Highly Efficient Catalytic Nitration of Phenolic Compounds by Nitric Acid with a Recoverable and Reusable Zr or Hf Oxychloride Complex and KSF

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Phenolic compounds can be nitrated with 60 % nitric acid (1.2 equiv.) in the presence of catalytic amounts of a Zr or Hf oxychloride complex and montmorillonite KSF to give the corresponding nitrated products in good yields in a heterogeneous catalytic system. The co-catalyst and montmorillonite can be easily recovered and reused in the next batch of nitration. This is a practical process for the nitration of phenolic compounds in a clean way.

Introduction

The replacement of current chemical processing techniques with more environmentally benign alternatives is an increasingly attractive subject.[1] Nitration of aromatic compounds is one of the most important industrial processes[2] and is the subject of a large body of literature.[3] Nitrated phenolic compounds, in particular, are very useful intermediates in the preparation of fine chemicals.[4] Nitration of aromatic compounds typically requires a mixture of concentrated or fuming nitric acid with sulfuric acid, which leads to large amounts of acid waste and added expense.[5] The obvious disadvantages of the commercial manufacturing process currently used has led to a substantial effort to develop viable alternatives, especially by using solid acid catalysts, other sources of NO_2^+, organic nitrating agents, other acids to replace sulfuric acid, etc.[6] However, none of them have found practical industrial uses thus far. Recently, it was reported that lanthanide triflates (l–10 mol-%) [$Ln(OTf)_3$, Ln = Yb, Sc, Y. etc.] can catalyze the nitration of a range of simple aromatic compounds in good to excellent yield in the presence of stoichiometric quantities of 69 % nitric acid; the only by-product is water and the catalyst can be readily recycled by simple evaporation.[7] Moreover, in 2000, Susanta reported a nitration of aromatic compounds using a bismuth (Bi) compound as the nitration reagent and montmorillonite KSF as the catalyst.[8] In our ongoing investigations on the nitration of aromatic compounds, including phenolic substrates,[9,10] we found that $Bi(NO_3)_3$/KSF is a good catalyst in the nitration of phenolic substrates.[10c] In fact, we used $Bi(NO_3)_3$/KSF as a catalyst to nitrate resorcinol and other phenolic compounds in diethyl ether or THF with 60% nitric acid to give good yields of the corresponding nitrated products under mild conditions, although the stability of $Bi(NO_3)_3$/KSF during nitration is still not sufficient because $Bi(NO_3)_3$ itself is a nitration reagent. We also found that the $Bi(NO_3)_3$/KSF catalyst gradually loses its catalytic efficiency during recycling. Moreover, the loss of the active components in the $Bi(NO_3)_3$/KSF catalyst into the water phase occurred during recycling. Encouraged by these findings, we attempted to seek out a more practical process for the nitration of phenolic compounds using stoichiometric or a small excess of nitric acid under mild conditions because the development of environmentally friendly practical procedures for the nitration of aromatic compounds is highly desirable. We describe here a highly efficient catalytic nitration of phenolic compounds in the presence of a small excess of nitric acid (1.2 equiv.) in the presence of a hydrolytically more stable zirconium or hafnium oxychloride complex and montmorillonite KSF.

Results and Discussion

We prepared the zirconium and hafnium oxychloride complexes by hydrolysis of $ZrCl_4$ and $HfCl_4$ with water.[11] Their structures were assigned on the basis of X-ray diffraction data and elemental analysis. An ORTEP representation of the Hf is shown in Figure 1, and the crystal packing in the solid state is shown in Figure 2. The tetranuclear hydroxo Zr^{IV} complex has been well studied by ^{17}O and ^{1}H NMR spectroscopy in aqueous solution and by X-ray crystallography.[12] These interesting tetrameric complexes were used as catalysts in the nitration of phenolic compounds after heating at 120 °C in an oven. With resorcinol as a substrate (1.0 mmol) and the Hf oxychloride complex (1.5 mol-%) and montmorillonite KSF (500 mg) as the cat-

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alyst, we carried out the nitration n the presence of 1.2 equiv. of 60% nitric acid at room temperature in a variety of solvents. The results are summarized in Table 1. As can be seen from Table 1, this nitration process proceeds smoothly in a variety of solvents such as diethyl ether, DME, or THF (Table 1, entries 1, 4, and 5). The mononitrated product **1** was obtained in 66% yield in diethyl ether after 1 h and in 80% yield after 16 h (Table 1, entries 1 and 2). In THF, the yields of **1** reached 68% and 87%, respectively, after the same times (Table 1, entries 3 and 4). With the Zr oxychloride complex (1.5 mol-%) and montmorillonite KSF (500 mg) as the catalyst, under otherwise identical conditions, **1** was obtained in 78% and 86% yields in diethyl ether and THF, respectively (Table 1, values in parentheses in entries 3 and 4). In ethylene glycol dimethyl ether (DME), **1** was obtained in 82% yield after 16 h. However, in dichloromethane or nitromethane the yields of **1** were low (Table 1, entries 6 and 7). The best result was obtained in THF with the Hf oxychloride complex as catalyst.

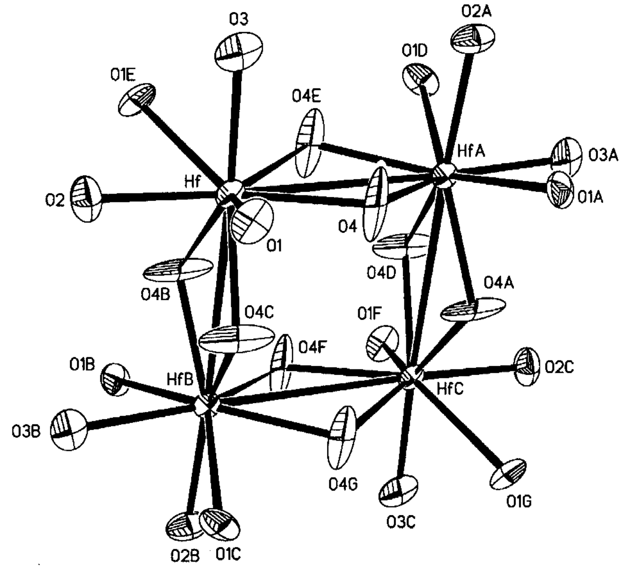


Figure 1. An ORTEP drawing of the hafnium oxychloride complex.

Control experiments indicated that no nitration occurs in the absence of montmorillonite KSF (Table 2, entry 1). At high temperature (under reflux in THF), however, **1** was obtained in 51% yield in the absence of montmorillonite KSF (Table 2, entry 2). In the presence of montmorillonite KSF under reflux, **1** was obtained in 62% yield (Table 2, entry 3). These isolated nitrated products are deeply colored and contain inseparable over-nitration and competitive oxidation products.[9c,9d] The replacement of montmorillonite KSF with other carriers such as SiO_2 and 4-Å molecular sieves gave no catalytic activity at room temperature (Table 2, entries 4 and 5). At high temperature (70 °C), Hf oxychloride complex/SiO_2 gave the nitrated product in 75% yield as a deeply colored product (Table 2, entry 6). The best catalyst for nitration of phenolic substrates at room temperature in THF is therefore Hf oxychloride complex/KSF with a slight excess of nitric acid (1.2 equiv.).

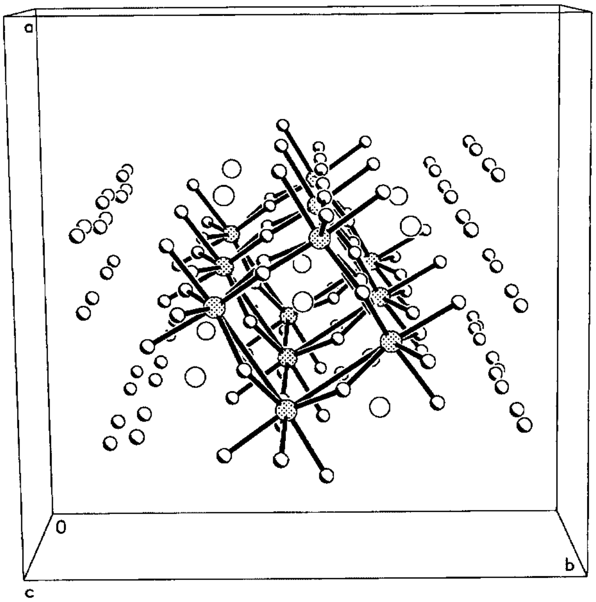
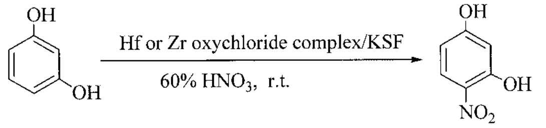


Figure 2. Crystal packing diagram of the hafnium oxychloride complex.

Table 1. Nitration of resorcinol catalyzed by Hf or Zr oxychloride complex (1.5 mol-%)/KSF (500 mg).



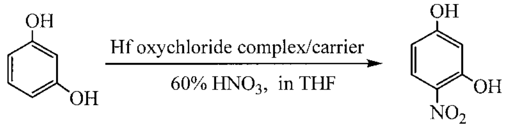
1

entry	solvent	time/h	yield/(%)[a]
1	Et_2O	1.0	66
2	Et_2O	16	80 (78)[b]
3	THF	1.0	68
4	THF	16	87 (86)[b]
5	DME	16	82
6	CH_2Cl_2	16	20
7	CH_3NO_2	16	35

[a] Isolated yields. [b] Zr oxychloride complex was used as a catalyst.

We also compared the effect on this catalytic nitration reaction of using different amounts of montmorillonite KSF and concentrations of nitric acid under otherwise identical conditions. With 60% nitric acid, 500 mg of montmorillonite KSF is required in order to get high yields of **1** (Table 3, entries 1–4), whereas with 20% nitric acid 1.0 g of montmorillonite KSF is required to give the nitrated phenol in 66% yield (Table 3, entries 5 and 6). These results suggest that montmorillonite KSF is a key material in this catalytic nitration process. It is well known that montmorillonite clays like KSF can be very acidic and these clays, when further doped with Lewis acids, are effective catalysts for Friedel–Crafts alkylations or acylations.[13] We believe that the montmorillonite KSF catalyst doped with the Zr or Hf

Table 2. Nitration of resorcinol catalyzed by Hf oxychloride complex (1.5 mol-%)/carrier.



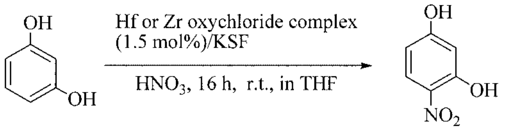
1

entry	carrier	temp.(°C)	yield/(%)[a]
1	–	r.t. (20)	NR
2	–	70	51
3	KSF	70	62
4	SiO_2	r.t.	NR
5	MS 4A	r.t.	NR
6	SiO_2	70	75

[a] Isolated yields.

complex is a strong Lewis acid that is able to activate aromatic compounds towards nitration with 60% nitric acid under mild conditions. When 95% nitric acid was used, the nitration process became faster (Table 3, entries 7 and 8), and the nitration reaction was complete at 0 °C in 80% yield (Table 3, entry 7). Upon increasing the reaction temperature to room temperature (20 °C), however, the yield of nitrated product decreased (Table 3, entry 8). These isolated nitrated products with 95% nitric acid are also deeply colored and also contain inseparable over-nitration and competitive oxidation products.

Table 3. Nitration of resorcinol with different concentrations of nitric acid.



1

entry	percent of nitric acid	temp./(°C)	amount of KSF	yield/(%)[a]
1	60%	20	100 mg	NR
2	60%	20	300 mg	34
3	60%	20	500 mg	87
4	60%	20	700 mg	83
5	20%	20	500 mg	NR
6	20%	20	1000 mg	66
7	95%	0	500 mg	80
8	95%	20	500 mg	65

[a] Isolated yields.

It should be emphasized here that this catalytic nitration is a heterogeneous catalytic process and the Hf oxychloride complex/KSF catalyst can be easily recovered from the reaction mixture by filtration. The catalyst can be reused many times without degradation after it has been reactivated by heating in an oven at 120 °C. The powder XRD scans of montmorillonite KSF and the Hf oxychloride complex are shown in Figures 3 and 4, respectively. The powder XRD analyses of the unused and recovered catalyst shown in Figures 5 and 6, respectively, are essentially identical. We have reused this catalyst ten times with no loss of catalytic activity (Table 4).

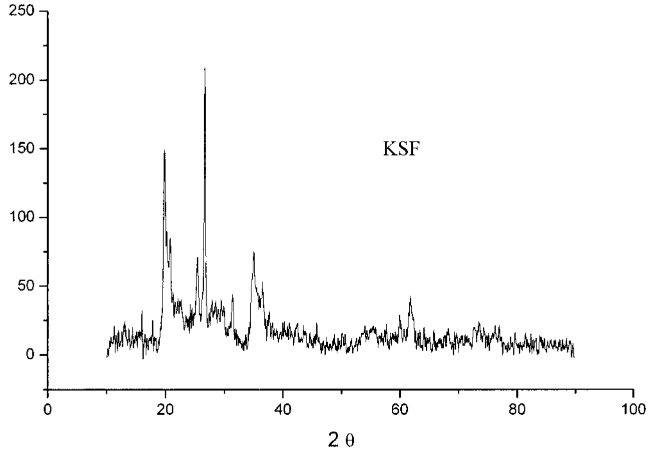


Figure 3. Powder XRD scan of the employed montmorillonite KSF.

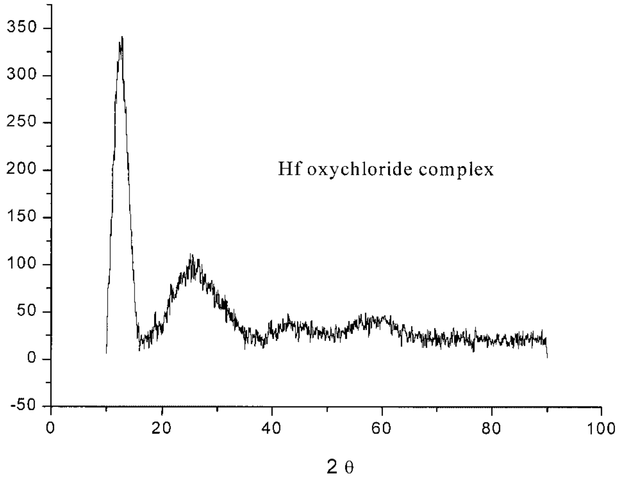


Figure 4. Powder XRD scan of the Hf oxychloride complex.

In order to further clarify the effects of the Hf oxychloride complex/KSF catalyst with other phenolic compounds, control experiments were carried out with Hf oxychloride complex, montmorillonite KSF, and Hf oxychloride complex/KSF as the catalysts in the nitration of *p*-chlorophenol. The results are shown in Table 5 and Figure S1 (see Supporting Information). We found that the nitration of *p*-chlorophenol does not occur in the absence of catalyst or only in the presence of the Hf oxychloride complex with 60% nitric acid in THF (Table 5, entry 1). The Hf oxychloride complex/KSF combination is a better catalyst than montmorillonite KSF alone in this nitration process – the yield of **2b** reached 74% after 3 h with Hf oxychloride complex/KSF (Table 5, entry 3), whereas is was only 29% in the presence of montmorillonite KSF under otherwise identical conditions (Table 5, entry 2). The difference in the catalytic

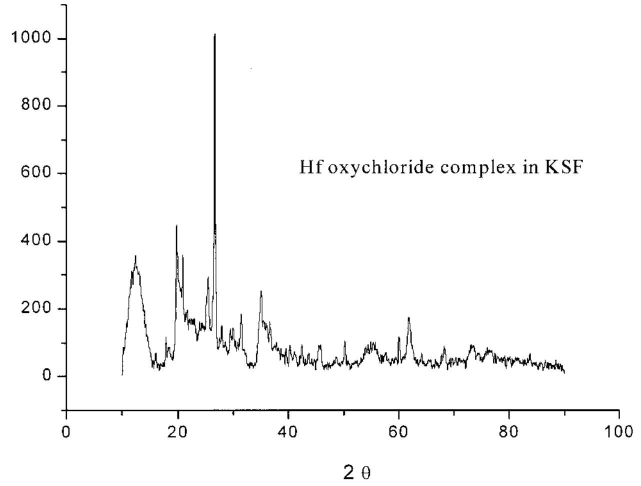


Figure 5. Powder XRD scan of the Hf oxychloride complex in montmorillonite KSF.

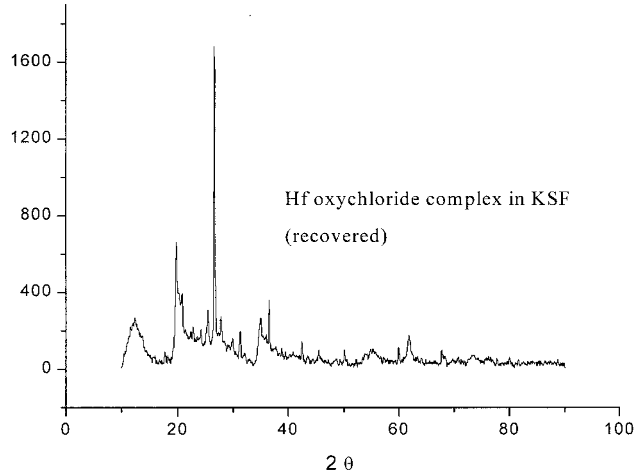
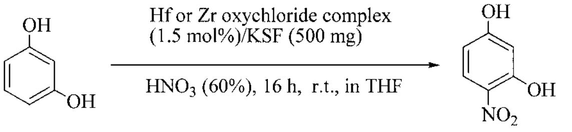


Figure 6. Powder XRD scan of the recovered Hf oxychloride complex in montmorillonite KSF.

Table 4. Recovered catalyst in the nitration of resorcinol.



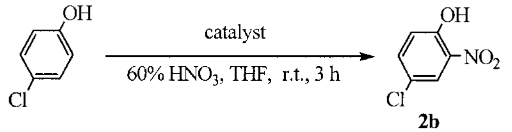
1

entry	yield/(%)[a]	entry	yield/(%)[a]
1	84	6[b]	84
2[b]	87	7[b]	87
3[b]	86	8[b]	88
4[b]	87	9[b]	86
5[b]	85	10[b]	84

[a] Isolated yields. [b] The recoverd catalyst was used.

abilities is remarkable. The yield of **2b** reached 98% after 16 h under mild conditions (Figure S1).

Table 5. Control experiments for the nitration of *p*-chlorophenol.



2b

entry	catalyst	yield/(%)[a] **2b**
1	only Hf oxychloride complex or no catalyst	no reaction
2	only KSF	29
3	Hf oxychloride complex/KSF	74

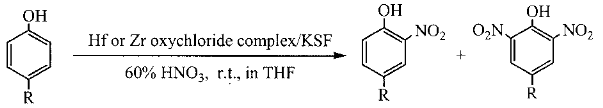
[a] Isolated yields.

This catalytic system is more effective and reusable than $Bi(NO_3)_3$/KSF and Bi_2O_3/KSF in the nitration of phenolic compounds because of its stability against strong hydrolytic reaction conditions in nitration. Based on the above investigations, we decided to use Hf oxychloride/KSF or Zr oxychloride/KSF as a catalyst to nitrate a variety of other phenolic substrates with 1.2 equiv. of 60% nitric acid. This electrophilic aromatic nitration reaction proceeded smoothly for many phenolic substrates; the results are shown in Table 6. With phenol as substrate the yield of nitrophenol was 84% (*para*/*ortho* = 40:44; Table 6, entry 1). If the nitration of phenol is attempted only with nitric acid, the product is a black solid and nitrophenol is not formed. *p*-Chlorophenol, *p*-bromophenol, and *p*-fluorophenol react smoothly to afford the mono-nitrated product in excellent yields (Table 6, entries 2–4). For the nitration of 4-*tert*-butylphenol, two products – mono-nitrated **2e** and dinitrated **3e** – were obtained in a combined 97% yield (Table 6, entry 5). In the case of the activated phenolic compound *p*-methoxyphenol, a single dinitrated product was obtained in 73% yield under identical conditions (Table 6, entry 6). We also examined the nitration of 1,4-dimethoxybenzene under the same conditions. The corresponding product [1,4-dimethoxy-2-nitrobenzene (**2g**)] was obtained in 84% yield. With Zr oxychloride/KSF as the catalyst the corresponding nitrated products were obtained in slightly lower yields under otherwise identical conditions (Table 6, entries 2–7).

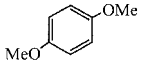
We also examined the nitration reaction of 2-cresol, 3-cresol and 4-cresol with 1.2 equiv. of 60% nitric acid in the presence of Hf oxychloride complex/KSF. In the case of 3-cresol, two mono-nitrated phenolic products (**4i** and **4i′**) were obtained in good yields (Table 7, entry 2). However, in the nitration of 4-cresol and 2-cresol, both mono- (**4h**, **4j**, **4j′**) and dinitrated (**5h**, **5j**) products were obtained in good combined yields (Table 7, entries 1 and 3).

We also investigated the nitration of 2-chlorophenol, 1,2-diethoxybenzene, and 2-ethoxyphenol with 60% HNO_3 (1.2 equiv.) in the presence of Hf or Zr oxychloride complex/KSF under identical conditions. The results are summarized in Table 8. We found that nitration of 2-chlorophe-

Table 6. Nitration of phenolic compounds catalyzed by Hf or Zr oxychloride complex (1.5 mol-%)/KSF (500 mg).

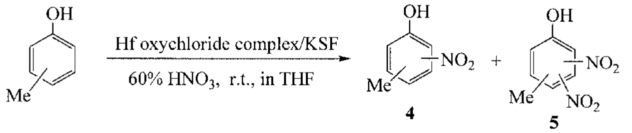


2 3

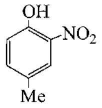
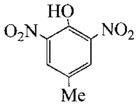
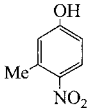
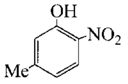
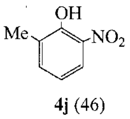
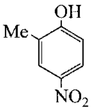
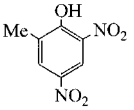
entry	R	time/(h)	yield/(%)[a]	
			2	3
1	H	16	**2a**, **2a'** (84)[b]	–
2	Cl	4	**2b** (98) (98)[e]	–
3	F	16	**2c** (86) (85)[c]	–
4	Br	16	**2d** (84) (81)[e]	–
5	*t*Bu	16	**2e** (40) (44)[e]	**3e** (57) (52)[e]
6	OMe	16	–	**3f** (73)[c] (71)[e]
7		4	**2g** (84)[d] (82)[e]	–

[a] Isolated yields. [b] The products are 2-nitrophenol **2a** (40%) and 4-nitrophenol **2a'** (44%). [c] 2.1 equiv. of nitric acid. [d] The produce is 1,4-dimethoxy-2-nitrobenzene **2g**. [e] Zr oxychloride complex is used as a catalyst.

Table 7. Nitration of cresol catalyzed by Hf oxychloride complex/KSF.



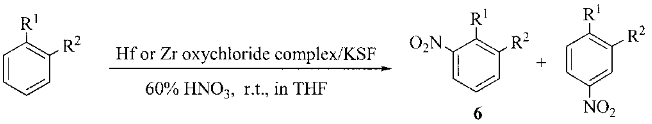
4 5

entry	cresol	time/(h)	yield/(%)[a]	
			4	5
1	4-MeC$_6$H$_4$OH	16	 **4h** (81)	 **5h** (6)
2	3-MeC$_6$H$_4$OH	16	 **4i** (58)  **4i'** (20)	–
3	2-MeC$_6$H$_4$OH	16	 **4j** (46)  **4j'** (36)	 **5j** (4)

[a] Isolated yields.

nol proceeds smoothly within four hours to give the mononitrated products **6a** and **7a** in high yields. Increasing the reaction time reduced the yields of **6a** and **7a** due to overoxidation by nitric acid (Table 8, entries 1 and 2). For nitration of 1,2-diethoxybenzene, the mono-nitrated product **7b** was obtained in 71% yield with 1.2 equiv. of 60% HNO$_3$ and 92% yield with 1.7 equiv. of 60% HNO$_3$ (Table 8, entries 3 and 4). For 2-ethoxyphenol, a similarly good result was obtained with Hf or Zr oxychloride complex/KSF under identical conditions (Table 8, entry 5).

Table 8. Nitration of aromatic compounds catalyzed by Hf or Zr oxychloride complex (1.5 mol-%)/KSF (500 mg).



6 7

entry	R^1	R^2	Time/h	Yield/(%)[a]	
				6	7
1	OH	Cl	4	**6a** (35)	**7a** (62)
2	OH	Cl	16	**6a** (32)	**7a** (44)
3	OEt	OEt	18	trace	**7b** (71)
4[b]	OEt	OEt	18	trace	**7b** (92)
5	OH	OEt	7	**6c** (45) (33)[c]	**7c** (53) (62)[c]

[a] Isolated yield. [b] 60% HNO$_3$ (1.7 equiv.). [c] Zr oxychloride complex was used as a catalyst.

In conclusion, we have found an environmentally friendly practical procedure for the nitration of phenolic compounds under mild conditions. In the presence of Zr or Hf oxychloride complex/KSF catalyst, 60% nitric acid can be used for the nitration of a variety of phenolic compounds to give the nitrated products in good yields. The use of a large excess of concentrated or fuming nitric acid can be avoided with this catalytic system. Moreover, the Zr or Hf oxychloride complex/KSF catalyst can be recovered and reused. This nitration procedure can be carried out in THF, an environmentally safer solvent, without the need for sulfuric acid. The nitration of *p*-chlorophenol under the optimized conditions has been successfully carried out on a one kilogram scale in THF at room temperature. Overall, this method is a safer and environmentally benign way of nitrating phenol compounds. No operational problems are foreseen for a large-scale version of this heterogeneous catalytic nitration process, and technical refinements should further improve the synthetic efficiency.

Experimental Section

General Remarks: Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solutions in CDCl$_3$ with tetramethylsilane (TMS) as internal standard; coupling constants are given in Hz. All the solid compounds reported in this paper gave satisfactory CHN microanalyses (Carlo–Erba 1106 analyzer). Mass spectra were recorded with an HP-5989 instrument and HRMS was measured with a Finnigan MA$^+$ mass spectrometer. Organic solvents were dried by standard methods when necessary. Montmorillonite KSF (C.A.S. number: 1318-93-0) was purchased from Acros Co. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. The orientation of nitration was determined by NMR analysis. Flash column chromatography was carried out using 200–300 mesh silica gel.

Preparation of the Zirconium and Hafnium Oxychloride Complex: $ZrCl_4$ or $HfCl_4$ (500 mg) was hydrolyzed with distilled water (2.0 mL) in a glass vessel. The water was then removed under reduced pressure by heating at 80 °C. Then, the product was dried at 120 °C for 24 h in an oven to give the zirconium or hafnium oxychloride complex as a white solid.

Zirconium oxychloride complex: M.p. $>$ 300 °C, 500 mg, yield: 98%. $Zr_4Cl_5O_{24}H_{24}$: calcd. Cl 18.65; found Cl 18.88 (X-ray crystal structure: see A. Clearfield, P. A. Vaughan, *Acta Crystallogr.* **1956**, *9*, 555).

Hafnium oxychloride complex: m.p. $>$ 300 °C, 487 mg, yield: 96%. $Hf_4Cl_5O_{24}H_{24}$: calcd. Cl 13.64; found Cl 14.99.

A single crystal of this complex was obtained by recrystallization from water. Therefore, this complex contains water in its crystal structure. Empirical formula: $H_{72}Cl_5Hf_4O_{48}$; formula mass: 1731.79; color, cabit: colorless, prismatic; dimensions: $0.366 \times 0.273 \times 0.186$ mm; crystal system: tetragonal; lattice type: primitive; lattice parameters: a = 17.0031(11), b = 17.0031(11), c = 7.6897(7) Å, α = 90°, β = 90°, γ = 90°, V = 2223.1(3) $Å^3$; space group: $P4/mnc$; Z = 2; $D_{\text{calcd.}}$ = 1.909 $g\,cm^{-3}$; F_{000} = 1152; diffractometer: Rigaku AFC7R; residuals: R, Rw: 0.0808, 0.2076. The crystal data have been deposited at Fachinformationszentrum (FIZ) Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, with deposition number CSD-414059.

General Procedure for the Nitration of Phenolic Compounds: Montmorillonite KSF (500 mg) was put into a glass vessel and then heated at 120 °C for 0.5 h under reduced pressure (0.1 Torr) to get rid of the absorbed water. A solution of resorcinol (110 mg, 1.0 mmol) and hafnium compound (20 mg) in THF (or other solvent, 5 mL) was added into the glass vessel. Nitric acid (60%, 0.095 mL, d = 1.3667, 1.2 mmol) was slowly added dropwise and the mixture was stirred for 16 h at room temperature. The reaction mixture was extracted with ethyl acetate or dichloromethane. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc, 10:1) to give the product.

4-Nitroresorcinol (1): Yellow solid, 135 mg, yield 87%. M.p. 117–119 °C. IR (KCl): $\tilde{\nu}$ = 1532, 1397 cm^{-1} (NO_2), 3354, 1255 cm^{-1} (OH). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 6.47 (dd, J = 9.2, 3.4 Hz, 1 H, Ar), 6.52 (d, J = 3.4 Hz, 1 H, Ar), 8.05 (d, J = 9.2 Hz, 1 H, Ar), 10.97 (s, 1 H, ArOH) ppm. MS (EI) m/z = 155 (47.40) [M^+], 125 (100) [M^+ – 30], 97 (94.90) [M^+ – 58], 77 (6.77) [M^+ – 78], 51 (65.02) [M^+ – 104]. $C_6H_5NO_4$: calcd. C 46.46, H 3.25, N 9.03; found C 46.48, H 3.44, N 9.02.

Supporting Information Available: ^1H NMR spectral and analytical data for nitrated products, experimental details, and Figure S1 (yields of nitrated p-chlorophenol vs. time).

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