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Hafnium(IV) and Zirconium(IV) Triflates as Superior Recyclable Catalysts for the Atom Economic Nitration of *o*-Nitrotoluene

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Abstract: The hydrated group 4 metal triflates, $Hf(OTf)_4$ and $Zr(OTf)_4$, were found to be excellent catalysts (10 mol%) for the mononitration of *o*-nitrotoluene using a single equivalent of concentrated (69%) nitric acid. The only side product is water and the catalysts are readily recycled from the aqueous phase and re-used. © 1998 Elsevier Science Ltd. All rights reserved.

We have recently reported the use of lanthanide(III) triflates[1] as recyclable catalysts for the atom econonic nitration of simple arenes.[2] A range of lanthanide(III) triflates were examined of which the ytterbium salt was found to be the most active: a catalytic quantity (1-10 mol%) of ytterbium(III) triflate was found to catalyse the nitration of simple aromatics with good to excellent conversions using a single equivalent of 69% nitric acid in refluxing 1,2-dichloroethane for 12h. The only by-product of the reaction is water and the catalyst can be recovered by simple evaporation of the separated aqueous phase and re-used repeatedly for further nitrations. However, the lower reactivity threshold of arenes that could be nitrated readily with this system was limited to mildly electron deficient aromatics and is set at approximate Hammett values of $\sigma_p^+ \approx +0.3$. With a specific programme aim of nitrating *o*-nitrotoluene in this manner ($\sigma_p^+ \approx +0.7$), other metal triflates were sought with greater catalytic activity and we turned our attention to tetrapositive metal centres; in this letter we report the use of hafnium(IV) and zirconium(IV) triflates as efficient catalysts for such a purpose.

Hafnium[3] and zirconium[4] triflates are known compounds and have been prepared as the anhydrous salts. Kobayashi has demonstrated the efficiacy of these species for Fries rearrangements[5] and Friedel-Crafts acylations (hafnium only)[3,6] where lanthanide triflates were less successful. For our purposes the anhydrous salts were not required and we have developed a facile synthesis of the hydrated materials by simple metathesis of the corresponding metal halide with the readily available silver triflate to afford the requisite hydrated metal(IV) triflates as strongly deliquescent white solids.[7]

Table 1. Nitration of *o*-Nitrotoluene with Metal Triflates[a]

Entry	Catalyst	mol%	Time/h	%Conversion[b]
1	$Yb(OTf)_3$	10	12	trace
2	$Yb(OTf)_3$	10	120	17
3	$Yb(OTf)_3$	100	14	88
4	$Hf(OTf)_4$	10	24	>95
5	$Zr(OTf)_4$	10	24	>95

a Reactions performed with 3 mmol *o*-nitrotoluene, 3 mmol 69% nitric acid with 2 ml 1,2-dichloroethane as solvent; *b* Determined by GCMS: the product ratio was found to be 65:35 ± 2 of 2,4-DNT:2,6-DNT in all cases.

The use of catalytic quantities (10 mol%) of $Yb(OTf)_3$ for the attempted nitration of *o*-nitrotoluene under the standard conditions was essentially ineffective (Table 1, entry 1) and a poor conversion was obtained even after exhaustive reflux (Table 1, entry 2). Stoichiometric quantites of $Yb(OTf)_3$ were found to mediate nitration but the reaction proceeded as a suspension.[8] When $Hf(OTf)_4$ was utilised at a 10 mol% loading[9] smooth nitration occurred over a period of 24 h (Table 1, entry 4); 2,4- and 2,6-dinitrotoluenes (DNT's) were isolated in 92% yield in a 63:37 ratio as determined by ^1H NMR integration. Only traces of *o*-nitrotoluene could be detected and no other significant products were apparent. Similarly, zirconium(IV) triflate was found

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to have comparable catalytic activity (Table 1, entry 5) and 2,4- and 2,6-DNT were isolated in 87% yield in a 66:34 ratio.

In the work utilising ytterbium(III) triflate as the nitration catalyst it was shown that the lanthanide salt could be recovered unchanged from a nitration and re-used with no loss of activity.[2] In an analogous fashion hafnium(IV) and zirconium(IV) triflates could be recycled and the results from three successive nitrations of *o*-nitrotoluene using the zirconium salt are shown in table 2.[10] The recycled material was found to have an identical IR spectrum to the freshly prepared material. However, after several runs the solid had taken on a yellow-brown appearance and an additional band was apparent at 1660 cm^{-1} in the IR spectrum which is tentatively assigned to the presence of nitrate bound species.

Table 2. Recycled Zirconium(IV) Triflate for the Nitration of *o*-Nitrotoluene

Run[a]	time / h	% conversion[b]	mass recovery / mg[c]
1	24	> 95 (87)	173 (86)
2	27	> 95 (80)	134 (67)
3	23	88 (76)	121 (61)

a All runs performed with 3 mmol *o*-nitrotoulene, 10 mol% zirconium(IV) triflate (200 mg) (run 1) and 1 equivalent of 69% nitric acid in refluxing 1,2-dichloroethane (2 ml); *b* GC analysis. The isomeric ratio of 2,4- and 2,6-DNT was unchanged throughout (65:35 respectively). The isolated yields shown in parenthesis; *c* Mass of zirconium(IV) triflate recovered from each run. The figures in parenthesis indicate the percentage recovery which were not optimised.

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References and notes

1. For a range of reactions catalysed by $Ln(OTf)_3$ see: (a) Marshmann, R. W. *Aldrichimica Acta* **1995**, *28*, 77. (b) Kobayashi, S. *Synlett* **1994**, 689. (c) Engberts, J. B. N. F.; Feringa, B. L.; Keller, E.; Otto, S. *Recl. Trav. Chim. Pays Bas* **1996**, *115*, 457.
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7. A solution of silver(I) triflate (2.05 g, 8.0 mmol) in water (15 mL) was added to a vigorously stirred solution of hafnium(IV) chloride (0.64 g, 2.0 mmol) in water (20 mL). The resulting precipitate of silver chloride was collected by suction filtration (1.10 g, 96% mass recovery) and the colourless filtrate was evaporated to give hydrated hafnium(IV) triflate as a white solid (1.81 g, theoretical anhydrous mass: 1.55g; theoretical mass allowing for hydration = 1.87 g *i.e.* 97% yield): IR (KBr) υ_{max} 3600-2700s, 1619w, 1259vs, 1184m, 1034s, 769w, 644s, 580w, 520m cm^{-1}.
8. Typically a liquid-liquid two-phase system is obtained where the catalyst is solubilised in the 69% nitric acid and a less dense organic phase comprising the substrate and solvent (1,2-dichloroethane).
9. Typical experimental procedure: Nitric acid (69%; 200 μL, 3.0 mmol) was added to a stirred suspension of hafnium(IV) triflate (350 mg, 0.30 mmol, 10 mol%) in 1,2-dichloroethane (2 ml). The suspension dissolved to give a two phase system in which the aqueous phase was the more dense. *o*-Nitrotoluene (354 μL, 3.0 mmol) was added and the stirred mixture was heated at reflux for 24 h. The solution was allowed to cool and partitioned between CH_2Cl_2 and water. The yellow organic phase was dried ($MgSO_4$) and evaporated to give dinitrotoluenes (502 mg, 92%). The pale yellow aqueous phase was evaporated to give hafnium(IV) triflate as a deliquescent off-white solid (385 mg, 98%).
10. When Hafnium(IV) triflate was recycled and re-used for the nitration of *o*-nitrotoluene, an 87% conversion to DNT's was obtained after 24h.