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Lewis acid catalysis by lanthanide complexes with tris(perfluorooctanesulfonyl)methide ponytails in fluorous recyclable phase[†]

Koichi Mikami,[a,*] Yutaka Mikami,[a] Yousuke Matsumoto,[a] Joji Nishikido,[b] Fumihiko Yamamoto[b] and Hitoshi Nakajima[b]

[a]*Department of Applied Chemistry, Tokyo Institute of Technology, Tokyo 152-8552, Japan*
[b]*The Noguchi Institute, Tokyo 173-0003, Japan*

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Abstract—Scandium and ytterbium tris(perfluorooctanesulfonyl)methide complexes are shown to be immobilized in fluorous recyclable phase and extremely efficient Lewis acid catalysts for alcohol acylation, Friedel–Crafts acylation, Diels–Alder reaction, and Mukaiyama aldol reaction by virtue of the highly electron-withdrawing effect of tris(perfluorooctanesulfonyl)methide ponytails without any hydrocarbon spacer.

Enzymatic reactions based on hydrogen bonding of gigantic protein enzymes have been recognized as models for catalytic organic reactions. A wide variety of Lewis acid complexes in minimal sizes, by contrast, have thus been developed by mimicking hydrogen bonding with the Lewis acid–base complexation in aprotic polar solvents.[1] However, the Lewis acid complexes have often been wasted in more than a stoichiometric amount. Therefore, it is desirable to decrease the amount of Lewis acid complex by developing a stronger Lewis acid catalyst and the recycle process thereof. Quite recently, the concept of fluorous bi-phasic catalysis (FBC) was introduced as an environmentally benign recycle process.[2] Phosphine or phosphite ligands with fluorous ponytails and hydrocarbon spacers have been developed to immobilize late transition metal catalysts for hydroformylation, hydride reduction, hydrogenation, alkene epoxidation and hydroboration in non-polar media.[3] The design and immobilization of strong Lewis acid catalysts are challenging in this unorthodox non-polar media for Lewis acid catalysis.[4] Numerous (nine) and long-enough (perfluorooctyl, C_8F_{17}) fluorous ponytails can be employed for fluorous phase immobilization of lanthanide catalysts (Fig. 1). The key to the success is the powerful electron-withdrawing effect of the perfluoroalkanesulfonylmethide group without any hydrocarbon spacer.[5] We report the 'super' Lewis acidities and the complete recycle of lanthanide(III) tris(perfluorooctanesulfonyl)methide complexes in the fluorous phase.

First, we examined the solubility of the scandium and ytterbium complexes in fluorous and/or non-fluorous solvents. The lanthanide complexes were soluble in

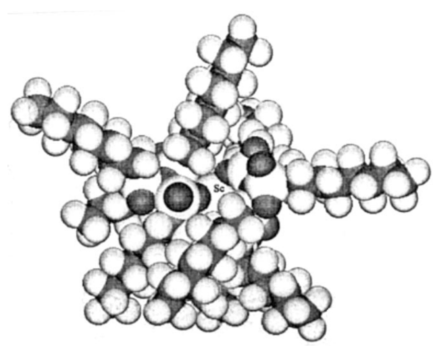

Figure 1. ScL'_3, $L' = C(SO_2C_8F_{17})_3$. The core structure of ScL_3, $L = C(SO_2CF_3)_3$ is optimized at the Hartree Fock level with 6-31 G basis set for C, F, S, O and with CEP-31G pseudo potential and basis set for Sc. Then the CF_3 group in the core structure is replaced with C_8F_{17} and those chains are optimized using UFF force field (Ref. 6).

Keywords: acylation; environmental benignity; fluorous phase; lanthanide; Lewis acid catalysis.

* Corresponding author.

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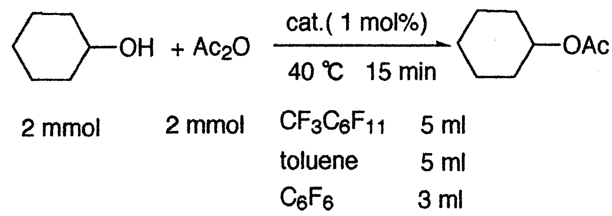


Scheme 1.

aromatic fluorocarbons but not so soluble in aliphatic fluorocarbons. However, fluoroaromatic solvents were miscible in non-fluorous solvents. Therefore, we examined the catalytic activities of the lanthanide complexes for alcohol acylation as a probe reaction in aliphatic fluorocarbon/non-fluorous solvents with or without fluoroaromatics; in the bi-phases or a homogeneous phase with fluoroaromatics at higher temperature.

The ester formation of cyclohexanol (2 mmol) with acetic anhydride (2 mmol) in perfluoromethylcyclohexane (5 ml), toluene (5 ml) and perfluorobenzene (3 ml) was completed within 15 min in the homogeneous phase at 40°C, with 1 mol% of scandium and ytterbium complexes (Scheme 1). Then, the reaction mixture was allowed to stand at 15°C for 3 min, so that the reaction mixture could separate into the upper phase (19.9% $CF_3C_6F_{11}$, 52.5% toluene, 27.6% C_6F_6) and the lower phase (69.9% $CF_3C_6F_{11}$, 13.8% toluene, 16.3% C_6F_6) (Fig. 2); cyclohexyl acetate was obtained in quantitative yield as calculated by GC analysis (Table 1). Scandium and ytterbium complexes were completely (>99%) recovered in the lower phase as determined by atomic emission spectrometry.

We then conducted the reaction and separation in the bi-phase (FBC) mode of perfluoromethylcyclohexane/toluene. The reaction of cyclohexanol (2 mmol) with acetic anhydride (2 mmol) in perfluoromethylcyclohexane (5 ml) and toluene (5 ml) was carried out at 30°C for 20 min in the presence of 1 mol% of lanthanide complexes (Scheme 2). Then, the heterogeneous two phases were separated within 10 seconds into toluene and the lower fluorous layers (Fig. 3). Cyclohexyl acetate was obtained in good isolated yield. Scandium and ytterbium complexes were completely (>99%) recovered and reused in the fluorous phase without isolation (Table 2).

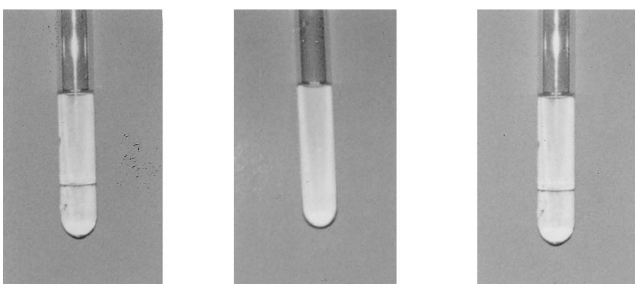
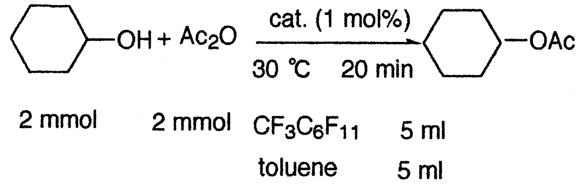


Figure 2. Before (15°C), during (40°C) and after (3 min, 15°C) the reaction.

Table 1. Esterification in homogeneous phase catalyzed by $Yb[C(SO_2C_8F_{17})_3]_3$ or $Sc[C(SO_2C_8F_{17})_3]_3$

% Yield[a]	
$Yb[C(SO_2C_8F_{17})_3]_3$	$Sc[C(SO_2C_8F_{17})_3]_3$
100	100 (95)[b]

[a] Calculated by GC analysis using n-nonane as an internal standard.
[b] Values in parentheses refer to the isolated yields.



Scheme 2.

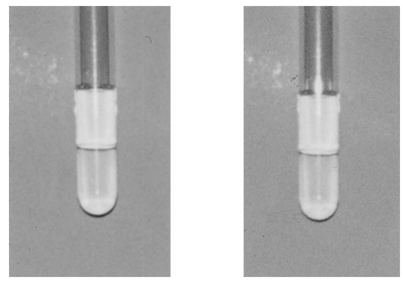


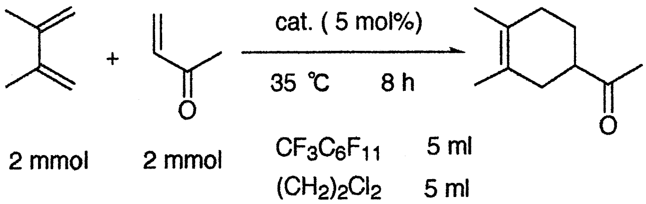
Figure 3. Before (25°C) and after (10 sec, 25°C) the reaction.

Then, the catalytic activities and recyclable use of the lanthanide complexes were examined for C–C bond forming (CCF) reactions. The Diels–Alder (D-A) reaction constitutes one of the most efficient construction processes of six-membered rings.[7] The D-A reaction of 2,3-dimethylbutadiene (2 mmol) with methyl vinyl ketone (2 mmol) in perfluoromethylcyclohexane (5 ml) and 1,2-dichloroethane (5 ml) was carried out at 35°C for 8 h in the presence of a catalytic amount (5 mol%) of scandium complex. Then, the heterogeneous two phases were separated to give acetylcyclohexene in good isolated yield (Scheme 3). Scandium methide complex was completely (>99.9%) recovered and reused in the recyclable fluorous immobilized phase (Table 3).

Table 2. Esterification in two phases catalyzed by $Yb[C(SO_2C_8F_{17})_3]_3$ or $Sc[C(SO_2C_8F_{17})_3]_3$

Cycle[a]	% Yield[b]	
	$Yb[C(SO_2C_8F_{17})_3]_3$	$Sc[C(SO_2C_8F_{17})_3]_3$
1	99	99
2	99 (96)[c]	100 (98)[c]
3	98	99
4	99	99
5	99 (96)[c]	100 (98)[c]

[a] The catalyst in the lower phase was recycled.
[b] Calculated by GC analysis using n-nonane as an internal standard.
[c] Values in parentheses refer to the isolated yields.

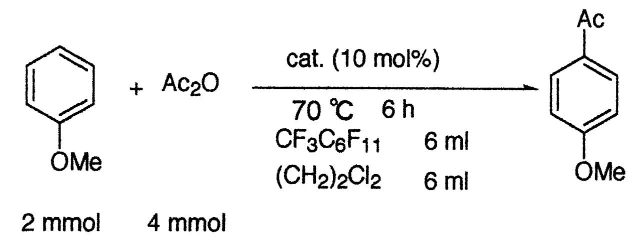


Scheme 3.

Table 3. Diels–Alder reaction catalyzed by $Sc[C(SO_2C_8F_{17})_3]_3$

Cycle[a]	% Yield[b]
1	95
2	94 (91)[c]
3	95
4	95 (92)[c]

[a] The catalyst in the lower phase was recycled.
[b] Calculated by GC analysis using *n*-nonane as an internal standard.
[c] Values in parentheses refer to the isolated yields.



Scheme 4.

The Friedel–Crafts (F-C) reactions constitute one of the most useful CCF processes in organic synthesis.[8] The F-C acylation reaction of anisole (2 mmol) with acetic anhydride (4 mmol) was also carried out in the presence of a catalytic amount (10 mol%) of the lanthanide complexes in perfluoromethylcyclohexane (6 ml) and 1,2-dichloroethane (6 ml) at 70°C for 6 h. The aromatic ketone product was obtained in good isolated yields (Scheme 4). Scandium complex was completely (99.8%) recovered and reused in the fluorous phase (Table 4).

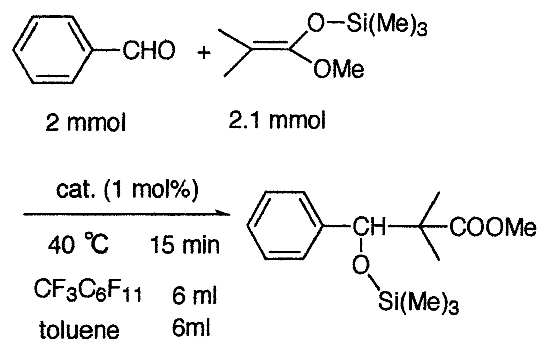
The Mukaiyama-aldol reaction is a synthetically and biologically important CCF process.[9] The aldol reaction of benzaldehyde (2 mmol) with trimethylsilyl enol ether derived from methyl 2-methylpropanoate (2.1 mmol) was completed within 15 min even in the presence of only 1 mol% of the lanthanide complexes in perfluoromethylcyclohexane (6 ml) and toluene (6 ml) at 40°C (Scheme 5). The aldol product was obtained in good isolated yields. Lanthanide methide complex was completely (99.8%) recovered and reused (Table 5).

In summary, we have disclosed lanthanide tris(perfluorooctanesulfonyl)methide complexes[10] as extremely efficient Lewis acid catalysts in the immobilized and recyclable fluorous phases by virtue of the powerful electron-withdrawing effect of the tris(perfluorooctanesulfonyl)methide ponytails without any hydrocarbon spacer.[11]

Table 4. Friedel–Crafts acylation reaction catalyzed by $Sc[C(SO_2C_8F_{17})_3]_3$

Cycle[a]	% Yield[b]
1	94 (87)[c]
2	93
3	93
4	92

[a] The catalyst in the lower phase was recycled.
[b] Calculated by GC analysis using *n*-decane as an internal standard.
[c] Values in parentheses refer to the isolated yield.



Scheme 5.

Table 5. Mukaiyama-Aldol reaction catalyzed by $Yb[C(SO_2C_8F_{17})_3]_3$ or $Sc[C(SO_2C_8F_{17})_3]_3$

Cycle[a]	% Yield[b]	
	$Yb[C(SO_2C_8F_{17})_3]_3$	$Sc[C(SO_2C_8F_{17})_3]_3$
1	84	88 (84)[c]
2	85	88
3	83	86

[a] The catalyst in the lower phase was recycled.
[b] Calculated by GC analysis using *n*-nonane as an internal standard.
[c] Values in parentheses refer to the isolated yield.

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