Notes

Tris(trifluoromethanesulfonyl)methide ("Triflide") Anion: Convenient Preparation, X-ray Crystal Structures, and Exceptional Catalytic Activity as a Counterion with Ytterbium(III) and Scandium(III)

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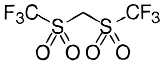
The lanthanide(III) triflates are the focus of much current research.[1] Recently we have reported the use of lanthanide(III) triflates[2] and the superior tetrapositive group IV metal triflates, hafnium and zirconium,[3,4] as recyclable atom economic catalysts for aromatic nitration. In an attempt to further enhance the catalytic activity of these salts for nitrations, we sought to modify the triflate counterion.[5] On the basis of our current mechanistic understanding[6] of our lanthanide(III) catalyzed nitration protocol we sought a counterion that should be (i) a conjugate base of a very strong acid, (ii) unaffected by strongly oxidizing conditions, i.e., not oxidized by concentrated nitric acid, (iii) nonoxidizing itself, precluding the use of, for example, perchlorate, (iv) hydrolysis resistant, ruling out counterions such as PF_6^- and SbF_6^-, and (v) of increased solubility in organic solvents compared to triflate itself. Thus, our attention was drawn to Seppelt's seminal paper[7] which details the preparation of tris(trifluoromethylsulfonyl)methane, $HC(SO_2CF_3)_3$ **1a**, a remarkably strong organic C−H Brønsted acid.[7,8] Its lithium salt, $LiC(SO_2CF_3)_3$ **1b**, has been extensively employed as an electrolyte in nonaqueous high voltage batteries,[9] displaying high anodic stability,[10] and so the tris(trifluoromethanesulfonyl)methide anion seemed ideally suited for our purposes as a triflate replacement.

$[(CF_3SO_2)_3C]_nM$

1a, n=1; M = H
1b, n=1; M = Li
1c, n=1; M = Cs
1d, n=3; M=Yb
1e, n=3; M=Sc



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Seppelt's preparation of **1a** calls for the use of trifluoromethanesulfonyl fluoride (bp −21 °C) as an electrophilic triflyl source.[7] Aside from the inconvenience of handling gaseous reagents, CF_3SO_2F is not commercially available and is typically prepared via electrochemical fluorination with anhydrous HF,[12] a highly hazardous undertaking in most standard laboratories. We were intrigued by the possibility of using readily available triflic anhydride in lieu of CF_3SO_2F especially since the failure of organometallic reagents to add cleanly to triflic anhydride is well-documented.[12,13] Herein we report a practical and convenient two-step preparation of the tris(trifluoromethanesulfonyl)methide anion (which we have given the trivial name of "triflide"), conveniently isolated as its cesium salt **1c**, employing triflic anhydride as the electrophilic triflyl source. Additionally we report the preparation of the corresponding ytterbium(III) and scandium(III) salts, **1d** and **1e**, respectively, and compare their catalytic competence for aromatic nitration of *o*-nitrotoluene with ytterbium(III) and scandium(III) triflates.

Results and Discussion

Slow addition of triflic anhydride to a stirred solution of trimethylsilylmethyllithium in pentanes at 0 °C resulted in smooth reaction as evidenced by the gradual precipitation of lithium triflate with only a slight increase in the internal temperature (max. ≈10 °C). Basic aqueous quench, extraction with dichloromethane, and strong acidification (concentrated HCl) of the remaining aqueous phase followed by extraction with dichloromethane led

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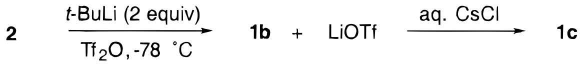
Scheme 1

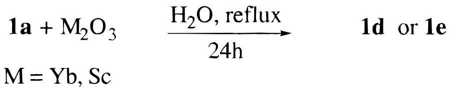


$$\mathbf{2} \xrightarrow[\text{Tf}_2\text{O}, -78\ ^\circ\text{C}]{t\text{-BuLi (2 equiv)}} \mathbf{1b} + \text{LiOTf} \xrightarrow{\text{aq. CsCl}} \mathbf{1c}$$

to the isolation of methyleneditriflone **2**[7,14] as a yellow oil which was essentially pure by ^{1}H NMR but could be obtained as a low-melting white solid after vacuum sublimation. The acidic nature of **2**, which has been estimated to have a pK_a of −1,[14a] allows for easy purification via acid−base extraction as above and this procedure allows gram quantities to be prepared in a reproducible 50−55% yield.

Triflylation of **2** with triflic anhydride was carried out by double deprotonation[7,14a] with *tert*-butyllithium followed by the addition of triflic anhydride (Scheme 1). The expected reaction product, **1b**, would, by the precondition of employing triflic anhydride, be contaminated with at least stoichiometric quantities of lithium triflate and a suitable separation regime was required. After quenching with aqueous base, acidification, and extraction with dichloromethane to remove all neutral organic side products, lithium triflide and triflate could be extracted effectively from the aqueous phase with diethyl ether. The triflide anion was completely freed from any triflate anion by selective precipitation with cesium chloride in water as determined by negative ion electrospray mass spectrometry. Purification was effected by vacuum sublimation of the cesium salt from concentrated sulfuric acid (generating the free acid **1a**) and reprecipitation with cesium chloride followed by recrystallization, giving **1c** as an analytically pure white solid. The cesium salt **1c** is a convenient way to store the triflide anion and does not decompose or color on standing at room temperature. Simple vacuum sublimation from sulfuric acid using a modification of Seppelt's procedure[7] generates the free acid **1a** which is best handled as an aqueous solution.

Scheme 2



$$\mathbf{1a} + \text{M}_2\text{O}_3 \xrightarrow[\text{24h}]{\text{H}_2\text{O, reflux}} \mathbf{1d} \text{ or } \mathbf{1e}$$

M = Yb, Sc

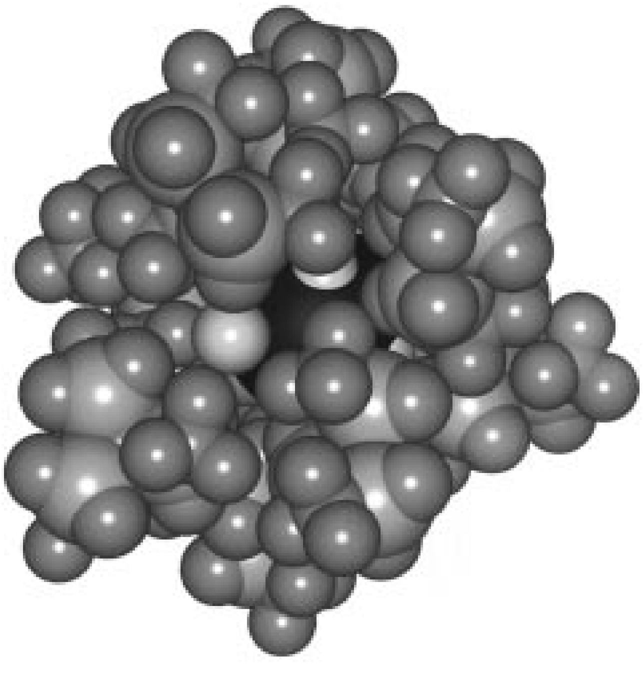


Figure 1. A space-filling representation of **1d** showing the encapsulation of the Yb(OH$_2$)$_8$ core (dark) and the included water molecule (light) by the nine triflide anions (light gray).

Ytterbium(III) and scandium(III) triflides were obtained by an analogous protocol employed for the triflate series viz. the metal oxides were heated to reflux with the free acid in water.[15] Thus, heating at reflux Yb$_2$O$_3$ or Sc$_2$O$_3$ in an aqueous solution of **1a** provided the metal triflides **1d** and **1e** in essentially quantitative yields as white powders after drying for 24 h (Scheme 2). Recrystallization furnished single crystals of the aqua complexes of both **1d** (from water−methanol) and **1e** (from water) suitable for X-ray crystallography. An initial examination showed the two compounds to have the same space group and very similar unit cell parameters, with those of the ytterbium complex being, on average, slightly larger than those of the scandium species. The immediate assumption was that the two compounds were isomorphous and that the small difference in lattice parameters were a consequence of the different ionic radii of the two metals. However, single-crystal structural analysis of the ytterbium complex revealed the metal atom to be eight coordinate, being bonded to eight aqua ligands. The structure is disordered, there being two principal metal coordination geometries distributed throughout the crystal. The major occupancy geometry (60%) is square antiprismatic, while that of the minor occupancy component (40%) is bicapped trigonal prismatic; the major occupancy Yb−O distances are in the range 2.27(2)−2.38(2) Å. In contrast, in the scandium complex the metal was found to be only seven coordinate (bonded to seven aqua ligands) in a geometry that can be considered as either distorted monocapped trigonal prismatic or distorted pentagonal biprismatic. In this latter geometry the five "equatorial" atoms are coplanar only to within 0.47 Å with the scandium atom lying 0.07 Å out of this plane. As in the ytterbium complex the structure is disordered, the crystals containing a minor component (20%) with a slightly different distorted monocapped trigonal prismatic geometry; the major occupancy Sc−O distances are in the range 2.113(13)−2.222(10) Å. The remainder of the structure in both complexes is virtually identical, with in each case an included water molecule hydrogen bonded to the ytterbium/scandium aqua coordination spheres (the coordinates of this water molecule are effectively the same in the two structures). The resulting Yb/Sc(OH$_2$)$_n$·H$_2$O unit is, in both complexes, completely encapsulated by a total of nine triflide anions (Figure 1), and the resulting assemblage is cemented by hydrogen bonds between the aqua ligands, the included water molecule and the sulfone oxygen atoms.[16] A consequence of this "total encapsulation" is large Yb···Yb and Sc···Sc separations throughout the crystal, the shortest internuclear distances being 10.69 and 10.62 Å, respectively. Despite

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(16) Failure to locate the positions of the hydrogen atoms on either the aqua ligands or the included water molecule precluded detailed analysis of the hydrogen bonding geometries. However, there are in the ytterbium complex, for example, some fourteen O···O contacts between the aqua ligands and either the included water molecule or the triflide anions of less than 3 Å.

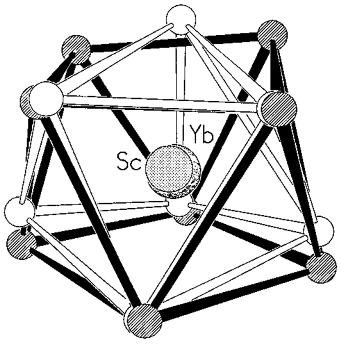

Figure 2. The mapping of the distorted monocapped trigonal prismatic scandium coordination polyhedron in **1e** (open bonds and open spheres) onto the ytterbium square antiprismatic polyhedron (filled bonds and shaded spheres) in **1d** showing the near superimposition of six of the aqua ligands.

the difference in the coordination geometries of the two species, the principal coordination polyhedra map remarkably well onto each other with six of the eight apexes of the ytterbium square antiprism being virtually superimposable onto those of the scandium monocapped trigonal prism (Figure 2).

While $Yb(OTf)_3$ was essentially ineffective for the nitration of *o*-nitrotoluene (ONT) to dinitrotoluenes (DNT's) giving 8% conversion under our standard conditions (i.e. 10 mol % catalyst, 1.05 equiv of 69% HNO_3, 1,2-DCE, reflux, 24 h), *10 mol % $Yb(CTf_3)_3$ **1d** was found to mediate the nitration of ONT to 93% conversion in 24 h*. The use of 10 mol % $Sc(OTf)_3$ gave a 50% conversion to DNT's in 24 h although the reaction mixture was found to darken considerably. In contrast, $Sc(CTf_3)_3$ **1e** was found to give a 91% conversion within the same time period, and no darkening was observed. In all cases, the ratio of 2,4-:2,6-DNT's was found to be 65:35.

In conclusion, we have demonstrated a convenient two-step preparation of the triflide anion (isolated as its cesium salt **1c**) from readily available materials. **1c** can be converted to an aqueous solution of the free acid **1a** which is used directly for the preparation of ytterbium(III) and scandium(III) triflides **1d** and **1e**. The dramatic increase in activity of the triflide salts versus the corresponding triflates for the aromatic nitration of the electron deficient arene *o*-nitrotoluene clearly demonstrates the utility of the triflide anion. Presumably, this is a direct result of the remarkable acidity of the free acid and hence the weakly coordinating properties of its conjugate base. These preliminary findings, coupled with its ease of preparation reported herein, should see the triflide anion find many applications[17] as an alternative counterion in the arena of homogeneous metal catalysis.

Experimental Section

General Procedures. Trimethylsilylmethyllithium and *tert*-butyllithium were purchased from the Aldrich Chemical Co. as 1.0 M and 1.7 M solutions in pentanes, respectively, and titrated against 2-pentanol with 1,10-phenanthroline as the indicator in dry Et_2O at 0 °C. Trifluoromethanesulfonyl (triflic) anhydride was purchased from Avocado and distilled from phosphorus(V) oxide directly before use. Cesium chloride, ytterbium oxide, and scandium oxide were obtained from the Aldrich Chemical Co. and used as received.

Methyleneditriflone (2).[14] Triflic anhydride (7.5 mL, 45 mmol) was added dropwise over 1 h by means of a syringe pump to a stirred solution of trimethylsilylmethyllithium in pentane (107 mL, 0.83 M, 90 mmol) under argon at 0 °C. The solution was allowed to stir for 1 h and quenched with saturated aqueous $NaHCO_3$ solution (100 mL). The layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (3×75 mL) and then acidified with concentrated hydrochloric acid (50 mL) [**care**: vigorous effervescence] and reextracted with CH_2Cl_2 (3×100 mL). The latter combined organic extracts were dried ($MgSO_4$), filtered, and evaporated to give a yellow solid which was subjected to vacuum sublimation (70 °C, 0.5 mmHg), yielding **2** as a white solid, 3.36 g (53% based on triflic anhydride): mp 33−35 °C (lit.[14a] 35 °C); ^1H NMR (300 MHz; $CDCl_3$) δ 4.98 (br s, 2H); ^{13}C NMR (75 MHz; $CDCl_3$) δ 118.7 (q, $J = 327$ Hz), 64.0; ^{19}F (376 MHz; $CDCl_3$) δ −75.1.

Cesium Tris(trifluoromethylsulfonyl)methide (1c).[7] *tert*-Butyllithium (4.56 mL, 1.84 M, 8.4 mmol) was added dropwise to a stirred solution of **2** (1.13 g, 4.0 mmol) in Et_2O (25 mL) at −78 °C under argon. The pale yellow solution was allowed to stir at −78 °C for 1 h when triflic anhydride (1.0 mL, 6.0 mmol) was added dropwise and the solution allowed to warm to room temperature over 2 h. The solvent was removed under reduced pressure, and the dark brown semisolid residue was taken up in saturated aqueous $NaHCO_3$ solution (60 mL) and extracted with CH_2Cl_2 (3×60 mL), acidified with concentrated hydrochloric acid (50 mL), and reextracted with CH_2Cl_2 (3×60 mL). The latter CH_2Cl_2 extracts were combined, dried ($MgSO_4$), and evaporated yielding 220 mg of a red oil (recovered **2**). The yellow aqueous phase was extracted with Et_2O (3×60 mL) and the yellow ethereal extracts were combined, dried ($MgSO_4$), filtered, and evaporated to give a yellow oil. The oil was taken up in distilled water (10 mL) and treated with an aqueous solution of cesium chloride (2.0 g, 12 mmol). The orange-brown precipitate was collected by filtration and vacuum-sublimed (130 °C, 0.5 mmHg) from concentrated sulfuric acid (2 mL), and the volatile $(CF_3SO_2)_3CH$ **1a** was taken up in distilled water and reprecipitated with cesium chloride. The solid was recrystallized from water (2 crops) to give **1c** as white platelets (1.0 g, 46% based on **2**): mp 324−326 °C; IR (KBr) 1374, 1360, 1336, 1233, 1197, 1131, 1123, 972, 694, 610, 585, 516; ^{13}C NMR (75 MHz; CD_3CN) δ 121.7 (q, $J = 326$ Hz), 83.8; ^{19}F (376 MHz; CD_3CN) δ −76.6; MS (electrospray, negative ions) 410.9 (Tf_3C^-).

Tris(trifluoromethylsulfonyl)methane (1a).[7] To cesium salt **1c** (0.744 g, 1.37 mmol) in a sublimation pot was added H_2SO_4 (sp. gr. 1.835, 0.7 mL, approximately 10 equiv) and the slurry sublimed in vacuo (1.5 mmHg, 100 °C rising to 160 °C). Liberated free acid **1a** was taken up in H_2O (2 mL) and treated with a saturated aqueous solution of $BaCl_2$ (6 mL) to remove sulfate impurities. The resulting white precipitate in a colorless solution was extracted with Et_2O (3×50 mL), and the aqueous component saturated with solid NaCl and reextracted with Et_2O (50 mL). The combined ethereal extracts were concentrated, and the residue was sublimed in vacuo (1.5 mmHg, 100 °C). The resultant purified free acid **1a** was taken up in H_2O (25.00 mL) and titrated (4×0.2 mL aliquots) against a standard NaOH solution (0.9995 M, phenolphthalein indicator). In a series of separate experiments the titrations revealed that aqueous solutions of the free acid **1a** had been produced in 88−98% yield from **1c**.

Ytterbium(III) Tris(trifluoromethylsulfonyl)methide (1d). Yb_2O_3 (99 mg, 0.25 mmol) was added to free acid **1a** (1.27 mmol) in H_2O (22.4 mL) and the milky suspension heated to reflux for 24 h. The resultant colorless solution was filtered (to remove traces of unreacted Yb_2O_3), evaporated, and dried under vacuum to provide **1d** (0.59 g, 0.42 mmol, 100% based on **1a**) as a white powder: IR (KBr) 3500−2800, 1631, 1376, 1336, 1204, 1123, 982, 689, 628, 585, 515 cm^{-1}; ^{13}C NMR (100 MHz; D_2O) δ 122.7 (q, $J = 325$ Hz), 84.1; ^{19}F NMR (376 MHz; CD_3CN) δ −76.5. Crystal data for $[Yb(OH_2)_8][C(SO_2CF_3)_3]_3 \cdot H_2O$: $M = 1568.8$, monoclinic, $P2_1/c$ (no. 14), $a = 19.241(4)$, $b = 13.442(2)$, $c = 18.094(4)$ Å, $b = 92.84(1)°$, $V = 4674(2)$ Å^3, $Z = 4$, $D_c = 2.229$ g cm^{-3}, μ(Mo−Kα) = 25.9 cm^{-1}, $F(000) = 3052$, $T = 293$ K; clear platy prisms, $0.73 \times 0.53 \times 0.17$ mm, Siemens P4/PC diffractometer, ω-scans, 7611 independent reflections. The structure was solved by the Patter-

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(17) For the interesting use of the triflide counteranion in diazonium salts and their decomposition products, see: (a) Zhu, S.-Z.; DesMarteau, D. D. *Inorg. Chem.* **1993**, *32*, 224. (b) Yagupolskii, Y. L.; Pavlenko, N. V.; Yurev, I. I.; Iksanova, S. V. *Zh. Org. Khim.* **1990**, *26*, 682.

son method, and the major occupancy non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give $R_1 = 0.060$, $wR_2 = 0.140$ for 5215 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$] and 769 parameters (CCDC-115480).

Scandium(III) Tris(trifluoromethylsulfonyl)methide (1e). Sc_2O_3 (52.8 mg, 0.38 mmol) was added to free acid **1a** (2.30 mmol) in H_2O (4.0 mL) and the milky suspension heated to reflux for 18 h. The resultant colorless solution was filtered (to remove traces of unreacted Sc_2O_3), evaporated, and dried under vacuum to provide **1e** (1.01 g, 0.79 mmol, 103% based on **1a**) as a white powder: IR 3600−2800, 1627, 1373, 1333, 1202, 1123, 981, 689, 628, 585, 515 cm^{-1}; ^{13}C NMR (100 MHz; D_2O) δ 122.6 (q, J = 325 Hz), 84.0; ^{19}F NMR (235 MHz; D_2O) δ −75.9. Crystal data for $[Sc(OH_2)_7][C(SO_2SCF_3)_3]_3 \cdot H_2O$: $M = 1422.8$, monoclinic, $P2_1/c$ (no. 14), $a = 18.954(2)$, $b = 13.503(2)$, $c = 17.957(3)$ Å, $b = 92.42(1)°$, $V = 4592(1)$ Å^3, $Z = 4$, $D_c = 2.058$ g cm^{-3}, $\mu(Cu{-}K\alpha) = 70.3$ cm^{-1}, $F(000) = 2816$, $T = 293$ K; clear platy prisms, 0.60 × 0.43 × 0.13 mm, Siemens P4/PC diffractometer, ω-scans, 6240 independent reflections. The structure was solved by the Patterson method and the major occupancy non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give $R_1 = 0.095$, $wR_2 = 0.238$ for 3472 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 120°$] and 757 parameters (CCDC-115479).

Nitration of *o*-Nitrotoluene with Ytterbium(III) and Scandium(III) Triflates or Triflides. Nitric acid (69%; 135 mL, 2.1 mmol) was added to a stirred suspension of catalyst (10 mol %) in 1,2-dichloroethane (2.0 mL). The suspension dissolved to give a two-phase system in which the aqueous phase was the more dense. *o*-Nitrotoluene (236 mL, 2.0 mmol) was added, and the stirred mixture was heated at reflux for 24 h. The mixture was allowed to cool and diluted with water (5 mL). The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organics were dried ($MgSO_4$) and evaporated to yield dinitrotoluenes (see main text). The aqueous phase was evaporated to yield the recovered catalyst (90−100%).

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Supporting Information Available: X-ray crystallographic data for the hydrated forms of **1d** and **1e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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