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A Cationic Distannoxane Catalyst. Synthesis and Applications to Carbon−Carbon Bond Forming Reactions

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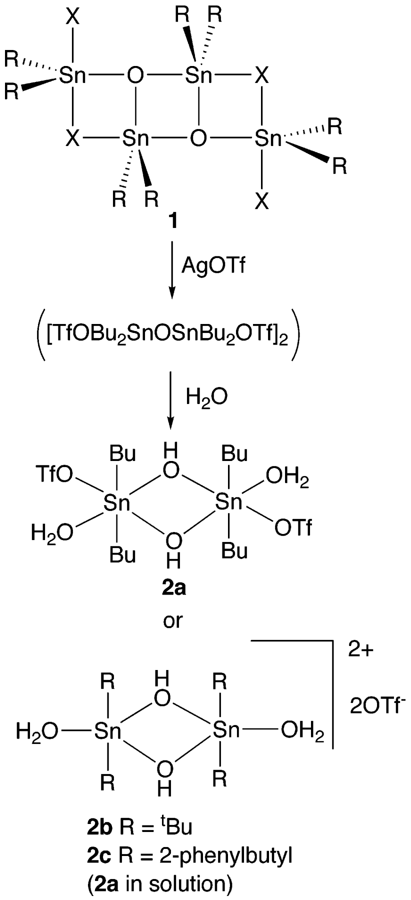
Summary: Incorporation of perfluorooctanesulfonate groups at 1,3-positions provides a cationic distannoxane which is acidic enough to catalyze efficient carbon−carbon bond forming reactions for the first time for this class of compounds.

1,3-Dihalotetraalkyldistannoxanes (**1**), having a unique ladder structure, are stable, easy-to-handle Lewis acids[1] and have been employed as catalysts for various functional group transformations such as (trans)esterification, acetalization, deacetalization, etc.[2] The mild acidity of these catalysts works favorably for giving rise to high chemoselectivity. On the other hand, the acidity is not strong enough to induce carbon−carbon bond forming reactions. Thus, for the purpose of expanding the scope of availability, it is of great significance to increase the acidity of these compounds. One such way to this end is to incorporate electron-withdrawing groups. Along this line, we attempted to replace 1,3-halogens with triflate groups. However, no desired product was obtained, but the skeleton was modified, leading to μ-hydroxo dimers **2** by spontaneous hydrolysis (Scheme 1).[3] In the solid state, both a neutral structure for **2a** and a dicationic structure for **2b** and **2c** were revealed by X-ray analysis, while **2a** was found to undergo dissociation into dicationic species in solution on the basis of conductivity. The resulting cationic organotin species seemed to us to be strongly acidic but was actually not so; for instance, acetylation was effected under mild conditions, whereas attempts for carbon−carbon bond forming reactions caused unsatisfactory outcomes (vide infra). Now, we have found that use of the perfluorooctanesulfonate (PFOS) group in place of the triflate group causes no change of the ladder framework to provide a novel cationic species which, for the first time for this class of compounds, allows carbon−carbon bond formation in a practical, acceptable manner upon treatment with various stannyl and silyl nucleophiles.

Scheme 1



Treatment of dimeric 1,3-dichlorotetrabutyldistannoxane (**1a**) with $C_8F_{17}SO_3Ag$ (4 equiv) in acetone furnished the corresponding perfluorooctanesulfonato derivative **1b** in a hydrated form, $[(PFOS)Bu_2SnOSnBu_2(PFOS)]_2 \cdot nH_2O$ (Scheme 2).[4] The hydration number was variable, depending on the conditions. ^{1}H NMR (in dry

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[1] $[ClBu_2SnOSnBu_2Cl]_2$ is commercially available from Aldrich Chemical Co. Inc.

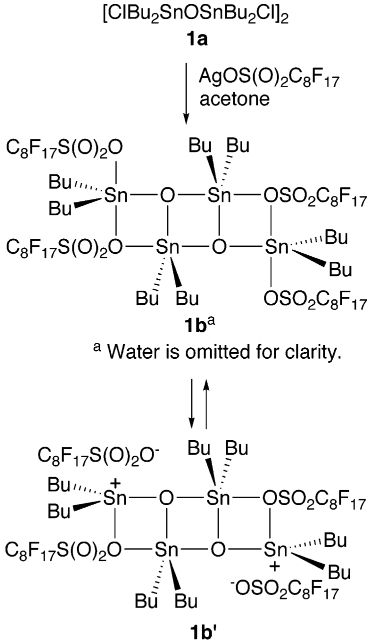
[2] (a) Otera, J. In *Advances in Detailed Reaction Mechanism*; Coxon, J. M., Ed., JAI Press: London, 1994; Vol. 3, p 167. (b) Otera, J. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: London, 1995; Vol. 2, p 1140. (c) Mascaretti, O. A.; Furlán, R. L. E. *Aldrichim. Acta* **1997**, *30*, 55. (d) Otera, J. *Acc. Chem. Res.* **2004**, *37*, 288.

[3] (a) Sakamoto, K.; Hamada, Y.; Akashi, H.; Orita, A.; Otera, J. *Organometallics* **1999**, *18*, 3555. (b) Sakamoto, K.; Ikeda, H.; Akashi, H.; Fukuyama, T.; Orita, A.; Otera, J. *Organometallics* **2000**, *19*, 3242.

[4] Synthesis of **1b**·nH$_2$O: to an acetone solution (10 mL) of **1a** (553 mg, 0.5 mmol as dimer) was added $AgOS(O)_2C_8F_{17}$ (1.214 g, 2.0 mmol). The mixture was stirred at room temperature for 3 h and filtered to remove AgCl. The filtrate was evaporated, and the residue was dissolved in acetone (2 mL). The solution was added dropwise to CH_2Cl_2 (50 mL), and the mixture was filtered. The solid obtained was recrystallized from 1/3 EtOAc/hexane to give **1b**·4H$_2$O (1.05 g, 71%): mp 108−111 °C; ^{1}H NMR (CD$_3$CN) δ 0.93 (t, 24H), 1.37−1.41 (m, 16H), 1.63−1.78 (m, 32H), 3.34 (br s, 8H); ^{19}F NMR (acetone-d_6) δ −79.2 (t, 12F), −112.2 (t, 8F), −118.6 (m, 8F), −119.7 to −120.0 (m, 24F), −120.9 (m, 8F), −124.3 to −124.4 (m, 8F); ^{119}Sn NMR (acetone-d_6) δ −162.5, −203.0. The tetrahydrate was pumped in vacuo at room temperature for 2 days to give the partially dehydrated product **1b**·0.5H$_2$O, which was subjected to elemental analysis. Anal. Calcd for $C_{64}H_{73}F_{68}O_{14.5}S_4Sn_4$: C, 25.89; H, 2.48. Found: C, 25.86; H, 2.46. The ^{1}H NMR spectrum exhibited a broad singlet at 4.68 ppm (1H) for the H$_2$O.

10.1021/om050212a CCC: $30.25

Scheme 2

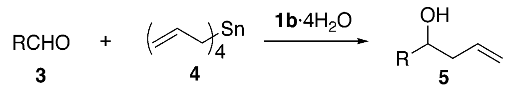


^{a} Water is omitted for clarity.

CD$_3$CN) proved the freshly prepared sample after recrystallization from EtOAc/hexane (1:3) to contain approximately one H$_2$O molecule per tin atom ($n = 4$), and the water content increased up to $n =$ ca. 6 (on the basis of ^{1}H NMR spectroscopy) upon standing in open air. On the other hand, pumping in vacuo for 2 days at room temperature caused dehydration, giving rise to $n =$ ca. 0.5. Elemental analysis of this sample was consistent with this composition. ^{119}Sn NMR of **1b** exhibited two signals at δ −162.5 and −203.0 ppm in acetone-d_6, diagnostic of the dimeric formulation.[5] However, ionic dissociation in solution was shown by conductivity measurements. The conductivity of **1b**·4H$_2$O (149.5 μS cm^{-1} in CH$_3$CN (0.5 mmol/L) at 25 °C; molar conductivity (Λ) = Λ ($^1/_4$[(PFOS)Bu$_2$SnOSnBu$_2$(PFOS)]$_2$) 74.8 μS cm^{-1} mol^{-1}) is nearly on a level with that of dicationic **2a** (165.5 μS cm^{-1} in CH$_3$CN (1 mmol/L) at 25 °C; molar conductivity (Λ) = Λ ($^1/_2$[Bu$_2$Sn(OTf)(OH)·H$_2$O]$_2$) 82.8 μS cm^{-1} mol^{-1}), yet a somewhat lower Λ value of **1b** suggests incomplete, partial dissociation into ionic species such as **1b′** in solution.[6] It should be pointed out, however, that formation of a dicationic μ-hydroxo structure such as **2b** or **2c** is not plausible, because it should give rise to a single peak in ^{119}Sn NMR due to the symmetrical structure.

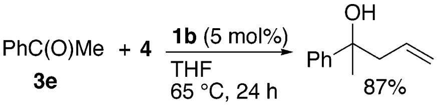
Notably, despite the hydration and ionic dissociation in solution, solid **1b** is stable enough to be stored in open air for months and is highly soluble in common organic solvents. These characteristic features together with increased acidity encouraged us to conduct carbon−carbon bond forming reactions. First, reaction of benzaldehyde (**3a**) with tetraallyltin (**4**) was screened in various solvents (Table 1, entries 1−5). The aldehyde was exposed to **4** in the presence of a catalytic amount of **1b**·4H$_2$O in a solvent. The reaction occurred smoothly in THF, CH$_2$Cl$_2$, and CH$_3$CN and rather sluggishly in diethyl ether and hexane. The catalyst is highly active, and the catalyst concentration can be reduced to 0.05 mol %. Remarkably, the solvents in these reactions were used as received. No dry solvents are needed, because of the tolerance of **1b** toward hydrolysis.[7] Note that only a 17% yield was obtained in the absence of the catalyst under otherwise the same conditions, an explicit indication of the effectiveness of the catalyst. The reaction gave good yields of homoallyl alcohols **5** in THF with aromatic aldehydes with electron-donating and -withdrawing groups together with an aliphatic aldehyde (entries 6−8). Ketones are less reactive: no reaction occurred at room temperature with acetophenone (**3e**), but the corresponding homoallyl alcohol was obtained in 87% yield at 65 °C with 5 mol % catalyst concentration (eq 1). On the other hand, no reaction occurred with acetals and cyclohexenone.

Table 1. Allylation of Aldehydes with Tetraallyltin (4) Catalyzed by 1b^a



entry	**3**	solvent^b	**1b**·4H$_2$O/ mol %^{c}	reacn time/h	yield of **5**/%^{d}
1	PhCHO (**3a**)	THF	0.05	12	98
2	**3a**	CH$_2$Cl$_2$	0.5	12	97
4	**3a**	Et$_2$O	0.25	6	34
5	**3a**	hexane	0.25	6	26
6	p-CH$_3$C$_6$H$_4$CHO (**3b**)	THF	0.05	12	97
7	p-CF$_3$C$_6$H$_4$CHO (**3c**)	THF	0.025	12	92
8	C$_5$H$_{11}$CHO (**3d**)	THF	0.025	12	73

^{a} Reaction conditions: **3** (1 mmol); **4** (0.3 mmol); solvent (3 mL); room temperature. ^{b} Solvents were used as received. ^{c} Concentration based on the dimeric formulation. ^{d} Determined by GLC.



(1)

Mukaiyama aldol and Michael reactions are also catalyzed by **1b**.[8] The enol silyl ether **6** reacted with aldehydes smoothly to give aldol products **7a** (Table 2, entries 1−3). THF, which is a somewhat better solvent than other solvents such as CH$_2$Cl$_2$ and CH$_3$CN, could be used as received directly from the bottle. In contrast to **4**, no reaction took place between **6** and ketone, but acetals and ketal **8** underwent facile reaction (entries 4−6). In these reactions, CH$_3$CN was found to be the best solvent.

Ketene silyl acetals **9** reacted with aldehydes similarly to afford **10** (Table 3). Because of their higher reactivity, reaction with aldehydes took place with a smaller amount of catalyst and even ketone **3e** was employable. Acetals also underwent smooth reaction.

Upon exposure of both **6** and **9** to cyclohexenone (**11**) under analogous conditions, Michael addition products

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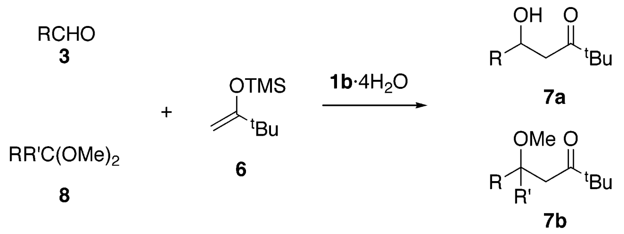
[5] (a) Otera, J.; Yano, T.; Nakashima, K.; Okwara, R. *Chem. Lett.* **1984**, 2109. (b) Yano, T.; Nakashima, K.; Otera, J.; Okawara, R. *Organometallics* **1985**, *4*, 1501.

[6] It is not likely that all PFOS ligands are dissociated to give highly positive species, and thus the structure **1b′** represents merely one possible ionic species. It is not clear at the moment which structure, covalent or ionic, prevails in the solid state.

[7] The same reaction catalyzed by HCl in H$_2$O/THF: (a) Yanagisawa, A.; Inoue, H.; Morodome, M.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 10356. (b) Yanagisawa, A.; Morodome, M.; Nakashima, H.; Yamamoto, H. *Synlett* **1997**, 1309.

[8] For relevant reactions in water, see:P (a) Kobayashi, S.; Manabe, K. *Acc. Chem. Res.* **2002**, *35*, 209. (b) Manabe, K.; Kobayashi, S. *Chem. Eur. J.* **2002**, 8, 4095 and references therein.

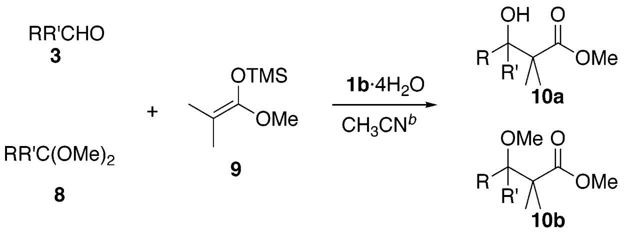
Table 2. Mukaiyama Aldol Reaction with Enol Silyl Ether 6 Catalyzed by 1b[a]



entry	3 or 8	solvent[b]	$\mathbf{1b}\cdot 4H_2O$/mol %[c]	reacn time/h	yield of **5**/%[d]
1	**3a**	THF	2.5	6	85
2	**3b**	THF	2.5	6	80
3	**3c**	THF	2.5	5	87
4	$PhCH(OMe)_2$ (**8a**)	CH_3CN	0.05	3	93
5	$C_7H_{15}CH(OMe)_2$ (**8b**)	CH_3CN	0.05	3	89
6	**8c**[e]	CH_3CN	0.05	3	81

[a] Reaction conditions: **3** or **8** (1 mmol); **6** (1.3 mmol); solvent (3 mL); room temperature. [b] Solvents were used as received. [c] Concentration based on the dimeric formulation. [d] Isolated yield after column chromatography. [e] Cyclohexanone dimethyl acetal.

Table 3. Mukaiyama Aldol Reaction with Ketene Silyl Acetals 9 Catalyzed by 1b[a]



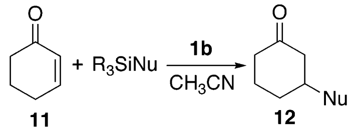
entry	3 or 8	$\mathbf{1b}\cdot 4H_2O$/mol %[c]	reacn time/h	yield of **10**/%[d]
1	**3a**	0.5	3	>99[e]
2	**3b**	0.5	3	>99[e]
3	**3e**	1.0	10	90
4	**8a**	1.0	8	93
5	**8b**	1.0	8	86

[a] Reaction conditions: **3** or **8** (1 mmol); **9** (1.3 mmol); CH_3CN (3 mL); room temperature. [b] CH_3CN was used as received. [c] Concentration based on the dimeric formulation. [d] Isolated yield after column chromatography. [e] Detemined by ^1H NMR.

(**12**) were exclusively obtained without formation of 1,2-addition products (Scheme 3).

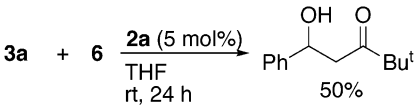
With regard to metal sulfonate catalysis, it must be taken into account that a sulfonic acid arising in situ during the reaction may possibly work as an active species.[9] Thus, the reaction between **3a** and **6** (the same as Table 2, entry 1) was conducted in the presence of $C_8F_{17}SO_3H$[10] (5 mol %). The reaction was not clean, because many spots appeared on TLC, and only a 17% yield of the aldolate was obtained. Apparently, **1b** is responsible for the smooth reactions shown above.

Scheme 3



R_3SiNu = **6**; $\mathbf{1b}\cdot 4H_2O$ (5 mol%); THF; rt; 12 h: yield 86%
R_3SiNu = **9**; $\mathbf{1b}\cdot 4H_2O$ (1 mol%); CH_3CN; rt; 6 h: yield 95%

Previously, we reported that dibutyltin bis(triflate) (**13**) is so mild that aldehydes, ketones, and their acetals could be discriminated in Mukaiyama aldol reactions.[11] In this respect, **1b** is somewhat too acidic to allow such subtle discrimination. However, in contrast to hygroscopic **13**, it is a great convenience that **1b** is stable in open air. The effectiveness of the cationic distannoxane is highlighted by comparison with μ-hydroxo cationic species. The Mukaiyama aldol reaction between **3a** and **6** in the presence of 5 mol % of **2a** furnished only the aldol product in 50% yield even after 24 h under similar conditions (eq 2). Obviously, the distannoxane is more active than the μ-hydroxo species, even though both are cationic. Since **1b** is weaker in cationic character than **2a** due to a smaller degree of dissociation on the basis of conductivity, the ladder skeleton probably plays an important role in the high catalytic activity.[2]



(2)

In summary, incorporation of perfluorooctanesulfonate groups at 1,3-positions provides a cationic distannoxane which enables the formation of a variety of carbon–carbon bonds with stannyl and silyl nucleophiles. The reaction requires no purification of solvents. On account of its stability as well as storability, **1b** should find a broad range of utility.

OM050212A

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[9] It was suggested that in some metal triflate catalyzed acetylation of alcohols, in situ generated triflic acid plays an important role: Dumeunier, R.; Markó, I. E. *Tetrahedron Lett.* **2004**, *45*, 825.

[10] Pure $C_8F_{17}SO_3H$ was prepared from $C_8F_{17}SO_3Ag$ and aqueous HCl.

[11] Sato, T.; Otera, J.; Nozaki, H. *J. Am. Chem. Soc.* **1990**, *112*, 901.