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Synthesis and Structure of an Extremely Air-Stable Binuclear Hafnocene Perfluorooctanesulfonate Complex and Its Use in Lewis Acid-Catalyzed Reactions

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Abstract: An extremely air-stable μ^2-hydroxy-bridged binuclear hafonocene perfluorooctanesulfoante complex was successfully synthesized. This complex showed high catalytic efficiency in the esterification of alcohols, phenol, thiol, and amines, in the Friedel–Crafts acylation of alylaryl ethers, in the Mukaiyama aldol reaction, and in the allylation of aldehydes and could be reused.

Keywords: hafnocenes • homogeneous catalysis • Lewis acids • perfluorooctanesulfonate

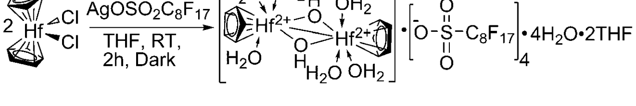
Introduction

Much attention has been paid to cationic hafnocene (Hf) compounds in recent years[1] due to their application in areas such as polymerization,[2] N_2 activation,[3] glycosylation,[4] and metal complexation.[5] The most interesting of these compounds is hafnocene dichloride ($[Cp_2HfCl_2]$; Cp = cyclopentadiene; **2**) and its derivatives because they are regarded as organometallic compounds that are somewhat stable and catalytically highly reactive. However, $[Cp_2HfCl_2]$ has seldom been used as a Lewis acid in organic synthesis on account of its weak acidity. To overcome this shortcoming, $AgClO_4$, a potentially explosive material, is added for glycosylation[4d] and a cocatalyst is needed for polymerization.[2a,b] In general, to enhance the activity, an organometallic Lewis acid should be as strongly acidic as possible. The dilemma is that with an increase in acidity, the compound becomes more susceptible to hydrolysis. For example, Angus-Dunne reported the incorporation of a triflate ion as the counteranion to $[Cp_2HfCl_2]$ for the generation of hafnocene bis(triflate) (**3**), which was employed in the polymerization of THF.[6] Unfortunately, the compound was extremely unstable in air due to facile hydrolysis. From the standpoint of the practical utilization of cationic hafnocene derivatives as catalysts, it is highly desirable to lower the hygroscopic character while improving the Lewis acidity of the substance.

Recently, Otera and co-workers postulated that the incorporation of long-chain perfluoroalkylsulfonate and perfluoroarylsulfonate groups to organometallic (i.e., Sn, Zr, and Ti) cations could result in an enhancement of acidity and stability.[7] These findings led us to envision that perfluorooctanesulfonate groups can help to overcome the hydrolytic instability of other cationic organometallic species. Herein, we report the synthesis and characterization of the air-stable cationic μ^2-hydroxy-bridged binuclear complex $[\{CpHf(OH_2)_3\}_2(\mu^2\text{-}OH)_2][OSO_2C_8F_{17}]_4{\cdot}x\,H_2O{\cdot}y\,THF$ (**1**$\cdot x\,H_2O\cdot y\,THF$) and an assessment of its Lewis acidity and catalytic activity.[8]

Results and Discussion

The synthesis of binuclear hafnocene perfluorooctanesulfonates (**1**$\cdot x\,H_2O\cdot y\,THF$) is shown in Scheme 1. The treatment



Scheme 1. Synthesis of **1**$\cdot 4\,H_2O\cdot 2\,THF$.

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of $[Cp_2HfCl_2]$ with silver perfluorooctanesulfonate ($AgOSO_2C_8F_{17}$; 2 equiv) in THF afforded the corresponding complexes as hydrates. The water molecules in the complex originated from air or the solvent, and the hydrate numbers x and solvating ligands THF y varied according to the reaction conditions. The results of ^1H NMR spectroscopic (in dry $[D_6]$acetone) and elemental analyses proved that in the freshly prepared sample after recrystallization x was approximately equal to four and y equal to two. After exposure to air for two days, the sample showed $y=0$ with the solvating ligand THF replaced by water molecules and the water content increased to $x=6$. When **1**$\cdot 4H_2O\cdot 2THF$ was kept for one week at room temperature under vacuum (created through pumping), there was partial dehydration of the sample ($x=0$) and removal of the solvating ligand THF ($y=0$). We found that **1**$\cdot 4H_2O\cdot 2THF$ remained as dry crystals or powder and suffered no color change over one year in air. Therefore, this complex can be considered to be extremely air stable at ambient environment and has a great advantage over hafnocene triflates from an operational point of view.

The cationic structure of **1**$\cdot 4H_2O\cdot 2THF$ in the solid state was confirmed by X-ray diffraction analysis. Single crystals of **1**$\cdot 4H_2O\cdot 2THF$ could be obtained by diffusion of hexane into a saturated solution of the complex in THF. An ORTEP plot of the structure of the cation, a ball-and-stick view of the crystal cell, and selected bonds and angles are shown in Figure 1. The data shows that the hafnium atoms have a distorted octahedral coordination with the Cp group *trans* to the OH unit, such as in the case of $[\{CpHf(OH_2)_3\}_2(\mu^2\text{-}OH)_2]^{4+}$.[9] The Hf–O lengths in **1**$\cdot 4H_2O\cdot 2THF$ are 2.086(4), 2.122(5), 2.151(4), 2.177(5), and 2.179(5) Å, respectively; the Hf–C(Cp) lengths range from 2.477(7) to 2.512(7) Å and the average length is 2.493 Å. The two Cp rings are parallel, the Hf-O1-HfA angle is 111.13(17)°, and the Hf···HfA distance is 3.4952 Å, thus suggesting that the Hf···HfA interaction is very weak. The $C_8F_{17}SO_3^-$ ions, the dissociated H_2O molecules, and solvating ligand THF are packed around the complex cation in such a way that the oxygen atoms of these species point towards the H_2O ligands. The C_8F_{17} side chains of the anions, on the other hand, are clustered together to form the hydrophobic domains.

The thermal behavior of complex **1** was investigated by thermogravimetric–differential scanning calorimetry (TG–DSC) in argon and oxygen (Figure 2). The TG–DSC curves show 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 300°C, after which two overlapping weight losses of an exothermic nature

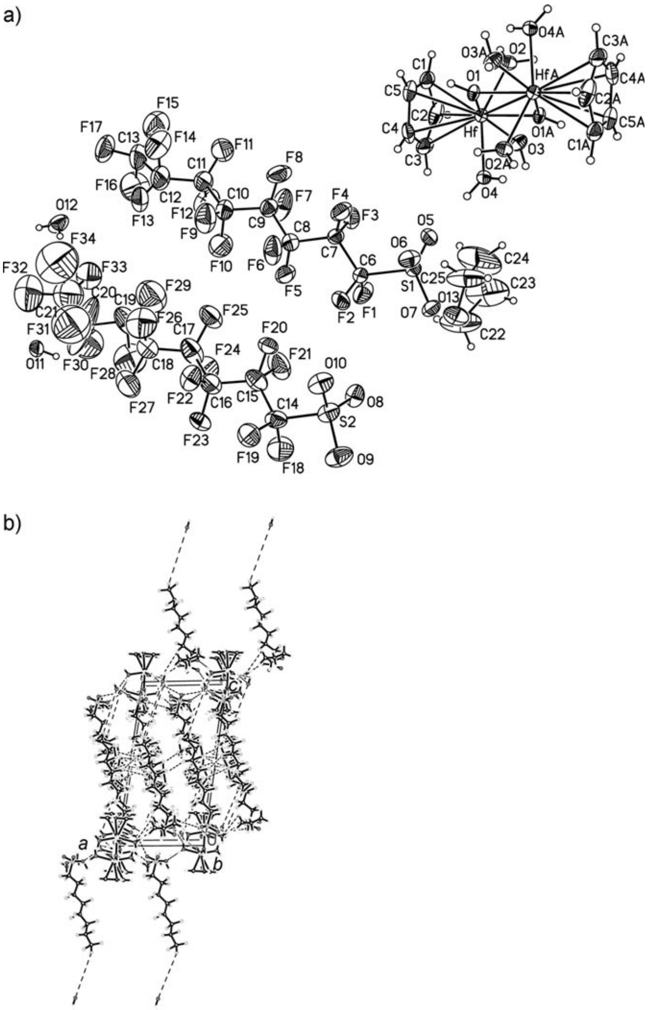


Figure 1. a) OTREP view of the novel cationic structure of $[\{CpHf(OH_2)_3\}_2(\mu^2\text{-}OH)_2]^{4+}$; b) and a ball-and-stick view of the crystal structure of $[\{CpHf(OH_2)_3\}_2(\mu^2\text{-}OH)_2][OSO_2C_8F_{17}]_4\cdot 4H_2O\cdot 2THF$ (**1**$\cdot 4H_2O\cdot 2THF$). The displacement of ellipsoids is drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Selected bonds [Å] and angles [°]: Hf–O1 2.086(4), Hf–O2 2.122(5), Hf–O1A 2.151(4), Hf–O4 2.177(5), Hf–O3 2.179(5), Hf–C4 2.477(7), Hf–C3 2.481(8), Hf–C2 2.496(8), Hf–C5 2.498(7), Hf–C1 2.512(7), Hf–HfA 3.4952(5); O1-Hf-O2 95.17(18), O1-Hf-O1A 68.87(17), O2-Hf-O1A 79.19(18), O1-Hf-O4 90.40(18), O2-Hf-O4 152.21(19), O1A-Hf-O4 77.51(17), O1-Hf-O3 149.61(18), O2-Hf-O3 82.3(2), O1A-Hf-O3 80.96(17), O4-Hf-O3 79.28 (19). The two Cp ring planes are parallel.

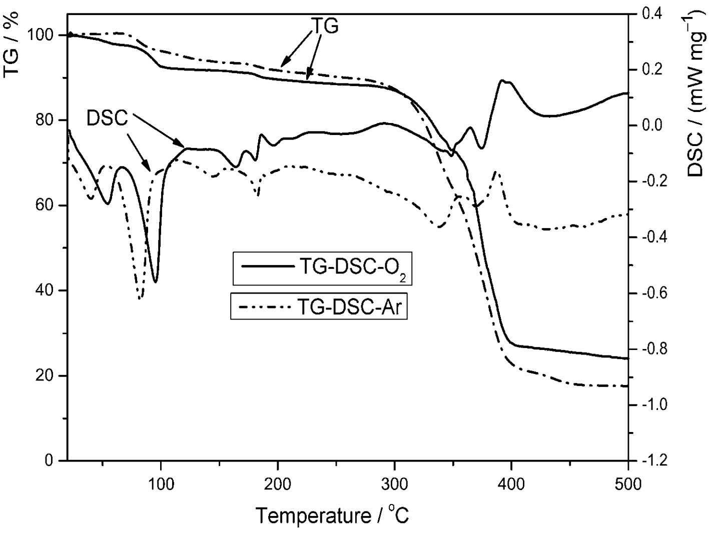


Figure 2. TG–DSC curves of complex **1**.

appear, plausibly due to the oxidation of organic entities. At 400°C, we observed the removal of pentafluorooctanesulfuryl ligands, thus leaving hafnium fluoride compounds. The results of the TG–DSC analysis are in agreement with those obtained from the ^1H and ^{19}F NMR spectroscopic investigations (see the Supporting Information). The empirical formula of this complex can be written as $\mathbf{1}\cdot 6\,H_2O$.

Based on the results from conductivity measurements (Table 1), $\mathbf{1}\cdot 4\,H_2O\cdot 2\,THF$ can be partially dissociated into ionic species in an anhydrous solution of CH_3CN and completely dissociated into ionic species in an aqueous solution of CH_3CN. The large molar conductivity value ($\Lambda = 327\ \mu S\,cm^{-1}mol^{-1}$; entry 4, Table 1) is consistent with the complete ionization of $\mathbf{1}\cdot 4\,H_2O\cdot 2\,THF$ into a 1:4 electrolyte.[10] Notably, the complex has relatively strong acidity with an acid strength of $3.3 < H_o \leq 4.8$ (H_o = Hammett acidity function).[11] In addition, this complex is highly soluble in methanol ($400\ g\,L^{-1}$; entry 1, Table 2) and in aqueous solutions of common polar organic solvents ($118–1793\ g\,L^{-1}$; entries 1–6, Table 2). The characterization of $\mathbf{1}\cdot 4\,H_2O\cdot 2\,THF$ stimulated us to evaluate its performance as a Lewis acid catalyst for reactions such as the esterification of alcohols, phenols, thiols, and amines; Friedel–Crafts acylation of alkylaryl ethers; the Mukaiyama aldol reaction; and the allylation of aldehydes.

Table 1. Conductivity of hafnocene perfluorooctanesulfonate ($\mathbf{1}\cdot 4\,H_2O\cdot 2\,THF$).[a]

Entry	V_{CH_3CN}/V_{H_2O}	Conductivity [$\mu S\,cm^{-1}$][b]	Entry	V_{CH_3CN}/V_{H_2O}	Conductivity [$\mu S\,cm^{-1}$][b]
1	5:0	55.6 (55.6)[c]	4	2:3	327 (327)[d]
2	4:1	192.6 (192.6)[d]	5	1:4	186.0 (186.0)[c]
3	3:2	221 (221)[d]	6	0:5	13.78 (13.78)[e]

[a] The complex was freshly prepared and recrystallized from a mixture of water and CH_3CN ($0.5\ mmol\,L^{-1}$) at 15 °C, and then left under vacuum at room temperature for 2 h. [b] The value given in the parentheses is the molar conductivity Λ [$\mu S\,cm^{-1}\,mol^{-1}$]. [c] The sample was not dissolved completely. [d] The sample was dissolved completely. [e] The sample was not dissolved.

Table 2. Solubility of $\mathbf{1}\cdot 4\,H_2O\cdot 2\,THF$ in organic solvents at 25 °C [$g\,L^{-1}$].[a]

Entry	Solvent	Pure[b]	Mixture[c]	Entry	Solvent	Pure[b]	Mixture[c]
1	MeOH	400	1783	6	CH_3CN	11	972
2	EtOAc	68	169	7	CH_2Cl_2	0	0
3	acetone	33	1082	8	toluene[f]	0	0
4	THF	20	483	9	hexane[f]	0	0
5	Et_2O	23	118[e]	10			

[a] Complex $\mathbf{1}\cdot 4\,H_2O\cdot 2\,THF$ was freshly prepared, recrystallized, and left under vacuum at room temperature for 2 h. [b] Pure organic solvent. [c] $V_{organic\ solvent}/V_{water} = 4{:}1$. [d] $V_{organic\ solvent}/V_{water} = 95{:}5$. [e] $V_{organic\ solvent}/V_{water} = 97{:}3$. [f] The organic solvent and water did not mix with each other.

The acetylation of alcohols, phenols, thiols, and amines has been one of the most frequently used strategies in organic synthesis and extensively investigated by organic chemists for nearly 100 years.[12] This reaction provides an efficient and inexpensive means for protecting hydroxy and amino groups in a multistep synthetic process. A number of Lewis acids, such as $Sc(OTf)_3$, trimethylsulfonate triflate (TMSOTf), and $Bi(OTf)_3$, are known to catalyze the acetylation of alcohols with acetic anhydride.[13] Unfortunately, most of the methods have one or more disadvantages, including low yield, poor chemoselectivity, functional intolerance, being environmental unfriendly, the need for organic solvents as reaction media, and the need for strictly anhydrous reaction conditions. Most of the catalysts are unrecoverable, air or moisture sensitive, and too low or too large in Lewis acidity.

The esterification reaction was investigated with structurally diverse alcohols, phenols, thiols, and amines with 1.2 equivalents of acetic anhydride in the presence of 1.0 mol % of $\mathbf{1}\cdot 4\,H_2O\cdot 2\,THF$ at room temperature under solvent-free conditions (Table 3). We observed that fast and effective acetylation occurred not only for alcohols (94–99 % yield; entries 1–4, Table 3) but also for amines (97–99 % yield; entries 10 and 11, Table 3). Phenol (94 % yield; entry 5, Table 3) and thiol (96 % yield; entry 9, Table 3) were also acetylated efficiently. Furthermore, in the cases of furan, methanol, and geraniol with a carbon–carbon double bond, $\mathbf{1}\cdot 4\,H_2O\cdot 2\,THF$ was found to be functionally tolerated (98–99 % yield; entries 6 and 7, Table 3). High chemoselectivities were achieved, and tertiary alcohols, such as triphenyl methanol, were almost unaffected; only trace amounts of the desired ester were detected.

Table 3. Yields from the nucleophilic substitution reactions of acetic anhydride with alcohols catalyzed by $\mathbf{1}\cdot 4\,H_2O\cdot 2\,THF$.[a]

$$\underset{\mathbf{4a\text{-}4k}}{ROH} + Ac_2O \xrightarrow[\text{RT, 5 mins to 12 h}]{1\cdot 4H_2O\cdot 2THF,\ 1-5\ mol\%} \underset{\mathbf{5a\text{-}5k}}{ROAc}$$

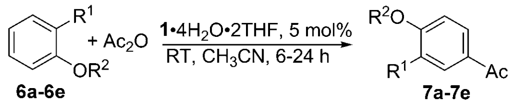
Entry	ROH		Time [min]	Product	Yield [%]
1	$PhCH_2OH$	(**4a**)	5	**5a**	99
2	$PhCH_2CH_2CH_2OH$	(**4b**)	30	**5b**	99
3	$PhCH(OH)CH_2CH_3$	(**4c**)	30	**5c**	97
4	$C_8H_{17}OH$	(**4d**)	5	**5d**	99
5[b]	PhOH	(**4e**)	120	**5e**	94
6	furanmethanol	(**4f**)	5	**5f**	98
7	geraniol	(**4g**)	5	**5g**	99
8[b]	Ph_3COH	(**4h**)	720	**5h**	<1
9[b]	PhSH	(**4i**)	300	**5i**	96
10	$PhNH_2$	(**4j**)	5	**5j**	99
11[b]	Ph_2NH	(**4k**)	60	**5k**	97

[a] Substrates: **4**, 1.0 mmol; Ac_2O, 1.2 mmol; catalyst: 0.01 mmol; room temperature; yields are given for the isolated products. [b] Catalyst: 0.05 mmol.

The Friedel–Crafts acylation of aromatic compounds is one of the most important reactions in organic chemistry.[14] Traditionally, $AlCl_3$ is used as a Lewis acid promoter, and a stoichiometric amount of $AlCl_3$ is needed due to the formation of stable adduct compounds that result from the interaction between the catalyst and the carbonyl oxygen atom of the ketone product. The compound $Sc(OTf)_3$ was applied in this reaction and a good result was obtained;[14b] however, the high price of $Sc(OTf)_3$ limited its utilization. Combinations of $Hf(OTf)_4/LiClO_4$ and $NbCl_5/AgClO_4$ were also reported as Friedel–Crafts acylation catalysts.[14c,d] However, larger equivalents of potentially explosive perchloride salts have to be used as cocatalysts. Furthermore, most of these Lewis acids are air and/or moisture sensitive.

We assessed **1**·4H_2O·2THF (5.0 mol%) as a catalyst for the Friedel–Crafts acylation of structurally diverse alkyl aryl ethers with 2.0 equivalents of acetic anhydride at room temperature in CH_3CN and good-to-excellent yields were obtained (81–87%; entries 1–5, Table 4). The electron-donating groups attached to the aromatic ring enhanced the reaction activity (85–87%; entries 4 and 5, Table 4). As expected, this reaction showed high regioselectivity (*para*-regioisomer: >99%). In addition, the activity of $AlCl_3$ was markedly low under the present mild reaction conditions. No product was obtained in the absence of the catalyst. Thus, complex **1** can be considered to be an excellent catalyst in terms of yield and *para*-regioselectivity in the Friedel–Crafts acylation.

Table 4. Yield from the Friedel–Crafts acylation of alkyl aryl ethers catalyzed by **1**·4H_2O·2THF.[a]



Entry	R^1	R^2		Time [h]	Product	Yield [%]
1	H	CH_3	(**6a**)	8	**7a**	81
2		*n*-C_4H_9	(**6b**)	12	**7b**	83
3		benzyl	(**6c**)	24	**7c**	84
4	CH_3	CH_3	(**6d**)	6	**7d**	85
5		*n*-C_4H_9	(**6e**)	10	**7e**	87

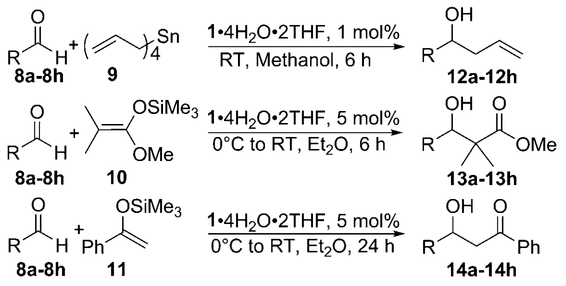
[a] Substrates: **6**, 1.0 mmol; Ac_2O, 2.0 mmol; catalyst: 0.05 mmol; solvent: CH_3CN, 2.0 mL; room temperature; yields are given for the isolated *para*-substituted product.

The allylation of aldehydes and the Mukaiyama aldol reaction mediated by a Lewis acid are one of the most convenient processes for the formation of carbon–carbon bonds in organic synthesis.[15] The addition reactions are intrinsically efficient in the production of useful building blocks, such as homoallylic alcohols[16] and β-hydroxy ketone or β-hydroxy ester derivatives,[17] because new stereogenic centers and new carbon–carbon bonds can be formed in a single operation. Several efficient Lewis acid catalysts based on boron, titanium, zirconium, copper, and so forth have been reported.[17b,18] In most cases, temperatures of −20 to −78 °C and strictly anhydrous conditions are required. In the present investigation, we address these problems by preparing the extremely air-stable hafnocene perfluorooctanesulfonate catalyst **1**·4H_2O·2THF and report the highly efficient catalytic activity of the catalyst in Mukaiyama aldol reactions and the allylation of aldehydes.

The reactions of aldehydes **8a**–**h** with nucleophiles, such as tetraallyltin (**9**), ketene silyl acetals **10**, and enol silyl ethers **11** were examined over **1**·4H_2O·2THF (Table 5). As expected, the reactions resulted in good yields of homoallyl alcohols **12a**–**h**, β-hydroxy esters **13a**–**h**, and β-hydroxy ketones **14a**–**h** (89–95, 75–94, and 65–90%, respectively) in methanol or diethyl ether. A similar tendency in the catalytic activity of complex **1** was observed when aliphatic aldehydes and aromatic aldehydes with electron-donating or -withdrawing groups were investigated.

Because of the high tolerance of **1**·4H_2O·2THF towards hydrolysis, the solvents adopted in these reactions were used as received and not subjected to any kind of drying procedure. Usually a highly reactive reagent would cause poor chemoselectivity. For example, Grignard, lithium, and titanium reagents often fail to discriminate between aldehydes and ketones. Over **1**·4H_2O·2THF, however, we observed good chemoselectivity. Ketones were less reactive: the addition reaction of acetophenone (**8i**) with nucleophiles **9**–**11** did not occur at room temperature, but the corresponding homoallyl alcohol **12i** was obtained in 85% yield at 65 °C over 24 h in the presence of **1**·4H_2O·2THF.

Table 5. Product yield for the reactions of aldehydes **8a**–**h** with nucleophiles **9**–**11** catalyzed by **1**·4H_2O·2THF.



Entry	RCHO	Yield [%]					
		12[a]		**13**[b]		**14**[c]	
1	PhCHO (**8a**)	**12a**	92	**13a**	89	**14a**	78
2	*p*-MeC_6H_4CHO (**8b**)	**12b**	91	**13b**	87	**14b**	75
3	*p*-$MeOC_6H_4CHO$ (**8c**)	**12c**	89	**13c**	86	**14c**	69
4	*p*-ClC_6H_4CHO (**8d**)	**12d**	93	**13d**	92	**14d**	83
5	*p*-$CF_3C_6H_4CHO$ (**8e**)	**12e**	95	**13e**	94	**14e**	90
6	$PhCH{=}CHCHO$ (**8f**)	**12f**	92	**13f**	85	**14f**	80
7	$PhCH_2CH_2CHO$ (**8g**)	**12g**	94	**13g**	81	**14g**	68
8	$C_7H_{15}CHO$ (**8h**)	**12h**	90	**13h**	75	**14h**	65

[a] Substrates: **8**, 1.0 mmol; **9**, 0.3 mmol; catalyst: 0.01 mmol; solvent: CH_3OH, 3.0 mL; RT, 6 h; yields are given for the isolated products. [b] Substrates: **8**, 1.0 mmol; **10**, 1.2 mmol; catalyst: 0.05 mmol; solvent: Et_2O, 3.0 mL; 0°C→RT, 6 h; yields are given for the isolated products. [c] Substrates: **8**, 1.0 mmol; **11**, 1.5 mmol; catalyst: 0.05 mmol; solvent: Et_2O, 3.0 mL; 0°C→RT, 24 h; yields are given for the isolated products.

To show the advantages of hafnocene perfluorooctanesulfonate (**1**·4H_2O·2THF) over [Cp_2HfCl_2] (**2**) and [$Cp_2Hf(OSO_2CF_3)_2$] (**3**), the catalytic activities of **1**·4H_2O·2THF and **2** and **3**, as control cationic species, were assessed in the acetylation of 2-phenylethanol and anisole and in the allylation and Mukaiyama aldol reactions of benzaldehyde (see Table 6 for the yields). High yields were constantly attained over **1**·4H_2O·2THF (up to 99%), whereas the other catalysts resulted in much lower yields (down to 13%), plausibly due to their lower Lewis acidity and/or greater air and moisture sensitivity. However, CF_3SO_3H, considered to be a powerful catalyst by Hollis and Bosnich, can be formed through the facile hydrolysis of **3**,[19] and an enhancement of catalytic activity results. It is worth pointing out that only a 35% yield of homoallyl alcohol **12a** and no desired aldoate products **13a** and **14a** were obtained in the absence of a catalyst under similar conditions, thus explicitly indicating the effectiveness of the catalysts. With regards to metal sulfonate catalysis, it must be taken into account that a sulfonic acid that arises in situ during the reaction may possibly work as an active species.[20] Thus, the reaction of **8a** with **9**, **10**, or **11** could be conducted in the presence of $C_8F_{17}SO_3H$ (5 mol%). The reaction was rather complex because many spots were detected in TLC analysis and only 17–19% yield of the desired products was reported.[7c]

Table 6. Yield [%] for the reactions of carbonyl compounds with nucleophiles catalyzed by **1**·4H_2O·2THF, **2**, and **3**.

Entry	RC(O)R′	Nu-R″	Product	Catalyst		
				(**1**)[f]	**2**	**3**
1[a]	Ac_2O	**4a**	**5a**	99	25	99
2[b]	Ac_2O	**6a**	**7a**	81	14	71[g]
3[c]	**8a**	**9**	**12a**	92	39	90
4[d]	**8a**	**10**	**13a**	89	25	75
5[e]	**8a**	**11**	**14a**	78	13	53

[a] Substrates: **4a**, 1.0 mmol; Ac_2O, 1.2 mmol; catalyst: 0.01 mmol; RT, 5 min; yields are given for the isolated products. [b] Substrates: **6a**, 1.0 mmol; solvent: Ac_2O, 2.0 mmol; catalyst: 0.05 mmol; solvent: CH_3CN, 2 mL; RT, 8 h; yields are given for the isolated *para*-substitute products. [c] Substrates: **8a**, 1.0 mmol; **9**, 0.3 mmol; catalyst: 0.01 mmol; solvent: CH_3OH, 3.0 mL; RT, 6 h; yields are given for the isolated products. [d] Substrates: **8a**, 1.0 mmol; **10**, 1.2 mmol; catalyst: 0.05 mmol; Et_2O, 3.0 mL; 0°C→RT, 6 h; yields are given for the isolated products. [e] Substrates: **8a**, 1.0 mmol; **11**, 1.5 mmol; catalyst: 0.05 mmol; solvent: Et_2O, 3.0 mL; 0°C→RT, 24 h; yields are given for the isolated products. [f] (**1**) = **1**·4H_2O·2THF. [g] Mixture of *ortho*- and *para*-isomer products.

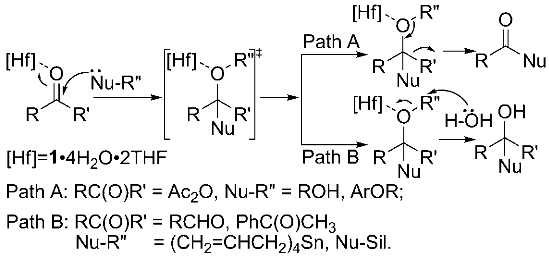
To test the reusability of the catalyst and reproducibility of the catalytic performance, **1**·4H_2O·2THF was subjected to cycles of addition reactions of benzaldehyde with nucleophiles **9**–**11**, respectively (Table 7). It was detected that the change in product yield (i.e., **12a**: 91–93%; **13a**: 86–89%; **14a**: 74–78%) was minimal in a trial of five cycles, thus indicating that the catalyst is stable and suitable for reuse. Therefore, **1**·4H_2O·2THF has the advantage of being high in activity, selectivity, stability, and reusability.

Table 7. Yields for the nucleophilic addition of benzaldehyde **8a** with nucleophiles **9**–**11**[a] catalyzed by recovered catalyst **1**·4H_2O·2THF.

Cycle number	Yield [%][b]	Catalyst [%][c]	Yield [%][b]	Catalyst [%][c]	Yield [%][b	Catalyst [%][c]
	8a+**9**→**12a**		**8a**+**10**→**13a**		**8a**+**11**→**14a**	
1	92	99	89	99	78	99
2	93	99	88	98	77	97
3	91	98	87	99	76	97
4	90	97	88	97	74	95
5	91	97	86	98	76	97

[a] Substrates: **8a**, 10 mmol; **9**, 0.3 equiv (or **10**, 1.2 equiv or **11**, 1.5 equiv); catalyst loading: 0.05 equiv; RT. [b] Yield of the desired isolated product. [c] Yield of the recovered isolated catalyst.

According to the findings reported so far, the mechanism of the nucleophilic reaction of carbonyl compounds, such as acetic anhydride and aldehydes, over solid **1**·4H_2O·2THF in a solution of an organic solvent is postulated (Scheme 2). When solid **1**·4H_2O·2THF is added to the reaction solution, the hafnium cationic groups dissociate and hydration occurs immediately. At this stage, there are frequent intra- and intermolecular exchanges between water and the organic solvent. The carbonyl compound coordinates with the metal cations and is activated. Then nucleophiles such as alcohols and alkyl aryl ethers attack the activated carbonyl compounds (i.e., acetic anhydride) to produce the desired ester and *para*-alkoxylarylketone derivatives, whereas nucleophiles such as tetraallyltin (**9**), ketene silyl acetals **10**, and enol silyl ethers **11** attack the activated carbonyl compounds (aldehydes or ketones) to produce the corresponding homoallyl alcohols and β-hydroxy ester or β-hydroxy ketone derivatives. The catalyst **1**·4H_2O·2THF is renewed with the intake of one molecule of water or solvating ligand. At the present stage of investigation, we are still not sure of the transient intermediates that are possibly formed during the reaction. Further work is still being conducted to understand this aspect.



Scheme 2. A proposed mechanism of reaction of carbonyl compounds with various nucleophiles catalyzed by **1**·4H_2O·2THF.

Conclusions

In summary, we have successfully synthesized and characterized a cationic μ^2-hydroxy-bridged binuclear hafnocene perfluorooctanesulfonate complex. This Lewis acid is strongly acidic and is extremely air stable. It shows high catalytic activity in the esterification of alcohols, phenol, thiol, and amines; the Friedel–Crafts acylation of alkylaryl ethers; the Mukaiyama aldol reaction; and the allylation of aldehydes and could be reused. On account of its stability and storability, the compound should find broad catalytic applications in organic synthesis.

Experimental Section

General: The chemicals used were purchased from Aldrich. Co. Ltd and other chemical companies and were used as received unless otherwise specified. The preparation of the catalyst was carried out in a nitrogen atmosphere with freshly distilled solvents unless otherwise noted. THF was distilled from sodium/benzophenone and CH_3CN was distilled from CaH_2. Acetone was heated to reflux with $KMnO_4$ for 4 h, distilled, dried with K_2CO_3, distilled, and kept inside a dry box. The catalytic reactions were carried out in air, and the solvents are used as received. The NMR spectra were recorded at 25 °C on INOVA-400M (USA) calibrated with tetramethylsilane (TMS) as an internal reference. Elemental analyses were performed over VARIO EL III (Germany). Conductivity was measured on a REX conductivity meter DDS-307 (China). The IR spectra were recorded on a NICOLET 6700 FTR spectrophotometer (Thermo Electron Corporation). The TG–DSC analysis was performed on a NETZSCH-STA-449C machine (operating conditions: O_2 or Ar atmosphere; heating rate: 5 °C min^{-1}). X-ray single-crystal diffraction analysis was performed on SMART-APEX equipment at the Shanghai Institute of Organic Chemistry (China Academy of Science). The acidity of the catalyst was measured by using the Hammett indicator method. The indicators employed included crystal violet, dimethyl yellow, and methyl red ($pK_a = 0.8$, 3.3, and 4.8, respectively), as described previously.[11] The strength of the acid was expressed by the Hammett acidity function (H_0), which was scaled by the pK_a value of the indicators. The hydrate molecular structure and solubility were determined according to previous reports.[7b]

Preparation of 1·4H$_2$O·2THF: A solution of $AgOSO_2C_8F_{17}$[7b] (1.214 g, 2.0 mmol) in THF (10 mL) was added to a solution of $[Cp_2HfCl_2]$ (0.379 g, 1.0 mmol) in THF (20 mL). After the mixture was stirred at 25 °C for 2 h in the absence of light, it was filtered. The filtrate was placed in a small jar, which was put into a larger jar containing dry hexane (40 mL). The larger jar was sealed and refrigerated for 24 h. Colorless crystals of complex **1**·$4H_2O$·2THF were obtained (1.222 g, 86 % yield of the isolated product). Recrystallization of this complex in THF/hexane produced good crystals suitable for X-ray analysis. Moreover, the treatment of **1**·$4H_2O$·2THF under vacuum for 1 week and exposure to air for 2 days yielded complexes **1** and **1**·$6H_2O$, respectively. **1**·$4H_2O$·2THF: ^1H NMR (400 MHz, [D$_6$]acetone, 25°C, TMS): $\delta = 6.81$ (s, 3H; Cp), 6.62 (s, 1H; Cp), 6.55 (s, 1H; Cp), 3.61 to 3.64 (m, 4H; THF), 3.39 (s, 10H; H_2O), 1.78–1.85 ppm (m, 4H; THF); ^{19}F NMR (376 MHz, [D$_6$]acetone, 25°C): $\delta = -121.12$ to -121.21 (m, 2F; -CF_2-), -117.69 (s, 2F; -CF_2-), -116.54 to -116.85 (d, 6F; -$(CF_2)_3$-), -115.46 (s, 2F; -CF_2-), -109.40 (s, 2F; -CF_2-), -76.07 to -76.12 ppm (m, 3F; CF_3-); IR (KBr): $\tilde{\nu} = 3566$, 3520, 3450, 3402, 3388, 2362, 1647, 1370, 1251, 1150, 107, 1040, 942, 846, 659, 625, 530, 477, 428 cm^{-1}; elemental analysis calcd (%) for $C_{50}H_{48}F_{68}Hf_2O_{26}S_4$: C 21.13, H 1.70; found: C 21.19, H 1.72. Complex **1**: ^1H NMR (400 MHz, [D$_6$]acetone, 25°C, TMS): $\delta = 6.80$ (s, 3H; Cp), 6.61 (s, 1H; Cp), 6.55 (s, 1H; Cp), 3.42 ppm (s, 6H; H_2O); elemental analysis calcd (%) for $C_{42}H_{24}F_{68}Hf_2O_{20}S_4$: C 19.21, H 0.92; found: C 19.25, H 0.92. Complex **1**·$6H_2O$: ^1H NMR (400 MHz, [D$_6$]acetone, 25°C, TMS): $\delta = 6.81$ (s, 3H; Cp), 6.62 (s, 1H; Cp), 6.55 (s, 1H; Cp), 3.42 ppm (s, 12H; H_2O); elemental analysis calcd (%) for $C_{42}H_{36}F_{68}Hf_2O_{26}S_4$: C 18.45, H 1.33; found: C 18.48, H 1.33. Crystal data for **1**·$4H_2O$·2THF: $C_{25}H_{24}F_{34}HfO_{13}S_2$; $M_r = 1421.05$; triclinic; space group: P-1; $a = 10.4394(10)$, $b = 11.0730(10)$, $c = 20.2914$ (19) Å; $\alpha = 97.945(2)$, $\beta = 98.005(2)$, $\gamma = 97.246(2)°$; $V = 2275.0(4)$ Å^3; $T = 293(2)$ K; $Z = 2$; $D_{calcd} = 2.074$ Mg m^{-3}; reflections collected/unique, 12065/8352, $R_{int} = 0.05791$; final R indices [$I > 2\sigma(I)$], $R1 = 0.0463$, $wR2 = 0.1164$; R indices (all data), $R1 = 0.0521$, $wR2 = 0.1226$; GOF = 1.019. CCDC-660034 (**1**·$4H_2O$·2THF) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Typical procedure for the esterification of 2-phenylethanol (4a) with acetic anhydride catalyzed by 1·4H$_2$O·2THF: 2-Phenylethanol (**4a**; 122 mg, 1.0 mmol), acetic anhydride (122 mg, 1.2 mmol), and a catalytic amount of **1**·$4H_2O$·2THF (14 mg, 0.01 mmol, 1.0 mol % based on the alcohol) were added to a 50-mL round-bottomed flask. The reaction mixture was stirred at room temperature for 5 min and was monitored with TLC analysis until the alcohol was consumed completely. The residue was diluted with petroleum ether. The catalyst was precipitated and collected by filtration. The filtrate was evaporated under vacuum and the residue was subject to column chromatography on silica gel. A colorless liquid (**5a**) was obtained (160 mg, 99 % yield of the isolated product).

Typical procedure for the Friedel–Crafts acylation of anisole (6a) with acetic anhydride catalyzed by 1·4H$_2$O·2THF: Anisole (**6a**; 108 mg, 1.0 mmol), a solution of **1**·$4H_2O$·2THF (70 mg, 0.05 mmol) in CH_3CN (2.0 mL), and acetic anhydride (204 mg, 2.0 mmol) were added to a 50-mL round-bottomed flask by a syringe. The reaction mixture was stirred at room temperature for 8 h. The mixture was subjected to column chromatography on silica gel. The Friedel–Crafts acylation product (**7a**) was obtained (121 mg, 81 % yield of the isolated product).

Typical procedure for the allylation of benzaldehyde (8a) with tetraallyltin (9) catalyzed by 1·4H$_2$O·26THF: Complex **1**·$4H_2O$·2THF (70 mg, 0.05 mmol) was added to benzaldehyde (**8a**; 106 mg, 1.0 mmol) in methanol (3.0 mL). Tetraallyltin (**9**) (85 mg, 0.3 mmol) was added to the reaction mixture at room temperature and stirred for 6 h with monitoring by TLC analysis. The reaction mixture was evaporated in vacuum at room temperature and hexane (3×10 mL) was added to the residue. The catalyst precipitated and was recovered by filtration for the next reaction cycle. The combined hexane portions were concentrated, MeOH and HCl (aq) were added, and the resulting mixture stirred for 15 min. $NaHCO_3$ (aq) was added for neutralization and the mixture was evaporated. The as-obtained solids were dissolved in AcOEt and water, extracted with AcOEt (3×10 mL), and the organic layer was washed with NaCl(aq) and dried over $MgSO_4$. After evaporation, the yield was measured by GLC. Otherwise, the residue was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1). A colorless oil (**12a**) was obtained (136 mg, 92 % yield of isolated product).

Typical procedure for the Mukaiyama aldol reaction of benzaldehyde (8a) with ketene silyl acetal 10 catalyzed by 1·4H$_2$O·2THF: Complex **1**·$4H_2O$·2THF (70 mg, 0.05 mmol) and (1-methoxy-2-methylprop-1-enyloxy)trimethylsilane (**10**; 209 mg, 1.2 mmol) were added to benzaldehyde (**8a**; 106 mg, 1.0 mmol) in diethyl ether (3.0 mL) at 0 °C. The temperature of the reaction mixture was slowly raised to room temperature and stirred for 6 h with monitoring by TLC analysis. The reaction mixture was evaporated in vacuum at room temperature and the residue was dissolved in hexane (3×10 mL). The catalyst was collected by means of filtration for the next cycle of the reaction. MeOH and HCl (aq) were added to the combined hexane portions, and the mixture was stirred for 15 min. $NaHCO_3$ (aq) was added for neutralization and the reaction mixture was evaporated. The solids thus obtained were dissolved in AcOEt and water, extracted with AcOEt (3×10 mL), and the organic layer was washed with NaCl (aq) and dried over $MgSO_4$. After evaporation, the yield was measured by GLC. Otherwise, the residue was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). Colorless crystals (**13a**) were obtained (185 mg, 89 % yield of isolated product).

Typical procedure for the Mukaiyama aldol reaction of benzaldehyde (8a) with enol silyl ether 11 catalyzed by 1·4H$_2$O·2THF: Complex **1**·$4H_2O$·2THF (70 mg, 0.05 mmol) and (1-methoxy-2-methylprop-1-enyloxy)trimethylsilane (**11**; 230 mg, 1.2 mmol) were added to benzaldehyde (**8a**; 106 mg, 1.0 mmol) in diethyl ether (3.0 mL) at 0 °C. The temperature of the reaction mixture was raised slowly to room temperature and stirred for 24 h with monitoring by TLC analysis. The reaction mixture was evaporated in vacuum at room temperature and the residue was dissolved in hexane (3×10 mL). The catalyst was collected by filtration for the next cycle of the reaction. MeOH and HCl (aq) were added to the combined hexane portions and the reaction mixture was stirred for 15 min. $NaHCO_3$ (aq) was added for neutralization and the mixture was evaporated. The solids thus obtained were dissolved in AcOEt and water, extracted with AcOEt (3×10 mL), and the organic layer was washed with NaCl (aq) and dried over $MgSO_4$. After evaporation, the yield was measured by GLC. Otherwise, the residue was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1). Colorless crystals (**14a**) were obtained (176 mg, 78 % yield of isolated product).

The reagent alcohols, phenol, amines, alkylaryl ethers, aldehydes, and acetophenone (i.e., **4a–k**, **6a–e**, and **8a–i**) and the nucleophiles acetic anhydride and **9–11** are commercially available. All the products (i.e., **5a–k**, **7a–e**, **12a–i**, **13a–h**, and **14a–h**) have been reported. The experimental details are given in the Supporting Information, including the ^1H NMR spectral data of the products and the ^1H and ^{19}F NMR spectra of complex **1** (crystal sample after recrystallization and calcined sample after heating at 250 °C for 10 min in a nitrogen atmosphere).

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