Facile preparation of metallic triflates and triflimidates by oxidative dissolution of metal powders†

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Various metallic triflates and triflimidates were prepared by the straightforward oxidative dissolution of the corresponding metal powder in DMSO under an atmospheric pressure of O_2 in the presence of stoichiometric amounts of triflic or triflimidic acid.

An array of metallic triflates, $M(OTf)_n$, and triflimidates, $M(NTf_2)_n$, belonging to the class of Lewis superacids have been described as efficient catalysts in many organic reactions. Recent examples of organic reactions catalysed by indium(III),[1–3] tin(II),[4,5] tin(IV),[6] rare earth metals,[7] and bismuth(III) triflates have been reported.[8–11] In the triflimidate series, indium(III),[12,13] and tin(IV) triflimidates[14] for example, have been used in various reactions.[15] Some metallic triflates and triflimidates are commercially available, usually as hydrates of general formula $M(OTf)_n \cdot xH_2O$ or $M(NTf_2)_n \cdot xH_2O$, where x is sometimes omitted, and rarely determined with accuracy. Their preparation may be achieved from metal oxides, hydroxides, carbonates or halides and triflic or triflimidic acid in aqueous media or directly in water,[16–18] providing the salts as hydrates. In the triflate series, $B(OTf)_3$, $Ga(OTf)_3$, and $Al(OTf)_3$ have been prepared from the corresponding metal bromides and chlorides and 3 equivalents of HOTf at $-78\ ^\circ C$.[19] Dubac and Le Roux have proposed several methods for the preparation of $Bi(OTf)_3$. In all instances, these methods involve the action of stoichiometric HOTf on a bismuth(III) compound, $BiPh_3$ in CH_2Cl_2, involving an unusual cleavage of metal–carbon bonds by the superacid,[20] or Bi_2O_3 in $EtOH–H_2O$[17] or in chlorobenzene.[16] Bismuth(III) triflate could also be obtained from bismuth oxide and stoichiometric HOTf in Tf_2O,[21] or from $Bi(OAc)_3$ and excess triflic acid.[22] In the triflimidate series, the same displacement strategy has been used to prepare alkali metal triflimidate salts from alkali metal carbonates in the presence of $HNTf_2$ in methanol,[23] $Mg(NTf_2)_2$ from $Mg(OH)_2$ and $HNTf_2$,[24] lanthanide triflimidates from carbonates and stoichiometric $HNTf_2$ or from oxides and excess $HNTf_2$ in refluxing water,[18] ytterbium and yttrium triflimidates from the corresponding metal oxides and 3 equivalents of $HNTf_2$ in refluxing water,[25] and $Bi(NTf_2)_3$ from triphenylbismuth and stoichiometric $HNTf_2$ in dichloromethane.[26] A metathesis reaction involving 2 equivalents of

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$NaNTf_2$ and $MgSO_4 \cdot 6H_2O$ in Et_2O was also used to prepare $Mg(NTf_2)_2 \cdot 8H_2O$.[27]

Although many metallic triflates and triflimidates are active Lewis acids even in an aqueous environment, some reactions are not water-tolerant and the preparation of nearly anhydrous metal salts may be desirable. It is worth noting that triflate-based counteranions are likely to decompose at temperature above $100\ ^\circ C$, therefore limiting the efficiency or applicability of oven drying.[22,28]

We have described an electrochemical method for the preparation of anhydrous metallic triflates and triflimidates based on the anodic oxidation of the corresponding metal in the presence of triflic or triflimidic acid.[29,30] This method has the advantage of yielding the metallic salts as solvates with organic solvent molecules instead of water, thereby providing an access to anhydrous salts. In the course of mechanistic studies on the oxidation of internal epoxides by metallic bismuth in the presence of triflic acid, we observed that the bismuth metal powder was dissolved in DMSO at $100\ ^\circ C$ under an atmospheric pressure of O_2 to form bismuth(III) triflate.[31] This interesting phenomenon prompted us to examine the behaviour of various metals of low standard reduction potential[32] under these oxidative conditions.

We present here a simple and efficient method for the preparation of metallic triflates and triflimidates based on the oxidative dissolution of metal powders in the presence of HOTf or $HNTf_2$ superacids, respectively, in DMSO under O_2. To our knowledge, no method has been reported to date to obtain such salts from metallic powders.

When metallic bismuth, a black powder, was heated at $100\ ^\circ C$ in DMSO under O_2 at atmospheric pressure in the presence of three equivalents of triflic acid (HOTf), a slow disappearance of the powder was observed and a homogeneous pale yellow solution was obtained after 24 h (Table 1, entry 1). Removal of the solvent was achieved in a bulb-to-
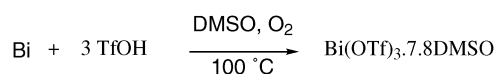
Table 1 Effect of temperature, solvent and atmosphere on the oxidative dissolution of metallic bismuth powder in the presence of HOTf (3 equiv.)[a]

Entry	Solvent	Atmosphere	$T/^\circ C$	t/h	Yield
1	DMSO	O_2	100	24	Quant.
2	DMSO	N_2	100	24	—
3	DMSO	O_2	20	24	—
4	CH_3CN	O_2	80	48	—

[a] Conditions: Bi (10 mmol, 2.09 g), HOTf (30 mmol, 4.50 g) in 10 mL of anhydrous solvent.

$$\text{Bi} + 3\,\text{TfOH} \xrightarrow[100\ ^\circ\text{C}]{\text{DMSO, O}_2} \text{Bi(OTf)}_3 \cdot 7.8\,\text{DMSO}$$

Scheme 1

bulb oven by heating under reduced pressure to yield a white–grey powder. After washing with cold dichloromethane under nitrogen, and drying overnight at 10 mbar, a white solid was obtained. ^{19}F-NMR spectrum of this solid in [D$_6$]acetone at 20 °C indicated a single singlet, centered at −79.4 ppm. The ^{1}H-NMR spectrum under the same analytical conditions displayed a singlet at 2.98 ppm. The latter was attributed to the methyl groups of DMSO molecules solvating the metallic salt, the coordination resulting in a shift of 0.38 ppm downfield compared to the chemical shift of free DMSO under the same analytical conditions. Elemental analysis was consistent with the formula Bi(OTf)$_3$·7.8DMSO. This reaction could be carried out on a multigram scale and was used as an alternative and convenient procedure to prepare Bi(OTf)$_3$ (Scheme 1).

In order to check if molecular oxygen was the sole oxidant of the system allowing the oxidation of metallic bismuth Bi^0 to Bi^{III} species (conditions Table 1, entry 1), the same reaction was conducted under a nitrogen atmosphere instead of oxygen. The metallic powder remained unchanged after 24 h (entry 2), and a sluggish mixture was obtained after 9 d, indicating that molecular oxygen was playing an important role. In DMSO at room temperature under molecular oxygen, no reaction of bismuth could be observed (entry 3). By changing DMSO for acetonitrile, the oxidative dissolution of bismuth was unsuccessful (entry 4). However, an exclusive oxygen atmosphere was not mandatory, since under air, the oxidative dissolution was also possible (not shown).

We further investigated the behaviour of other metals in oxidative dissolution in the presence of HOTf (Table 2). Similarly to bismuth, tin, copper, indium, magnesium, calcium, and iron were oxidatively dissolved in the presence of HOTf to form the corresponding salts, as confirmed by ^{1}H-, ^{19}F-NMR and elemental analysis. With samarium, the metal reacted vigorously with HOTf even at room temperature. A reaction time of 10 h at 100 °C was needed to observe the total dissolution of samarium metal (entry 6). Besides the redox reaction of the metal with O$_2$, an alternative reaction between

HOTf and samarium metal leading to the oxidation of samarium metal to samarium(III) and the reduction of H$^+$ to H$_2$ could not be ruled out. A light yellow solid was obtained after work-up, presenting a singlet at −79.1 ppm by ^{19}F-NMR, and was identified as Sm(OTf)$_3$·9.7DMSO by elemental analysis.

Aluminium and tungsten, in spite of their low standard reduction potentials (−1.66 V and −1.07 V vs. SHE, respectively) were not dissolved in the presence of HOTf. Passivation of the surface was probably an important factor in these cases, and was not circumvented by HCl activation.

When substoichiometric amounts of superacid were used, for example 1 equivalent of HOTf with copper, or 2 equivalents of HOTf with iron, a dark brown powder was obtained. The powder was almost insoluble in acetone, and ^{1}H-NMR analysis did not show the usual pattern of signals, but a broad signal from 4.5 to 6.0 ppm, attributed to non-identified acidic species.

This novel oxidative dissolution procedure was then carried out with a series of metals in the presence of HNTf$_2$. Similarly to what was obtained with HOTf, the corresponding triflimidate salts were formed quantitatively, except with aluminium (Table 3).

With both triflate and triflimidate salts, the solvating DMSO molecules were observed, during ^{1}H-NMR experiments in [D$_6$]acetone, as a singlet presenting a significant downfield shift. No trace of water was observed by ^{1}H-NMR either in [D$_6$]acetone or in [D$_6$]DMSO. Interestingly, the chemical shift of the solvating DMSO varied according to the nature of the metal cation, presenting a good correlation with the Pauling electronegativity value of the metal (Fig. 1).

The nearness of the DMSO molecules to the metal cation resulted in a close relationship between the electronic density of the DMSO molecule, as shown in the chemical shift of the methyl groups, and the electronic affinity of the metal, a characteristic included in the empiric Pauling electronegativity. Except with samarium, the only one having f orbitals, such a correlation was observed along the series examined.

FT-IR spectroscopy also indicated the presence of DMSO molecules (strong bands in the range 1200–980 cm^{-1}) and the absence of water for the triflate and triflimidate salts of tin and copper. We were further interested in how the DMSO molecules were bound to the cation and how these solvating DMSO could be displaced by other molecules, to allow the further use of these salts as catalysts. This effect was simply monitored by ^{1}H-NMR, bound DMSO displaying a singlet at 2.7–3.3 ppm while free DMSO presents a singlet at 2.5–2.7 ppm. For example, solvating DMSO molecules were almost instantaneously displaced when one drop of D$_2$O was

Table 2 Oxidative dissolution of various metals in the presence of HOTf in O$_2$–DMSO

Entry	Metal	E°/ V vs. SHE^a	TfOH (equiv.)	t/h	Product^b
1	Cu	0.34	2	18	Cu(OTf)$_2$·5DMSO
2	Sn	−0.14	4	24	Sn(OTf)$_4$·6.1DMSO
3	Bi	−0.23	3	24	Bi(OTf)$_3$·7.8DMSO
4	In	−0.34	3	22	In(OTf)$_3$·7DMSO
5	Fe	−0.44	3	24	Fe(OTf)$_3$·6.2DMSO
6	W	−1.07	6	24	—
7	Al	−1.66	3	24	—^{c}
8	Sm	−2.01	3	10	Sm(OTf)$_3$·9.7DMSO
9	Mg	−2.37	2	17	Mg(OTf)$_2$·3.9DMSO
10	Ca	−2.87	2	2	Ca(OTf)$_2$·6.4DMSO

^{a} Taken from ref. 32. ^{b} Quantitative yields. Formula determined from ^{1}H and ^{19}F-NMR, and elemental analysis. ^{c} Unsuccessful, even with HCl activation of aluminium prior to use.

Table 3 Oxidative dissolution of various metals in the presence of HNTf$_2$ in O$_2$/DMSO

Entry	Metal	Tf$_2$NH (equiv.)	t/h	Product^a
1	Cu	2	18	Cu(NTf$_2$)$_2$·4.4DMSO
2	Sn	4	7	Sn(NTf$_2$)$_4$·7.9DMSO
3	Bi	3	16	Bi(NTf$_2$)$_3$·10.8DMSO
4	Al	3	48	—
5	Mg	2	18	Mg(NTf$_2$)$_2$·5.0DMSO

^{a} Quantitative yields. Formula determined from ^{1}H and ^{19}F-NMR, and elemental analysis.

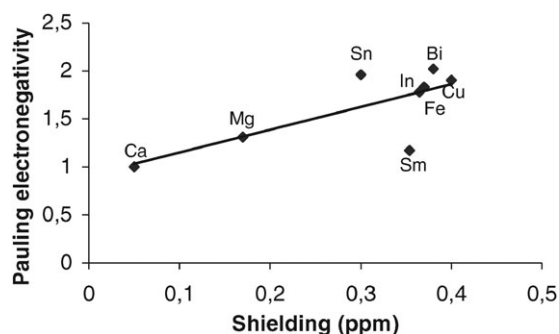**Fig. 1** Pauling electronegativity *vs.* ^{1}H-NMR shielding of DMSO in $M(OTf)_n \cdot x$DMSO.

added to a solution of $Sn(NTf_2)_4 \cdot 7.9$DMSO in $[D_6]$acetone with the DMSO signal shifting from 3.3 ppm to 2.7 ppm. When the analysis was performed in $[D_4]$methanol, the singlet of DMSO was observed at 2.8 ppm, suggesting that bound DMSO was released and replaced by MeOH around the metal centre. In deuterated THF and acetonitrile, no change was observed after 24 h. In an NMR experiment carried out with $Bi(NTf_2)_3 \cdot 10.8$DMSO in $[D_6]$DMSO with added water, the water signal was shifted downfield from 3.8 to 4.1 ppm, while DMSO signal was shifted upfield from 3.3 (value measured in $[D_6]$acetone) to 2.6 ppm, next to the pseudo quintuplet of deuterated DMSO centered at 2.5 ppm. This indicated that, here again, bound DMSO molecules were thus exchanged with free water molecules.

The activity of some of these salts was evaluated in catalytic reactions, previously described to be catalysed by metallic triflates and triflimidates prepared by the electrochemical method.[29,30] For example, tin(IV) triflate was used in the cycloisomerisation of bis-homoallylic alcohols.[33] After 1 h in refluxing acetonitrile, only 1 mol% of $Sn(OTf)_4 \cdot 6.1$DMSO quantitatively converted 6-methylhept-5-en-2-ol to 2,2,6-trimethyltetrahydropyran in quantitative yield. In the cycloisomerisation of 1,6-dienes,[14] diethyl diprenylmalonate **1** was efficiently cyclised to cyclohexane derivative **2** in 90% yield in the presence of only 2 mol% $Sn(NTf_2)_4 \cdot 7.9$DMSO after 3 h at 60 °C in nitromethane (Scheme 2).

In summary, we describe here a simple method for the preparation of metallic triflates and triflimidates from simple precursors and with high atom-economy on a multi-gram scale.[34] This method is convenient, yields quantitatively anhydrous salts, and should therefore be useful to organic chemists in many applications.
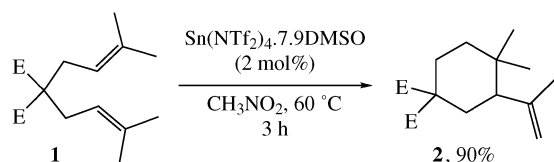
Scheme 2

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34 Preparation of $Bi(OTf)_3 \cdot 7.8$DMSO: Metallic bismuth (10 mmol, 2.09 g), is placed into a Schlenck flask containing a magnetic stirrer. The system is purged and placed under an O_2 atmosphere. Freshly distilled DMSO (10 mL) is introduced, followed by HOTf (30 mmol, 4.50 g) in three portions. The mixture is heated at 100 °C until disappearance of the powder. Removal of the solvent at 1–10 mbar using a bulb-to-bulb oven at 80 °C followed by quick washing with cold dichloromethane affords a white solid (12.8 g): NMR, $[D_6]$acetone, 20 °C: ^{19}F: −79.4 ppm, s. ^{1}H: 2.98 ppm, s. Elemental analysis: calcd %C = 17.8, %H = 3.8, %F = 13.4, %S = 27.5, and %Bi = 16.3 and experimental %C = 17.5, %H = 3.7, %F = 13.2, %S = 27.7, and %Bi = 16.2.