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Lanthanide Bis(trifluoromethylsulfonyl)amides as Effective Reusable Catalysts for Catalytic Friedel–Crafts Acylation†

Jin Nie,* Jun Xu and Guangyong Zhou

*Department of Chemistry, Huazhong University of Science & Technology, Wuhan 430074,
Hubei, P.R. China*

By using a catalytic amount of a lanthanide bis(trifluoromethylsulfonyl)amide, $\mathrm{Ln(NFf_2)_3}$, the Friedel–Crafts acylation of substituted benzene proceeds smoothly under mild conditions and the catalysts are easily recovered from the reaction mixture.

Some Lewis acid catalysts have been employed in the Friedel–Crafts acylation in place of aluminum trichloride.[1,2] Kobayashi and co-workers[3] have especially developed the lanthanide trifluoromethanesulfonates [lanthanide triflates, $\mathrm{Ln(OTf)_3}$] as effective and reusable Lewis acid catalysts for many organic reactions such as the aldol reactions, Diels–Alder and Michael reactions. For the Friedel–Crafts acylation the lanthanide triflates are also effective Lewis acid catalysts.[4] We have found that the metal salts of bis(trifluoromethylsulfonyl)amine [$\mathrm{HN(SO_2CF_3)_2}$ or $\mathrm{HNTf_2}$[5]] are effective Lewis acid catalysts for the Diels–Alder reaction of cyclopentadiene with methyl vinyl ketone in non-polar organic solvents[6,7] and the results indicated that lanthanide bis(trifluoromethylsulfonyl)amides are much more effective Lewis acid catalysts than lanthanide triflates. Mikami *et al.*[8] reported recently some new metal bis(trifluoromethanesulfonyl)amides as highly efficient Lewis acid catalysts for acylation reactions. We report here on the acylation reaction of substituted benzenes with acetic anhydride by using a catalytic amount of the lanthanide bis(trifluoromethylsulfonyl)amides, $\mathrm{Ln(NTf_2)_3}$

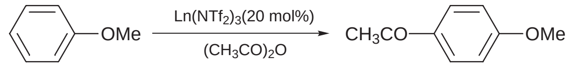
Results and discussion

The catalytic activities of various lanthanide bis(trifluoromethylsulfonyl)amides as Lewis acid catalysts were first examined in the acylation reaction of anisole with acetic anhydride (Table 1). In accordance with the results for lanthanide triflates,[4] $\mathrm{Yb(NTf_2)_3}$ was the most effective catalyst in this case and this is consistent with that what was found by Mikami *et al.*[8] The activities of $\mathrm{La(NTf_2)_3}$ were relatively low (Table 1, entries 1–5), however much higher than those of the corresponding lanthanide triflates.[4] The acetylation reaction of anisole catalysed by a catalytic amount of $\mathrm{Ln(NTf_2)_3}$ proceeded smoothly under very mild conditions and the differences among the catalytic activities of the lanthanide cations were consistent with their Lewis acidities, which was investigated by the halochromism of 2,4,4′,6-tetramethoxyazobenzene in toluene.[9]

Solvent effects on the acetylation reaction of anisole catalysed by ytterbium(III) tris[bis(trifluoromethylsulfonyl)amide] and optimization of the conditions in nitromethane are shown in Table 2. Although $\mathrm{Yb(NTf_2)_3}$ could be used as a homogeneous catalyst in acetonitrile, diethyl ether, acetic anhydride, nitromethane, and tetrahydrofuran under the same experimental conditions, totally different results were obtained (Table 2, entries 1, 3–4, and 9–10. Nitromethane was the best solvent for the acetylation reaction of anisole and, even if 1 mol% of catalyst was used, $\mathrm{Yb(NTf_2)_3}$ also showed higher catalytic activity to afford good yield at room temperature for 4 h (Table 2, entry 6). Interestingly, when the acetylation reaction of anisole was carried out in tetrahydrofuran for 10 min the reaction mixture gradually became sticky. Investigation of this result showed that the solvent, THF, had polymerized in the presence of the catalyst and meant that $\mathrm{Yb(NTf_2)_3}$ is a very strong Lewis acid catalyst.

To explore the scope of the above ytterbium(III) tris[bis(trifluoromethylsulfonyl)amide] catalysed acylation, the reaction was examined with several substituted benzenes and acetic anhydride (Table 3). The acylation of benzene was not detected and *m*-xylene was acetylated to the dimethylacetophenone in moderate yield under very mild conditions. The introduction of a methoxy group afforded high yields of the acylation products. The reactivity of several structurally diverse acid anhydrides was also checked

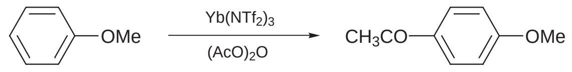
Table 1 $\mathrm{Ln(NTf_2)_3}$ catalysed Friedel–Crafts acylation of anisole in $\mathrm{CH_3NO_2}$[a]



Entry	Catalyst	$T/°\mathrm{C}$	t/h	Yield(%)[b]
1	$\mathrm{La(NTf_2)_3}$	25	4	55
2		25	10	60
3	$\mathrm{Sm(NTf_2)_3}$	25	4	85
4		25	8	90
5	$\mathrm{Yb(NTf_2)_3}$	25	4	99
6	$\mathrm{Yb(OTf)_3}$	50	18	99[c]

[a]Reaction conditions: anisole 1.25 mmol, $\mathrm{(CH_3CO)_2O}$ 2.5 mmol, $\mathrm{CH_3NO_2}$ 5 mL. [b]Determined by HPLC. [c]See ref. 4.

Table 2 Solvent effect on Friedel–Crafts acylation of anisole catalysed by $\mathrm{Yb(NFf_2)_3}$[a]



Entry	$\mathrm{Yb(NTf_2)_3}$ (equiv.)	$\mathrm{(AcO_2)_2O}$ (equiv.)	t/h	Solvent	Yield(%)[b]
1	0.2	2.0	4	$\mathrm{CH_3CN}$	n.d.[c]
2	0.2	2.0	4	$\mathrm{CCl_4}$	20
3	0.2	2.0	4	$\mathrm{Et_2O}$	24
4	0.2	excess	4	$\mathrm{Ac_2O}$	55
5	0.2	2.0	4	$\mathrm{CH_2Cl_2}$	80
6	0.01	2.0	4	$\mathrm{CH_3NO_2}$	66
7	0.05	2.0	4	$\mathrm{CH_3NO_2}$	77
8	0.1	2.0	4	$\mathrm{CH_3NO_2}$	85
9	0.2	2.0	4	$\mathrm{CH_3NO_2}$	99
10	0.2	2.0	0.5	THF	[d]

[a]Reaction conditions: anisole 1.0 equiv., solvent 5 mL, 25 °C. [b]Determined by HPLC. [c]Not detected. [d]The solvent THF was found to be polymerized in the presence of the catalyst.

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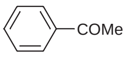
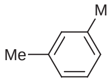
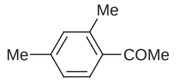
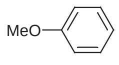
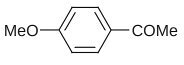
* To receive any correspondence (*e-mail*: niejin@wuhan.cngb.com).

† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

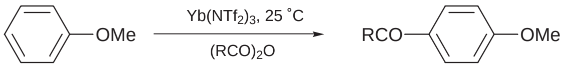
Table 3 $Yb(NTf_2)_3$ (20 mol%) catalysed Friedel–Crafts acylation at 25 °C[a]

$$Ar{-}H \; + \; (CH_3CO)_2O \xrightarrow{Yb(NTf_2)_3} Ar{-}COCH_3$$

Ar–H	Product	t/h	Yield(%)[b]
		24	n.d.[c]
		9	10
		4	99

[a]Reaction conditions: ArH 1.25 mmol, $(CH_3CO)_2O$ 2.5 mmol, CH_3NO_2 5 mL, 25 °C. [b]Determined by HPLC. [c]Not detected.

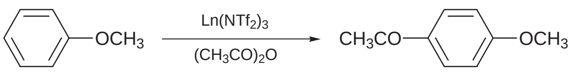
Table 4 $Yb(NTf_2)_3$ catalysed Friedel–Crafts acylation of anisole in CH_3NO_2[a] with structurally diverse acid anhydrides



Entry	Anhydride	Catalyst/mol%	t/h	Yield(%)[b]
1	$(CH_3CO)_2O$	10	2	86
2	$(CH_3CH_2CO)_2O$	10	2	87
3	$(CH_3(CH_2)_6CO)_2O$	20	2	99
4	$(PHCO)_2O$	20	24	–[c]

[a]Reaction conditions: anisole 1.25 mmol, $(CH_3CO)_2O$ 2.5 mmol, CH_3NO_2 2.5 mL. [b]Determined by ^{1}H NMR. [c]Product was not detected at 100 °C.

Table 5 Recycling of $Ln(NTf_2)_3$ in acylation of anisole[a]



Entry	Catalyst (mol%)	Yield(%)[b]	Recovery of catalyst(%)[c]
1	$La(NTf_2)_3$(20)	58	95 (1st)
2		56	93 (2nd)
3	$Sm(NTf_2)_3$(20)	80	91 (1st)
4		81	90 (2nd)
5	$Yb(NTf_2)_3$(20)	99	92 (1st)
6		99	90 (2nd)
7	$Yb(NTf_2)_3$(5)	77	90 (1st)
8		76	92 (2nd)
9		77	90 (3rd)

[a]Reaction conditions: anisole 1.0 equiv. $(CH_3CO)_2O$ 2.0 equiv., CH_3NO_2 5 mL, 25 °C, 4 h. [b]Determined in HPLC. [c]Determined by the ratio of the isolated amount of catalyst from the aqueous layer based on initial amount of $Ln(NTf_2)_3$.

(Table 4). For the aliphatic acid anhydrides, from acetic anhydride to octanoic acid anhydride the reactivity of acylations seemed to change little. However, the case of aromatic acid anhydrides for example benzoic anhydride the acylation of anisole did not occur even at 100 °C for 24 h.

Finally, the catalytic activities of recovered catalysts were examined. As shown in Table 5, from the yields of 4-methoxyacetophenone in the second and third uses of the catalyst it was obviously that the catalytic activities of the lanthanide bis(trifluoromethylsulfonyl)amides were almost same as that in the first use. Furthermore, more than 90% of the catalysts could be easily recovered from the aqueous layer by simple extraction.

In summary, lanthanide bis(trifluoromethylsulfonyl)amides are effective Lewis acid catalysts for Friedel–Crafts acylation and are stable in water, easily recovered, and reusable.

Experimental

The lanthanide bis(trifluoromethylsulfonyl)amides were prepared from the reaction of the amine acid, $HNTf_2$, with the corresponding oxides Ln_2O_3 in water.[6] A typical experimental procedure for the acylation reaction of anisole with acetic anhydride catalysed by ytterbium(III) tris[bis(trifluoromethylsulfonyl)amide], $Yb(NTf_2)_3$, is described as follow. A mixture of anisole (670 μL, 6.2 mmol) and acetic anhydride (1.16 mL, 12.4 mmol) was added to a solution of $Yb(NTf_2)_3$ (312.5 mg, 0.31 mmol) and dried nitromethane (5 mL) with stirring at 25 °C and the reaction carried out for 4 h at room temperature (25 °C). After dilution with water (10 mL), the reaction mixture was extracted with chloroform (3 × 10 mL). The acylation product, 4-methoxyacetophenone, was dissolved in the chloroform layer and the yield determined by HPLC (77%). The aqueous layer was then concentrated to give a solid residue, which was finally heated at 100 °C for 6.5 h under 1 mmHg to afford 281.3 mg of white powder of $Yb(NTf_2)_3$ (90%). The recovered catalyst was reused in the next acylation reaction.

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