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Metal bis{(trifluoromethyl)sulfonyl}amide complexes: highly efficient Friedel–Crafts acylation catalysts†

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A range of metal bis{(trifluoromethyl)sulfonyl}amide complexes, including many unreported ones, have been synthesised, most of which have been found to be excellent Friedel–Crafts acylation catalysts in the absence of solvent; these reactions have also been carried out in ionic liquids, which allow the catalysts to be recycled and reused.

The catalysis of chemical reactions is of major importance in chemistry, and explicitly green chemistry. The Friedel–Crafts acylation reaction involves the interaction of an acylating agent with an aromatic compound to give a ketone.[1] The reaction conventionally requires a Lewis acid "catalyst" such as aluminium(III) chloride, but suffers from a major disadvantage in that at least 1 molar equivalent of Lewis acid "catalyst" is needed.[1,2] The work-up of these reactions results in the destruction of the "catalyst", thus, in the majority of industrial processes, a minimum of four moles of HCl and one mole of hydrated aluminium waste are generated for every mole of product.[1] Kobayashi and co-workers have described the use of Group 13 metal perfluoroalkylsulfonates in the catalytic acylation of various aromatic compounds, using the aromatic compound as solvent.[3] In order to extend the range of catalysts for this reaction, we describe here the use of bis{(trifluoromethyl)sulfonyl}amine ($HN(SO_2CF_3)_2$ or $HNTf_2$) or new metal bistriflamide complexes, $M\{N(SO_2CF_3)_2\}_n$, as catalysts for Friedel–Crafts acylation reactions, both dissolved in the neat reagents and also in ionic liquid media. Ionic liquids are increasingly being used[4] as a means of dissolving catalysts, such that the catalyst can be recovered, recycled and reused.

Examples of metal bistriflamide catalysts include the polymerisation of styrene,[5] the reaction of silyl-enol ethers with allylic or benzylic acetates,[6] and the formation of acetals and ketals from carbonyl compounds (or enol ethers).[7] Aluminium, ytterbium and titanium bistriflamides have been used in the Friedel–Crafts reaction of acetic anhydride with anisole to give acetyl anisole,[8] in the flammable solvent nitromethane. Such a procedure is of very limited benefit as aromatics less reactive than anisole would require elevated reaction temperatures. Also, ytterbium(III) bistriflamide has been used as a Friedel–Crafts acylation catalyst and Diels–Alder catalyst in fluorous compounds such as 1,3,5-trifluorobenzene,[9] and lanthanide bistriflamides for the acylation of anisole in organic solvents.[10]

Metal bistriflamide catalysts do not require dangerous nitrated solvents (nitromethane) or toxic solvents (such as dichloroethane),[11] and the catalyst can be recycled and reused, which is not the case in the previous seven examples.[5–11] We report here that metal bistriflamide catalysts or $HNTf_2$ can be used in solvent-free conditions, or in ionic liquids. The use of ionic liquids gives the advantage that the metal bistriflamide catalyst is easier to recycle and the reactions can proceed with higher reaction rates. Some of the metal bistriflamide catalysts are sufficiently active that unreactive arenes (such as benzene, fluorobenzene, and chlorobenzene)[3] can be acylated.[12] The use of indium(III) bistriflamide in the acylation of chlorobenzene is reported to give low yields (5%).[11]

The metal bistriflamide catalysts were synthesised by a variety of routes.[12] These generally involved the reaction of a metal carbonate, hydroxide or oxide with bis{(trifluoromethyl)sulfonyl}amine in water. The water was then driven off by heating at 150 °C *in vacuo*.†[13] Some of the metal bistriflamide salts were found to be volatile, and were further purified by vacuum sublimation.[13] The structure of zinc(II) bistriflamide was determined by X-ray crystallography‡ and is shown in Fig. 1. The bistriflamide ligand coordinates to the zinc through the oxygen atoms. The structure consists of chains of $\{Zn[O,O'\text{-}(O_2SCF_3)_2N]_2\}$ units, with two chelating bistriflamide ligands in the same plane, linked in a complex pattern by *trans*-bridging *O*,*O*′-bidentate bistriflamide ligands.

The Friedel–Crafts reactions were carried out in two ways. The first is the addition of 1 mol% of a metal bistriflamide catalyst such as $Zn(NTf_2)_2$ to a mixture of an acylating agent and aromatic compound, and heating if necessary (Fig. 2). This can be achieved with no solvent, or in an ionic liquid. The second method is to generate the catalyst *in situ*, by taking a metal salt, not necessarily a bistriflamide salt (*e.g.* $ZnCl_2$ or $SnCl_4$) and dissolving it in a bistriflamide ionic liquid (*e.g.* [bmim][NTf_2], where $[bmim]^+$ = 1-butyl-3-methylimidazolium). To this mixture, the acylating agent and aromatic compound can be added. The separation of the products from the ionic liquid and catalyst was carried out by several means, including direct vacuum distillation (at 1 mm Hg) from the reaction vessel (Kugelrohr distillation). The reaction could be repeated by addition of fresh starting materials to the recovered catalytic system. The reactions in reused ionic liquids gave similar yields when performed in the ionic liquids (3 recycles), but gave successively poorer yields when no ionic liquid was present. The

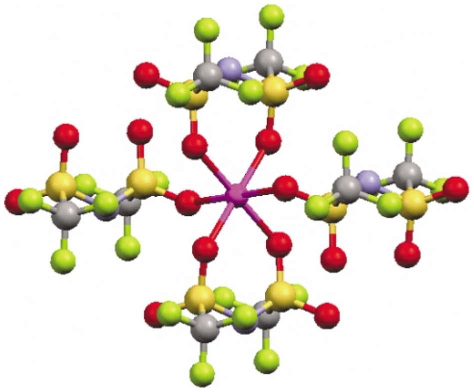

Fig. 1 The coordination environment around the metal in zinc(II) bis{(trifluoromethyl)sulfonyl}amide.

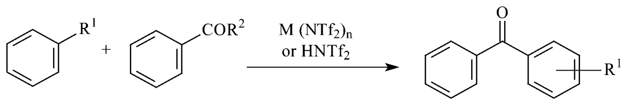

Fig. 2 The acylation reactions of aromatic compounds with bis{(trifluoromethyl)sulfonyl}amine or metal bistriflamide catalysts (R^1 = H, CH_3, Cl, F, OCH_3, R^2 = Cl, O_2CPh, OH).

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b4/b403650f/

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products can also be extracted with a solvent (*e.g.* cyclohexane, hexane, petroleum ether, or toluene), or by azeotropic separation of the products with steam (steam stripping). The hydrogen chloride by-product formed in the reaction was lost through the top of the condenser.

To determine the relative effectiveness of various metal bistriflamide catalysts, the reaction of benzoyl chloride with toluene was chosen as a model. The bistriflamide salts of magnesium(II), calcium(II), strontium(II), barium(II), tin(II), lead(II), manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) were prepared[12] and 1 mol% of each of these materials were heated with reactants for up to five days in the absence of solvent. The ionic liquid [bmim][NTf$_2$] (1 mol%), HNTf$_2$ (1 mol%) and lithium bistriflamide (1 mol%) were used as controls. All the reactions were monitored by GC, and some of the results are shown in Table 1. The reactions were also carried out successfully with a number of metal(III) and metal(IV) bistriflamide salts, such as those of aluminium(III), chromium(III), iron(III), indium(III), ytterbium(III), and cerium(IV), but these materials are poorly characterised, and their composition is not necessarily as claimed (see for example ref.[11]).

The rates of the acylation reactions varied considerably, depending on which metal bistriflamide was used. Surprisingly, metals that are not conventionally thought of as being Friedel–Crafts catalysts gave the best results. This is particularly the case for M(NTf$_2$)$_2$ (M = Mn, Co, Ni, or Pb), which for the reactions of acyl chlorides, give results significantly better than either lanthanide(III) bistriflamides[10,13] or triflates. When this acylation, with a cobalt(II) or nickel(II) bistriflamide, was performed in 1-ethyl-3-methylimidazolium bistriflamide [emim][NTf$_2$], the reaction time was reduced to 0.5 and 1 h, respectively, and the catalyst–ionic liquid combination could be recycled (95% yield on third recycle). Without the ionic liquid present, the catalyst gave successively poorer yields when reused (48% on 2nd and 21% on 3rd recycle for Co(NTf$_2$)$_2$. This activity was restored on addition of HNTf$_2$. It is interesting to note that HNTf$_2$ is a good acylation catalyst in its own right, and addition of this as a co-catalyst has been observed to increase the reaction rate. The isolation of the metal bistriflamide catalyst is not always necessary: the catalyst can be generated *in situ* by the addition of a metal compound (*e.g.* ZnCl$_2$) to a source of bistriflamide such as the ionic liquid [bmim][NTf$_2$], thus simplifying the experimental procedure (see Table 2). The acylation of chlorobenzene (Table 2) proceeds efficiently with cobalt(II) bistriflamide or indium(III) chloride in a bistriflamide ionic liquid. Other catalysts were found to be less effective. The acylation of fluorobenzene with 4-fluorobenzoyl chloride was carried out at 5 bar, and gave primarily 4,4′-difluorobenzophenone using zinc(II) chloride dissolved in [bmim][NTf$_2$]. The metal chloride dissolved in a bistriflamide ionic liquid was found to give similar yields compared with isolated metal bistriflamide catalysts. Metal bistriflamides also catalyse the acylation of aromatic compounds with carboxylic acids and anhydrides. Zinc(II) and cobalt(II) bistriflamide gave similar yields to lanthanide(III) bistriflamides, but at much lower reaction temperatures (140 °C compared with 250 °C).[14] This has the advantage that water is the only by-product, but longer reaction times are needed.

Table 1 The variation of yield with time for the reaction of benzoyl chloride (5 mmol) with toluene (7.5 mmol) at 110 °C with no solvent

Catalyst (1.0 mol%)	Time/h	Yield (%)
LiNTf$_2$	120	< 5
Mg(NTf$_2$)$_2$	48	99
Ca(NTf$_2$)$_2$	120	< 5
Sr(NTf$_2$)$_2$	120	31
Ba(NTf$_2$)$_2$	120	65
Mn(NTf$_2$)$_2$	5	99
Co(NTf$_2$)$_2$	3	99
Ni(NTf$_2$)$_2$	4	99
Cu(NTf$_2$)$_2$	72	99
Zn(NTf$_2$)$_2$	48	99
Sn(NTf$_2$)$_2$	48	91
Pb(NTf$_2$)$_2$	6	95
[bmim][NTf$_2$]	120	0
HNTf$_2$	48	97
Co(NTf$_2$)$_2$–HNTf$_2$	2	97

Table 2 The acylations of various aromatic compounds in [bmim][NTf$_2$] (1.0 g) after 18 h, unless otherwise stated

Aromatic (7.5 mmol)	Acylating agent (5 mmol)	Catalyst	Temp/°C	Yield (%)
Ph–Cl	PhCOCl	5% Zn(NTf$_2$)$_2$	130	55[a]
Ph–Cl	PhCOCl	5% Co(NTf$_2$)$_2$	130	95[a]
Ph–Cl	PhCOCl	15% InCl$_3$	130	87[abc]
Ph–F	4-FPhCOCl	5% ZnCl$_2$[bd]	160	98[e]
Anisole	PhCOCl	10% ZnCl$_2$[b]	110	80
PhCH$_3$	PhCOCl	1% SnCl$_4$	110	99[g]
m-Xylene	PhCO$_2$H	10% Zn(NTf$_2$)$_2$	140	40[f]
m-Xylene	PhCO$_2$H	10% Co(NTf$_2$)$_2$	140	82[f]
Anisole	(PhCO)$_2$O	5% In(OTf)$_3$	60	88
Anisole	(PhCO)$_2$O	5% Hf(OTf)$_4$	60	91

[a] *p*- : *o*-isomer ratio = 9 : 1. [b] [emim][NTf$_2$] ionic liquid used. [c] Reaction time 96 h. [d] Reaction carried out in an autoclave. [e] *p*- : *o*- : *m*-isomer ratio = 75 : 15 : 8. [f] Reaction carried out for 48 h. [g] 97% yield after 2 h.

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Notes and references

‡ Data were collected with a Bruker-AXS SMART diffractometer using the SAINT-NT[15a] software with graphite monochromated Mo–K$_\alpha$ radiation. A crystal was mounted onto the diffractometer at low temperature under nitrogen at *ca.* 120 K. The structure was solved using direct methods and refined with the SHELXTL version 5[15b] and the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen-atom positions were added at idealised positions with a riding model and fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded). The function minimised was $\Sigma[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2 |F_o|^2 + (g_1P)^2 + (g_2P)]$ where $P = [\max |F_o|^2 + 2|F_c|^2]/3$. Additional material available from the Cambridge Crystallographic Data Centre comprises relevant tables of atomic coordinates, bond lengths and angles, and thermal parameters.

Crystal data for $C_4F_{12}N_2O_8S_4Zn$: $M_r = 625.67$, monoclinic, space group $P2_1/n$, $a = 11.566(6)$, $b = 5.160(2)$, $c = 14.179(7)$ Å, $\beta = 100.753(10)$ °, $U = 831.1(7)$ Å^{-3}, $Z = 2$, $\mu = 2.154$ mm^{-1}, $R_{int} = 0.0904$, transmission range (max, min) = 0.928, 0.588. A total of 3810 reflections were measured for the angle range $4 < 2\theta < 50$ and 1439 independent reflections were used in the refinement. The final parameters were $wR2 = 0.1892$ and $R1 = 0.0664$ [$I > 2\sigma(I)$]. CCDC 219662. See http://www.rsc.org/suppdata/cc/b4/b403650f/ for crystallographic data in .cif or other electronic format.

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