2b** is high enough to trigger synthetically useful reactions.

With the above results in hand, we employed **2a** as a catalyst in synthetically important glycosylation reaction with glycosyl fluoride donor. As shown in Scheme 2, the reaction proceeded smoothly in the presence of **2a** · 3H$_2$O · THF (20 mol%) and molecular sieves 4A (MS 4A) to give high yields of the glycosylation products **5a–g**. Remarkably, only a catalytic amount of **2a** is enough to complete the glycosylation. This presents a striking contrast to metallocene triflates or percholorates which are used in large excess (2–5 equiv. relative to the donor) [9,11]. The *O*-glycosylation products were obtained exclusively with *p*-methoxyphenol and 2-naphthol in contrast to Cp$_2$HfCl$_2$/(AgClO$_4$)$_2$, which induced rearrangement from *O*-glycosides to *C*-glycosides at –20 °C with these phenols [11a,d]. Our catalyst is quite different in this respect, implying a unique influence of the perfluorooctanesulfonate counter-anion [17]. The present protocol is applicable to synthesis of disaccharide, and treatment of **4** with methyl 2,3,4-tri-*O*-benzyl-glucopyranoside provided **5f** in 89% yield. When 1,3,5-trimethoxybenzene was utilized as acceptor, the *C*-glycosylation took place exclusively from the β-face of **4** to afford **5g** in high yield.

In summary, long perfluoroalkanesulfonate groups have proved to work for stabilizing cationic metallocene complexes. The isolated species were fully characterized by NMR spectroscopy, X-ray diffraction, conductivity measurements, and ESR spectra. The perfluorooctanesulfonate derivatives exhibited strong Lewis acidity to trigger glycosylation in a catalytic manner. Further studies on synthesis of relevant compounds as well as their application to other reactions such as Mukaiyama–Aldol reaction and allylation will be reported in a full paper.

Scheme 1. Syntheses of Cp$_2$M(OSO$_2$C$_8$F$_{17}$)$_2$ and Cp$_2$M(OSO$_2$C$_4$F$_9$)$_2$ (M = Ti, Zr).

[M = Zr (**2a** · 3H$_2$O · THF), Ti (**2b** · 2H$_2$O · THF)] (after recrystallization from THF/hexane), Cp$_2$Zr(OPFBS)$_2$ · 2H$_2$O (**3a** · 2H$_2$O) (after recrystallization from Et$_2$O/toluene), and Cp$_2$Ti(OPFBS)$_2$ · 2H$_2$O (**3b** · 2H$_2$O) (after recrystallization from THF/Et$_2$O), as stable hydrated species. The hydration number (n) of **2** and **3** was variable upon standing (Scheme 1). ^{1}H NMR spectroscopy (in dry CH$_3$CN) and elemental analysis showed that freshly prepared samples after recrystallization contained two or three water molecules along with solvating THF for **2a** and **2b** while both **3a** and **3b** contained two water molecules only. Pumping these complexes in vacuo for a week at room temperature caused complete dehydration giving rise to n = 0. Standing the freshly prepared compounds **2a** and **2b** in open air for 2 days induced desolvation of the THF and the water content increased to n = 4. Under the same circumstances, the hydration number of **3a** and **3b** were also increased to n = 4. Such durability, though being hydrated, presents a sharp contrast to the corresponding triflate, Cp$_2$Zr(OTf)$_2$, which undergoes facile hydrolysis to dinuclear Cp$_2$Zr$_2$(H$_2$O)$_6$(μ^2-OH)$_2$(OTf)$_4$ · 4THF [3g]. Notably, **2** and **3** exhibited no sign of structural change after being kept in open air for three months. The solid samples remained as dry crystals or powder and suffered no color change. Therefore, the metallocene perfluoroalkanesulfonates are storable in open air, gaining a great advantage over the metallocene triflates or perchlorates from an operational point of view.

The cationic structure of **2a** · 3H$_2$O · THF in the solid state was confirmed by X-ray analysis. The crystals suitable for the X-ray diffraction were obtained by diffusion of hexane into saturated THF solution. The crystal structure and packing together with selected bond lengths and angles are shown in Fig. 1 [14]. The zirconium atom is coordinated by three water molecules and not by THF. Hence, the geometry of the [Cp$_2$Zr(H$_2$O)$_3$]$^{2+}$ moiety is similar to that of [Cp$_2$Zr(H$_2$O)$_3$]$^{2+}$(OTf$^-$)$_2$ [3b]. The three H$_2$O molecules lie on the plane that bisects the angle between the Cp ring planes. The Zr–O distances are 2.234(5), 2.236(6) and 2.247(6) Å. The PFOSO$^-$ anions and the THF molecule are packed around the zirconium cation in such a way that their oxygen atoms point towards the H$_2$O ligands. The C$_8$F$_{17}$ chains of the anion, on the other hand, are clustered together so as to produce hydrophobic domains in the crystal structure.

The ionic dissociation of **2** and **3** in solution was apparent from conductivity measurements (Table 1). The large molar conductivity values are consistent with complete ionization into a 1:2 electrolyte [15].

3. Experimental

3.1. General

All reactions were carried out under nitrogen atmosphere with freshly distilled solvents unless otherwise noted. THF was distilled from sodium/benzophenone. Acetonitrile was distilled from CaH$_2$. Acetone was refluxed for 4 h and distilled with KMnO$_4$, and then was dried with K$_2$CO$_3$, followed by distillation, and kept in the dry box. NMR spectra were recorded at 25 °C on INOVA-400 M (USA) calibrated with tetramethylsilane (TMS) as an internal reference. Elemental analyses were performed by VARIO EL III. Conductivity was measured on REX conductivity meter DDS-307. IR spectra were recorded on NICOLET 6700 FTIR spectrophotometer (Thermo Electron Corporation). X-ray single crystal diffraction analysis was performed with SMART-APEX and RASA-7A by Shanghai Institute Organic Chemistry, Chinese Academy of Science. AgOSO$_2$C$_8$F$_{17}$ and AgOSO$_2$C$_4$F$_9$ were prepared according to methods, which we reported earlier [13].
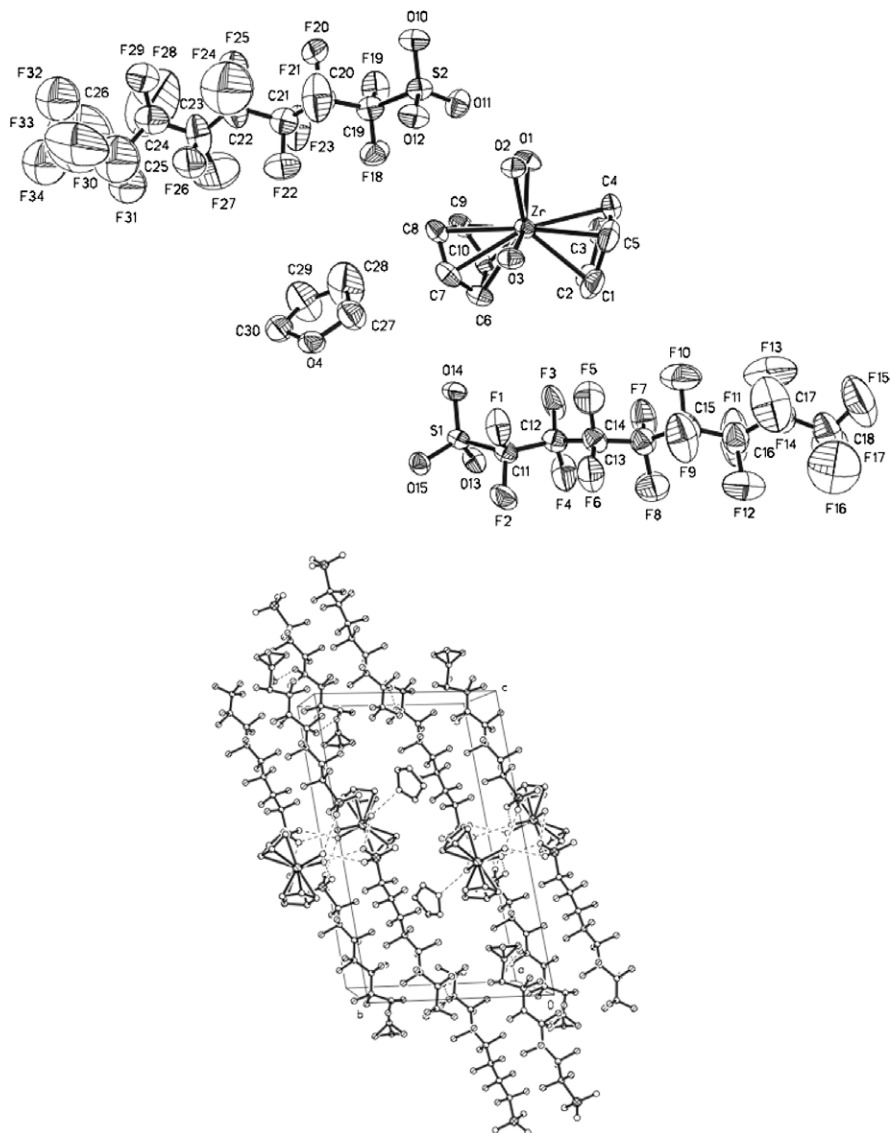
Fig. 1. An ORTEP view showing 50% probability ellipsoids and packing of $Cp_2Zr(H_2O)_3(OSO_2C_8F_{17})_2 \cdot 3H_2O \cdot THF$ (**2a** $\cdot$ 3H_2O $\cdot$ THF). Selected bond distances (Å) and angles (°): Zr–O(2), 2.234 (5); Zr–O(3), 2.236 (6); Zr–O(1), 2.247 (6); Zr–C(10), 2.467 (9); Zr–C(2), 2.469 (10); Zr–C(6), 2.479 (9); Zr–C(1), 2.479 (10); Zr–C(4), 2.491 (10); Zr–C(5), 2.494 (9); Zr–C(9), 2.498 (9); Zr–C(3), 2.504 (11); Zr–C(7), 2.511 (9). O(2)–Zr–O(3) 69.3 (2); O(2)–Zr–O(1) 72.0 (2); O(3)–Zr–O(1), 141.2 (2). The torsion angle between the two Cp ring planes is 53.83°.

Table 1
Conductivity of cationic metallocene perfluoroalkanesulfonates.[a]

Compound	Conductivity ($\mu S\ cm^{-1}$)
2a $\cdot$ 3H_2O $\cdot$ THF	136.1
2b $\cdot$ 2H_2O $\cdot$ THF	114.5
3a $\cdot$ 2H_2O	98.5
3b $\cdot$ 2H_2O	95.1

[a] In CH_3CN (1.0 mmol L^{-1}) at 15 °C.

3.2. $Cp_2Zr(OSO_2C_8F_{17})_2 \cdot 3H_2O \cdot THF$ (**2a** $\cdot$ 3H_2O $\cdot$ THF)

To a solution of Cp_2ZrCl_2 (292 mg, 0.99 mmol) in THF (20 mL) was added a solution of $AgOSO_2C_8F_{17}$ (1.21 g, 2.0 mmol) in THF (10 mL). The mixture was stirred in the dark at room temperature for 1 h, and filtrated. The filtrate was combined with dry hexane (40 mL). Then, the solution was stored in the refrigerator for 24 h to furnish colorless crystals (794 mg, 65%): M.p. 133–136 °C. ^{1}H NMR (300 MHz, CD_3CN) δ 1.77–1.81 (m, 4H, THF), 2.19 (s, 6H,
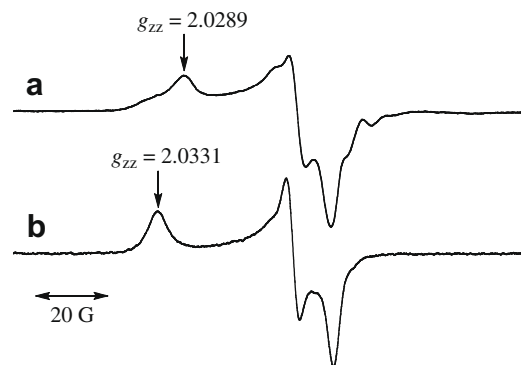
Fig. 2. ESR spectra of (a) O_2^-/Ti^{4+} (**2b** $\cdot$ 2H_2O $\cdot$ THF) and (b) O_2^-/Zr^{4+} (**2a** $\cdot$ 3H_2O $\cdot$ THF).

H_2O), 3.63 (t, J = 6.7 Hz, 4H, THF), 6.52 (s, 10H, Cp). ^{19}F NMR (283 MHz, CD_3CN) δ −81.45 (t, J = 9.6 Hz, 3F, CF_3-), −114.84 (s, 2F, -CF_2-), −120.86 (s, 2F, -CF_2-), −122.01 to −122.25 (m, 6F, -(CF_2)_3-),
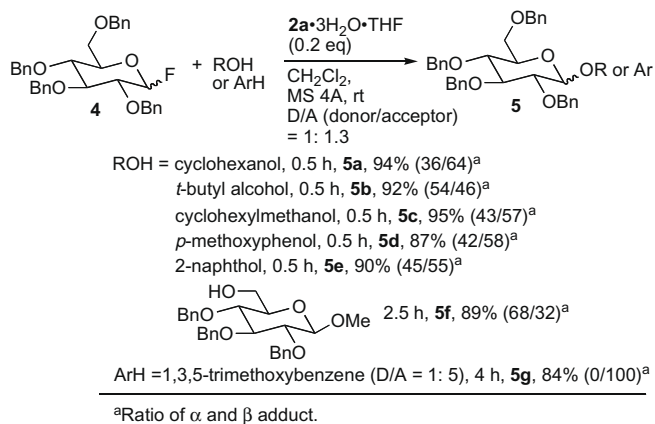
Scheme 2. Glycosylation with glycosyl fluoride catalyzed by 2a.

-123.10 (s, 2F, -CF$_2$-), -126.48 to -126.55 (m, 2F, -CF$_2$-). IR (KBr) 3543.8, 3505.8, 3474.8, 3420.8, 3409.8, 3905.2, 3229.0, 2359.0, 1662.9, 1427.7, 1370.6, 1331.5, 1242.4, 1150.7, 1074.1, 1041.1, 943.0, 819.6, 747.0, 707.5, 649.7, 628.8, 559.8, 531.6, 500.9 cm^{-1}. Cp$_2$Zr(OSO$_2$C$_8$F$_{17}$)$_2$ · 4H$_2$O (2a · 4H$_2$O) ^{1}H NMR (300 MHz, CD$_3$CN) δ 2.19 (s, 8H, H$_2$O), 6.52 (s, 10H, Cp). ^{19}F NMR (283 MHz, CD$_3$CN) δ -81.47 (t, $J = 9.6$ Hz, 3F, CF$_3$-), -114.91 (s, 2F, -CF$_2$-), -120.90 (s, 2F, -CF$_2$-), -122.00 to -122.27 (m, 6F, -(CF$_2$)-), -123.13 (s, 2F, -CF$_2$-), -126.54 to 126.65 (m, 2F, -CF$_2$-). Elemental Anal. for Cp$_2$Zr(OSO$_2$C$_8$F$_{17}$)$_2$ (2a) after pumping for a week: Calc. for C$_{26}$H$_{10}$F$_{34}$O$_6$S$_2$Zr: C, 25.60; H, 0.83; found: C, 25.67; H, 0.82%. Elemental Anal. for Cp$_2$Zr(OSO$_2$C$_8$F$_{17}$)$_2$ · 4H$_2$O (2a · 4H$_2$O) after standing in open air for 2 days: Calc. for C$_{26}$H$_{18}$F$_{34}$O$_{10}$S$_2$Zr: C, 24.18; H, 1.40; found: C, 24.34; H, 1.33%.

3.3. Cp$_2$Ti(OSO$_2$C$_8$F$_{17}$)$_2$ · 2H$_2$O · THF (2b · 2H$_2$O · THF)

To a solution of Cp$_2$TiCl$_2$ (249 mg, 0.99 mmol) in THF (20 mL) was added a solution of AgOSO$_2$C$_8$F$_{17}$ (1.21 g, 2.0 mmol) in THF (10 mL). The mixture was stirred in the dark at room temperature for 1 h, and filtered. The filtrate was combined with dry hexane (40 mL). Then, the solution was stored in the refrigerator for 24 h to furnish yellow needle crystals (693 mg, 54%): M.p. 206–210 °C. ^{1}H NMR (300 MHz, CD$_3$CN) δ 1.78–1.83 (m, 4H, THF), 3.56 (s, 4H, H$_2$O), 3.65 (t, $J = 6.6$ Hz, 4H, THF), 6.96 (s, 10H, Cp). ^{19}F NMR (283 MHz, CD$_3$CN) δ -81.33 (t, $J = 9.6$ Hz, 3F, CF$_3$-), -114.93 (s, 2F, -CF$_2$-), -120.98 (s, 2F, -CF$_2$-), -122.11 (m, 6F, -(CF$_2$)-), -122.99 (s, 2F, -CF$_2$-), -126.42 (m, 2F, -CF$_2$-). IR (KBr) 3648.9, 3586.9, 3536.4, 3505.3, 3443.4, 3416.5, 3120.1, 2363.6, 1662.9, 1440.4, 1370.1, 1246.3, 1152.6, 1073.9, 823.9, 642.0, 561.4, 526.5 cm^{-1}. Cp$_2$Ti(OSO$_2$C$_8$F$_{17}$)$_2$ · 4H$_2$O (2b · 4H$_2$O) ^{1}H NMR (300 MHz, CD$_3$CN) δ 3.19 (s, 8H, H$_2$O), 6.97 (s, 10H, Cp). ^{19}F NMR (283 MHz, CD$_3$CN) δ -81.32 (t, $J = 9.6$ Hz, 3F, CF$_3$-), -114.82 (s, 2F, -CF$_2$-), -120.90 (s, 2F, -CF$_2$-), -121.92 to -122.05 (m, 6F, -(CF$_2$)-), -122.91 (s, 2F, -CF$_2$-), -126.29 to -126.34 (m, 2F, -CF$_2$-). Elemental Anal. for Cp$_2$Ti(OSO$_2$C$_8$F$_{17}$)$_2$ (2b) after pumping for a week: Calc. for C$_{26}$H$_{10}$F$_{34}$O$_6$S$_2$Ti: C, 26.55; H, 0.86; found: C, 26.76; H, 0.86%. Elemental Anal. for Cp$_2$Ti(OSO$_2$C$_8$F$_{17}$)$_2$ · 4H$_2$O (2b · 4H$_2$O) after standing in open air for 2 days: Calc. for C$_{26}$H$_{18}$F$_{34}$O$_{10}$S$_2$Ti: C, 25.02; H, 1.45; found: C, 25.28; H, 1.42%.

3.4. Cp$_2$Zr(OSO$_2$C$_4$F$_9$)$_2$·2H$_2$O (3a · 2H$_2$O)

To a solution of Cp$_2$ZrCl$_2$ (146 mg, 0.50 mmol) in Et$_2$O (10 mL) was added a solution of AgOSO$_2$C$_4$F$_9$ (427 mg, 1.05 mmol) in Et$_2$O (5 mL). The mixture was stirred in the dark at room temperature for 1 h, and filtered. Evaporation furnished a residue, which was

diluted with Et$_2$O (2 mL) and toluene (5 mL). The solution was kept standing in a refrigerator for 24 h. White crystals were obtained (308 mg, 72%): M.p. 100–104 °C. ^{1}H NMR (500 MHz, CD$_3$CN) δ 2.36 (s, 4H, H$_2$O), 6.52 (s, 10H, Cp). ^{19}F NMR (283 MHz, CD$_3$CN) δ -81.67 (s, 3F, CF$_3$-), -115.52 (s, 2F, -CF$_2$-), -112.19 (s, 2F, -CF$_2$-), -126.56 (s, 2F, -CF$_2$-). IR (KBr) 3535.3, 3503.1, 3476.3, 3466.0, 3446.2, 3403.2, 3337.3, 2437.7, 1677.6, 1440.4, 1354.6, 1270.1, 1137.9, 1064.7, 1018.9, 835.0, 806.8, 739.6, 700.4, 685.2, 659.3, 617.5, 526.1, 439.0 cm^{-1}. Elemental Anal. for Cp$_2$Zr(OSO$_2$C$_4$F$_9$)$_2$ (3a) after pumping for a week: Calc. for C$_{18}$H$_{10}$F$_{18}$O$_6$S$_2$Zr: C, 26.38; H, 1.23; found: C, 26.28; H, 1.31%. Elemental Anal. for Cp$_2$Zr(OSO$_2$C$_4$F$_9$)$_2$ · 4H$_2$O (3a · 4H$_2$O) after standing in open air for 2 days: Calc. for C$_{18}$H$_{18}$F$_{18}$O$_{10}$S$_2$Zr: C, 24.25; H, 2.03; found: C, 24.37; H, 2.09%.

3.5. Cp$_2$Ti(OSO$_2$C$_4$F$_9$)$_2$ · 2H$_2$O (3b · 2H$_2$O)

To a solution of Cp$_2$TiCl$_2$ (124 mg, 0.50 mmol) in THF (10 mL) was added a solution of AgOSO$_2$C$_4$F$_9$ (427 mg, 1.05 mmol) in THF (5 mL). The mixture was stirred in the dark at room temperature for 1 h, and filtered. Evaporation furnished a residue, which was diluted with THF (1 mL) and Et$_2$O (5 mL). The yellow solid was obtained (276 mg, 68%): M.p. 117–121 °C. ^{1}H NMR (300 MHz, CD$_3$CN) δ 3.39 (s, 4H, H$_2$O), 6.95 (s, 10H, Cp). ^{19}F NMR (283 MHz, CD$_3$CN) δ -81.77 (t, $J = 9.6$ Hz, 3F, CF$_3$-), -115.41 to -115.45 (m, 2F, -CF$_2$-), -122.26 (s, 2F, -CF$_2$-), -126.47 to -126.70 (m, 2F, -CF$_2$-). IR (KBr): 3503.3, 3119.2, 1695.8, 1447.6, 1357.4, 1297.1, 1237.0, 1137.3, 1065.4, 1017.0, 850.4, 807.8, 740.8, 700.8, 658.1, 620.3, 598.5, 526.8 cm^{-1}. Elemental Anal. for Cp$_2$Ti(OSO$_2$C$_4$F$_9$)$_2$ (3b) after pumping for a week: Calc. for C$_{18}$H$_{10}$F$_{18}$O$_6$S$_2$Ti: C, 27.85; H, 1.30; found: C, 27.88; H, 1.37%. Elemental Anal. for Cp$_2$Ti(OSO$_2$C$_4$F$_9$)$_2$ · 4H$_2$O (3b · 4H$_2$O) after standing in open air for two days: Calc. for C$_{18}$H$_{18}$F$_{18}$O$_{10}$S$_2$Ti: C, 25.49; H, 2.14; found: C, 25.68; H, 2.03%.

3.6. Determination of hydration number

Molecular sieves (4 Å, 11.0 g, dried at 355 °C in a muffle furnace for 5 h) were added to CD$_3$CN (25.0 g), and the mixture was kept under nitrogen atmosphere overnight. In this CD$_3$CN, water was not detected by ^{1}H NMR spectroscopy. The dehydrated CD$_3$CN was added to a freshly prepared (2a · 3H$_2$O · THF) (10.0 mg, recrystallized from THF/hexane (3:4) followed by drying under reduced pressure for a week), and the solution was analyzed by ^{1}H NMR spectroscopy. Then the sample was subjected to elemental analysis.

3.7. ESR detection of O$_2^-$–2a complex

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 2a · 3H$_2$O · THF (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$_2^-$–2a 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 an Mn^{2+} marker, which was used as a reference.

3.8. Crystal data refinements details

Refinement of F^2 was against all reflections. The weighted R-factor wR and goodness of fit S are based on F^2, 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 calculating 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 will be even larger. 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.

3.9. Glycosylation

A suspension of **2a** · 3H$_2$O · THF (9.9 mg, 7.38 mmol) and powdered molecular sieves 4A (30.0 mg, dried in vacuo at 180 °C for 5 min prior to use) in CH$_2$Cl$_2$ (1.0 mL) was stirred at room temperature for 30 min. In another flask, a suspension of **4** (20.0 mg, 0.0369 mmol), methyl 2,3,4-tri-O-benzyl-glucopyranoside (22.2 mg, 0.0480 mmol), and powdered molecular sieves 4A (20.0 mg, dried in vacuo at 180 °C for 5 min prior to use) in CH$_2$Cl$_2$ (2.0 mL) was stirred at room temperature for 10 min. To the suspension of **2a** · 3H$_2$O · THF was transferred the suspension of **4** and methyl 2,3,4-tri-O-benzyl-glucopyranoside by a syringe, and the mixture was stirred at rt for 2.5 h. After aqueous solution of NaHCO$_3$ had been added, the mixture was filtered through a thin pad of Celite. The filtrate was extracted three times with ethyl acetate, and the combined organic layer was washed with brine and dried over MgSO$_4$. After evaporation, CH$_2$Cl$_2$ was added to the residue, and the mixture was filtered. After evaporation, the residue was purified by preparative TLC (silica gel, ethyl acetate/hexane (20%)) to give **5f** as colorless syrup (32.2 mg, 89%).

All the glycosylation products, glycosyl donors and acceptor **4** [18], **5a** [19], **5b** [18], **5c** [20], **5d** [21], **5e** [22], **5f** [23] and **5g** [24], were characterized spectroscopically by comparison of ^{1}H and ^{13}C NMR spectral data reported.

Acknowledgment

Appendix A. Supplementary material

CCDC 631296 contains the supplementary crystallographic data for **2a** · 3H$_2$O · THF. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.12.057.

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