# Scandium and Ytterbium Tris(perfluorobutanesulfonyl)methide Complexes: Extremely Efficient Lewis Acid Catalysts

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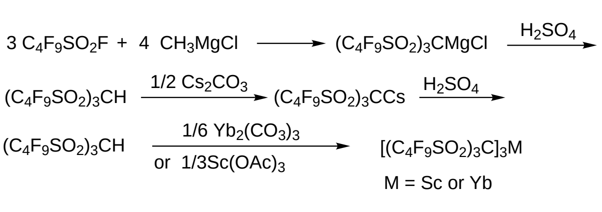
**Abstract**: Lanthanide tris(perfluorobutanesulfonyl)methides, scandium and ytterbium complexes in particular, were synthesized and shown to be water-tolerant and extremely efficient Lewis acid catalysts for the Friedel-Crafts acylation, Diels-Alder reaction, and Meerwein-Ponndorf-Verley reduction.

**Key words:** tris(perfluorobutanesulfonyl)methide, scandium, ytterbium, lanthanides, Lewis acid catalysis

Recently, a wide variety of Lewis acid complexes have been developed to realize unique reactivities and selectivities in reactions promoted therewith, and some of them have been applied in industrial processes.[1] However, the Lewis acid complexes have often been used in more than a stoichiometric amount. Therefore, it is desirable to decrease the amount of the Lewis acid complexes by developing an efficient catalyst and catalytic processes therewith. Amongst, the Friedel-Crafts reactions, which are one of the most important carbon-carbon bond forming processes in organic synthesis, are generally carried out by using Lewis acid complexes such as aluminum trichloride.[2] However, the Friedel-Crafts acylation reaction generally requires at least a stoichiometric amount of Lewis acid due to the complexation with the aromatic ketone product. In this respect, lanthanide(III) triflates have been reported as the catalysts of choice.[3,4] Furthermore, lanthanide(III) bis(perfluoroalkanesulfonyl)amide complexes have been found to be more active catalysts.[5] Quite recently, the syntheses and catalytic use of ytterbium and scandium tris(trifluoromethanesulfonyl)methides were reported for aromatic nitration.[6] We herein report the syntheses of lanthanide(III) tris(perfluorobutanesulfonyl)methide complexes and the remarkably high catalytic activities of the scandium and ytterbium complexes in carbon-carbon bond forming reactions such as the Friedel-Crafts acylation and Diels-Alder reaction.



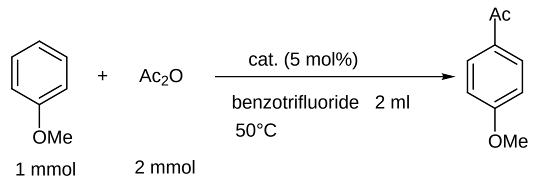
**Scheme 1**

First of all, the syntheses of the lanthanide(III) tris(perfluorobutanesulfonyl)methide complexes are worth mentioning (Scheme 1). Based on our precedent report on the higher catalytic activities of lanthanide(III) bis(perfluorobutanesulfonyl)amide complexes[5a] compared to bis(trifluoromethanesulfonyl)amide complexes, we focused our attention on the syntheses of the lanthanide(III) tris(perfluorobutanesulfonyl)methide complexes. According to Seppelt's original paper[7] on the preparation of tris(trifluoromethanesulfonyl)methane, $HC(SO_2CF_3)_3$, tris(perfluorobutanesulfonyl)methane, $HC(SO_2C_4F_9)_3$ was prepared through modification by using hydrogen fluoride-free and anhydrous perfluorobutanesulfonyl fluoride and the slow addition into a vigorously stirred solution of methylmagnesium chloride in tetrahydrofuran.[8] Acidic work up with sulfuric acid followed by the treatment with cesium carbonate gave the cesium salt of tris(perfluorobutanesulfonyl)methane, $CsC(SO_2C_4F_9)_3$ as a white solid. Upon protonation of $CsC(SO_2C_4F_9)_3$ with 100% sulfuric acid and vacuum-sublimation at 75 °C / 3 mmHg, to remove volatile materials, and then at 110 °C / 2 mmHg, a white crystalline $HC(SO_2C_4F_9)_3$ was obtained in 25% yield (lit.[8] 19% yield).

The lanthanide tris(perfluorobutanesulfonyl)methide complexes were synthesized in water using lanthanide(III) carbonates, acetates, or oxides. The ytterbium(III) tris(perfluorobutanesulfonyl)methide complex was prepared by mixing $HC(SO_2C_4F_9)_3$ (6 mmol) with a slightly excess amount of ytterbium(III) carbonate hydrate at room temperature for 3 hours and then at 70 °C for 2 hours in water. After filtration, evaporation and then drying at 90 °C / 0.01 mmHg for 6 hours, ytterbium(III) tris(perfluorobutanesulfonyl)methide complex was obtained as a hygroscopic white powder in 98% yield (5.42 g): $Yb[C(SO_2C_4F_9)_3]_3$ Anal.: Yb 6.2%, C 16.7%; Calcd.: Yb 6.3%, C 17.0%; $^{19}F$ NMR (dioxane-$d_8$) $\delta$ -126.1, -121.2, -107.3, -81.4 ppm. Likewise, the scandium(III) tris(perfluorobutanesulfonyl)methide complex was prepared by mixing $HC(SO_2C_4F_9)_3$ (6 mmol) with a slightly excess amount of scandium(III) acetate hydrate at room temperature for 3 hours and then at 70 °C for 3 hours in water. After filtration, evaporation and then drying at 90 °C / 0.01 mmHg for 6 hours, scandium(III) tris(perfluorobutanesulfonyl)methide complex was obtained as a hygroscopic white powder in 99% yield (5.21 g): $Sc[C(SO_2C_4F_9)_3]_3$ Anal.:1.6%, 17.4%; Calcd.: Sc 1.7%, C

17.8%; $^{19}$F NMR (dioxane-$d_8$) δ -126.4, -121.7, -107.8, -81.6 ppm.

Then, the catalytic activities of the scandium and ytterbium complexes were examined in carbon-carbon bond forming reactions such as the Friedel-Crafts acylation and Diels-Alder reaction. The Friedel-Crafts acylation reactions of anisole (1 mmol) with acetic anhydride (2 mmol) were carried out in the presence of a catalytic amount (5 mol%) of the lanthanide complexes in benzotrifluoride (2 ml) at 50 °C for 1-3 hours. Depending critically on the kind of the anionic ligands employed, the aromatic ketone product was obtained in low-to-good chemical yields as calculated by GC analysis using *n*-decane as an internal standard (Scheme 2, Table 1). Scandium tris(perfluorobutanesulfonyl)methide complex provides slightly higher chemical yield than that obtained by the ytterbium catalyst. In addition, the tris(perfluorobutanesulfonyl)methide complex affords comparable or even higher chemical yield than that obtained by the bis(perfluorobutanesulfonyl)amide complex. Thus, the order of the catalytic activities are as follows: $Sc[C(SO_2C_4F_9)_3]_3 \geq Yb[C(SO_2C_4F_9)_3]_3 \geq Yb[N(SO_2C_4F_9)_2]_3 > Sc(OSO_2CF_3)_3 > Yb(OSO_2CF_3)_3$.



**Scheme 2**

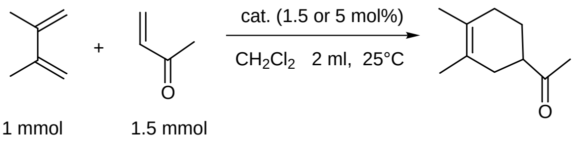
**Table 1** Friedel-Crafts Acylation reactions

| | %Yield a) | | | | |
|---|---|---|---|---|---|
| Time | YbOTf | ScOTf | YbC4am | YbC4me | ScC4me |
| 1h | 5% | 39% | 75% | — | 89% |
| 3h | 12% | 48% | 87% | 91% | 93% |

a) Calculated by GC analysis using *n*-decane as an internal standard.

YbOTf: Yb $(OSO_2CF_3)_3$ , ScOTf: $Sc(OSO_2CF_3)_3$
YbC4am: $Yb[N(SO_2C_4F_9)_2]_3$ YbC4me: $Yb[C(SO_2C_4F_9)_3]_3$
ScC4me: $Sc[C(SO_2C_4F_9)_3]_3$

The Diels-Alder reactions[9] of 2,3-dimethylbutadiene (1 mmol) with methyl vinyl ketone (1.5 mmol) were carried out in the presence of a catalytic amount (1.5 to 5 mol%) of scandium complexes in dichloromethane (2 ml) at 25 °C. Acetylcyclohexene was obtained in moderate-to-good chemical yield as calculated by GC analysis using *n*-nonane as an internal standard (Scheme 3, Table 2). Scandium methide complex affords the higher chemical yield than that obtained by scandium triflate complex.



**Scheme 3**

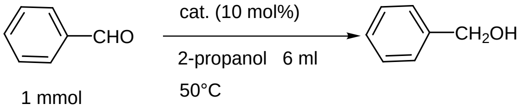
**Table 2** Diels-Alder reactions

| | %Yield a) | |
|---|---|---|
| Time | ScOTf(5 mol%) | ScC4me(1.5 mol%) |
| 10min | | 79% |
| 1h | 88% | 95% |
| 5h | 95% | |
| 20h | 97% | |

a) Calculated by GC analysis using *n*-nonane as an internal standard.

ScOTf: $Sc(OSO_2CF_3)_3$ , ScC4me: $Sc[C(SO_2C_4F_9)_3]_3$

Finally, the Meerwein-Ponndorf-Verley reductions[10] of benzaldehyde (1 mmol) with 2-propanol (6 ml) were examined in the presence of a catalytic amount (10 mol%) of lanthanide complexes at 50 °C for 1-3 hours. The benzylalcohol product was obtained in low-to-good yield as calculated by GC analysis using *n*-nonane as an internal standard (Scheme 4, Table 3). Ytterbium methide complexes provide higher chemical yields than those obtained by the ytterbium amide and triflate catalysts. Benzyl *iso*-propyl ether was also obtained as a by-product ($Yb[C(SO_2C_4F_9)_3]_3$:10%, $Yb[N(SO_2C_4F_9)_2]_3$:9%).



**Scheme 4**

**Table 3** Meerwein-Ponndorf-Verley Reductions

| | %Yield a) | | | | |
|---|---|---|---|---|---|
| Time | $AlCl_3$ | Al(OPr-*i*)$_3$ | YbOTf | YbC4am | YbC4me |
| 1h | — | — | 1% | 52% | 85%(97%)[b)] |
| 3h | trace | trace | 3% | — | — |

a) Calculated by GC analysis using *n*-nonane as an internal standard.
b) The value in parenthesis refers to the conversion of the starting benzaldehyde.

YbOTf: $Yb(OSO_2CF_3)_3$ YbC4am: $Yb[N(SO_2C_4F_9)_2]_3$
YbC4me: $Yb[C(SO_2C_4F_9)_3]_3$

In summary, we have disclosed herein that lanthanide tris(perfluorobutanesulfonyl)methide complexes such as the scandium and ytterbium complexes are synthesized and shown to be extremely efficient Lewis acid catalysts for the Friedel-Crafts acylation, Diels-Alder reaction, and Meerwein-Ponndorf-Verley reduction.

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