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C_3-Symmetric Ti(IV) Triphenolate Amino Complexes as Sulfoxidation Catalysts with Aqueous Hydrogen Peroxide

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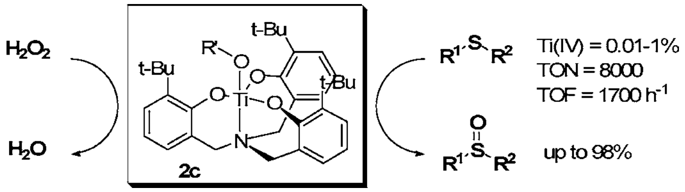
ABSTRACT



The Ti(IV) complex 2c bearing a C_3-symmetric triphenolate amine ligand is an air and moisture tolerant complex that efficiently catalyzes sulfoxidation reactions at room temperature without previous activation (catalyst loading down to 0.01%, TONs up to 8000, TOFs up to 1700 h^{-1}, quantitative yields). Reactions were performed with aqueous hydrogen peroxide as oxidant, which adds value to the methodology from the environmental viewpoint.

One of the current trends in catalyst design is the use of multidentate ligands for complexation of the metal.[1] Advantages include the high stability of the metal complexes, which often allows low catalyst concentrations without loss of catalyst integrity. Second, a nearly complete occupation of all coordination sites of the metal by a single ligand reduces the chances of formation of multimeric and often undefined metal-species under catalytic conditions. The presence of only a single catalytically active species greatly facilitates mechanistic studies and catalyst optimization. While C_2-symmetric bidentate ligands have been extensively used, C_3-symmetric ligands[2] have attracted more attention only recently[3] in spite of their advantages when octahedral complexes are involved in the catalytic process.[2a] We have a longstanding interest in the use of chiral C_3-symmetric Ti(IV)-trialkanolamine complexes **1** as oxidation catalysts (Figure 1).[3b,e,4] In the tetradentate complexes, coordination of Ti(IV) occurs through the three alkoxides and the tertiary amine, giving a high stability to the complex. In the presence of alkyl hydroperoxides these catalysts are able to catalyze the asymmetric oxidation of sulfides with ee values up to 93% and with turnover numbers (TON) up to 1000.[3a] Recently, we also showed that secondary amines are effectively oxidized to nitrones with high chemoselectivities, quantitative yields, and TONs reaching 1400.[3e] The high

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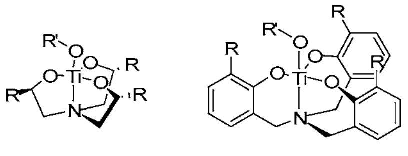


1 R = H, Me, Ph

2a R = H
2b R = Me
2c R = *tert*-Bu

Figure 1. Titanatranes from C_3-symmetric trialkoxyamine (**1**) and triphenolate amine ligands (**2**).

stability of **1** allows the incorporation of the catalysts in polyvinylidene difluoride membranes without affecting their performance even after 5-fold recycling of the catalytic membrane.[5]

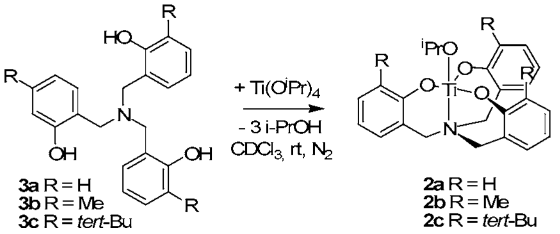
Ti(IV)-tri(phenolate) amino complexes **2** are structurally very similar to **1** when considering the trigonal bipyrimidal coordination geometry of Ti(IV) and the number and type of donor atoms (Figure 1). Because of the higher acidity of phenol compared to alcohol, this should have a beneficial effect on the stability of **2** with respect to **1** and thus allow higher TONs.

In the last years, a substantial number of publications have appeared regarding the synthesis and metal complexation behavior of triphenolate amino ligands **3**. Although complex formation of **3** with a wide variety of transition metals and main group elements (Ti(IV),[6] V (III),[7] V(V),[7] Zr(IV),[8] In-(III),[9] Ga(III),[9] Fe(III),[10] Ta(V),[6g,11] and Si(IV)[12]) has been reported, the number of reports that deal with the catalytic behavior of any of these complexes is very limited and is mainly in the context of polymerization reactions.[6b,d−f,j,7,11b] In fact, for a series of other organic transformations it has been reported that complexes **2** are poor Lewis acid catalysts and that activity is only observed after exchange of the apical isopropoxy ligand for a more labile triflate anion.[6d] V(V) complexes of triphenolate amino ligands have shown catalytic activity in epoxidation reactions, even if they afford very slow reactions (2−3 turnovers per day).[7]

Here we report that the in situ prepared Ti(IV) triphenolate amino complexes are very stable and highly efficient sulfoxidation catalysts which can be used without the need for prior activation. In addition, the catalysts are even highly active in the competitive solvent MeOH, using aqueous hydrogen peroxide as the primary oxidant. These reaction conditions are unprecedented for this kind of catalyst and make them far superior to the Ti(IV)-trialkanolamine complexes **1**.

Triphenolamines **3a**−**c** where prepared with a new synthetic strategy, recently developed by us, based on a 3-fold reductive amination of the corresponding substituted salicyl aldehyde.[13] Reaction of **3a**−**c** with Ti(O*i*-Pr)$_4$ in CHCl$_3$ under nitrogen yielded the corresponding mononuclear, C_3-symmetric Ti(IV) complexes **2a**−**c**[14] and free *i*-PrOH (3 equiv) is released in solution. Formation of the complexes is fast and quantitative, as confirmed by ^{1}H NMR spectra recorded a few minutes after mixing of the reagents. (Scheme 1).

Scheme 1. Synthesis of the Ti(IV) Complexes **2a**−**c**



3a R = H
3b R = Me
3c R = *tert*-Bu

2a R = H
2b R = Me
2c R = *tert*-Bu

The observed complexation behavior is in complete accordance with the structurally similar complexes described in the literature, which contain additional substituents para to the phenolic moiety.[6a,b,d,e]

Complex **2c** is air and moisture tolerant whereas complexes **2a** and **2b** tend to form aggregates in the presence of traces of water or after long standing in solution. This behavior is in agreement with previous studies by Kol et al. that have already shown that there is a significant dependence of the stability of complexes **2** on the steric size of the peripheral R-groups.[6a]

Stimulated by the remarkably stability of complex **2c** even in the presence of large excesses of water,[6a,g] we decided to

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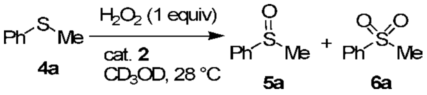
(14) For related titanatranes the racemization barriers, determined via VT NMR experiments (nitrobenzene-d_5), were found to be $\Delta G^{\ddagger} = 65.7$−74.4 kJ mol^{-1} (ref 6a). For a related phosphite-based systems see also ref 3a.

study the catalytic activity of **2a**−**c** in sulfoxidation reactions using aqueous hydrogen peroxide as oxidant. The use of hydrogen peroxide is highly advantageous, since it is nontoxic and inexpensive and yields water as the only side product.[15] A series of V(V)[16] and Fe(III)[17]/chiral Schiff base-based catalysts have been recently reported to be very effective in H_2O_2 activation for highly stereoselective sulfoxidations. On the contrary, only a few polynuclear Ti(IV) μ-oxo preformed complexes have been described that can activate H_2O_2 or its urea complex.[18]

To work under homogeneous conditions and follow the reaction course via ^{1}H NMR, the experiments were performed in methanol-d_4, using a 1% catalyst loading and a 1:1 ratio of thioanisole and H_2O_2 (30% in water) (Table 1 and Figure 2).

Table 1. Oxidation of Thioanisole by Aqueous Hydrogen Peroxide Catalyzed by **2a**−**c**[a]



entry	complex	$t_{1/2}$ (min)[b]	TOF (h^{-1})[c]	convn (%)[d]	SO:SO_2[d]
1	**2a**	4	740	92	92:8
2	**2b**	<3	1700	90	90:10
3	**2c**	17	170	96	98:2

[a] Reactions were carried out in CD_3OD at 28 °C with a 1:1 molar ratio of substrate/H_2O_2 and 1% catalyst at an initial substrate concentration of 0.5 M. [b] Time required for a 50% decrease of the initial concentration of oxidant. [c] Determined at 20% conversions. [d] Determined by ^{1}H NMR (CD_3OD, 300 MHz) and quantitative GC analysis on the crude reaction mixture after complete oxidant consumption (iodometric test).

We were pleased to find that in the presence of all complexes **2** thioanisole **4a** was smoothly and quantitatively oxidized to the corresponding sulfoxide and sulfone in high yields, good selectivities, and short reaction times (30−60 min).

The most active complex was **2b** affording TOFs = 1700 h^{-1} (Table 1, entry 2), followed by **2a** and **2c**. Even if catalyst **2c** (R = *t*-Bu) gave the slowest reaction (Table 1, entry 3), much better sulfoxide/sulfone selectivities were obtained (98:2) and the catalyst did not decompose in solution under turnover conditions. Signals relative to the catalyst could be observed by ^{1}H NMR spectroscopy until the end of the process, when relatively large amounts of water are present (450 equiv), the solution remaining clear until the end of the reaction.

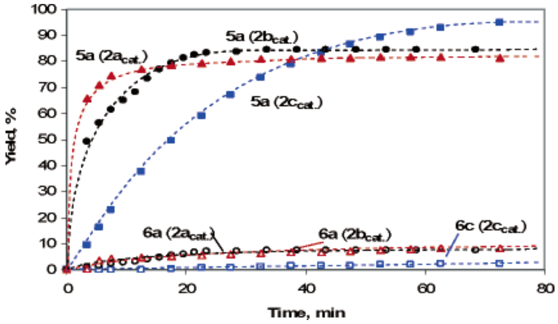


Figure 2. Oxidation of thioanisole (**4a**) to methyl phenyl sulfoxide (**5a**) and methyl phenyl sulfone (**6a**) with aq H_2O_2 (35%) in CD_3-OD at 28 °C catalyzed by **2a**−**c** (1%): $[\mathbf{4a}]_0 = [H_2O_2]_0 = 0.5$ M. Reaction catalyzed by **2a**: **5a** (●), **6a** (○). Reaction catalyzed by **2b**: **5a** (▲), **6a** (△). Reaction catalyzed by **2c**: **5a** (■), **6a** (□). Yields were determined by ^{1}H NMR; internal standard was 1,2-dichloroethane.

On the other side, in the reactions catalyzed by **2a** and **2b** extensive decomposition of the catalysts was observed after addition of aqueous hydrogen peroxide. After consumption of the oxidant no signals relative to the catalysts could be detected by ^{1}H NMR and the formation of a white sluggish gel was observed, hampering the possibility to increase the TONs and recycle the catalysts.

Due to the higher stability under reaction conditions of **2c** we decided to investigate its performance in more detail. The effect of substrate concentration, solvent, oxygen source, and catalyst loading on the oxidation of thioanisole **4a** is reported in Table 2. Working in the presence of 1% of catalyst in methanol, substrate concentrations were varied from 0.08 to 0.8 M (Table 2, entries 1−4).[19] Quantitative conversion of the oxidant was observed in all cases and in the more concentrated reaction, $[\mathbf{4a}]_0 = 0.8$ M, the reaction was complete after only 70 min (Table 2, entry 4).

The reaction was also carried out in other less coordinating solvents like acetone and acetonitrile (Table 2, entries 5 and 6). In both cases much slower reactions were obtained with only 50% conversion into the products, due to partial H_2O_2 and catalyst decomposition.

The catalyst loading was then decreased. Catalyst amount could be reduced down to 0.1% without affecting the efficiency and the SO/SO_2 ratio (Table 2, entry 7), while a further lowering (0.01%) led to significantly lower conversions (Table 2, entry 9). However, much better SO/SO_2 ratios were obtained (basically only sulfoxide **5a**) giving a total TON = 8000. The use of the urea−hydrogen peroxide adduct (Table 2, entry 8) gave a much higher selectivity toward the formation of the sulfoxide, although the reaction rate was sensibly slowed down.

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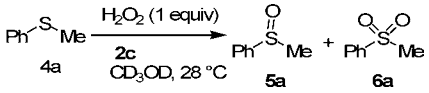
[19] Reaction with a larger catalyst loading (i.e. 10%) could not be performed due to the low solubility of **2c** in the reaction mixture.

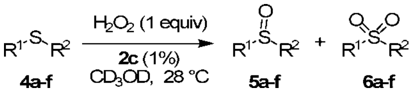
Table 2. Oxidation of Thioanisole (**4a**) by Aqueous Hydrogen Peroxide Catalyzed by **2c** and the Effect of Concentration, Solvent, Oxidant, and Catalyst Loading



entry	$[\mathbf{4a}]_0$ (M)	**2c** (%)	$t_{1/2}$ (h)[b]	convn (%)[c]	**5a**:**6a**[c]
1	0.08	1	2	92	94:6
2	0.2	1	1.6	90	93:7
3	0.5	1	0.3	96	98:2
4	0.8	1	0.2	94	95:5
5[d]	0.8	1		44	93:7
6[e]	0.8	1	3.3	52	>99:1
7	0.8	0.1	0.8	86	96:4
8[f]	0.8	0.1	24	89	99:1
9	0.8	0.01	5	79	99:1

[a] Reactions carried out at 28 °C with a 1:1 molar ratio of substrate/aq H_2O_2. [b] Time required for a 50% decrease of the initial concentration of oxidant. [c] Determined by ^1H NMR (CD_3OD, 300 MHz) and quantitative GC analysis on the crude reaction mixture after total oxidant consumption (iodometric test). [d] Reaction performed in acetone-d_6. [e] Reaction performed in acetonitrile-d_3. [f] Urea−hydrogen peroxide adduct was used as oxidant.

Table 3. Oxidation of Sulfides **4a**−**f** by Aqueous Hydrogen Peroxide Catalyzed by **2c**[a] (1%)



#	sub	R^1	R^2	convn (%)[b]	**5**:**6**[b]	yield (%)[d]
1	**4a**	Ph	Me	96	98:2	92
2[c]	**4a**	Ph	Me	97	98:2	93
3	**4b**	*p*-Tol	*n*-Bu	95	95:5	89
4	**4c**	Ph	Bu	91	93:7	84
5	**4d**	*n*-Bu	*n*-Bu	92	93:7	83
6	**4e**	*p*-MeO-C_6H_4	Me	94	94:6	86
7	**4f**	*p*-NO_2-C_6H_4	Me	77	85:15	61

[a] Reactions were carried out in CD_3OD at 28 °C using a molar ratio substrate/H_2O_2 1:1 and 1% catalyst at $[\mathbf{4a}-\mathbf{f}]_0 = 0.5$ M on 0.5 mmol scale. [b] Determined by ^1H NMR (CD_3OD, 300 MHz) and quantitative GC analysis on the crude reaction mixture after total oxidant consumption (iodometric test). [c] Reaction carried out on 7 mmol scale. [d] Isolated yields in sulfoxide **5**, based on the substrate, after radical chromatography.

The scope of the reaction was explored under the optimized conditions (Table 3). A series of arylalkyl and dialkyl sulfides were oxidized by using the reaction conditions of Table 2, entry 3. In analogy with what we observed for **4a**, in all cases the oxidation with H_2O_2 afforded a fast and quantitative conversion into the oxidized products with high selectivity for the formation of the sulfoxides. The reaction was also performed on preparative scale, giving comparable yields in isolated products (entry 2, Table 3). The effect of the introduction of electron-donating and electron-withdrawing substituents in the aryl ring was also studied in some detail (Table 3, entries 6 and 7). The introduction of an electron-withdrawing group like a nitro led to a decrease in the selectivity for sulfoxide formation, ([**5f**]:[**6f**] = 85:15) while no significant differences were obtained in the presence of a MeO-group.

These results seem to indicate that, in the second oxidation step from sulfoxide to sulfone with electron-poor substrates like **5f**, a concomitant metal-promoted nucleophilic oxidation of the sulfinyl moiety may be occurring, in analogy with what we previously observed with the titanatrane systems **1** with alkyl hydroperoxides.[20] Currently we are examining this aspect in more detail.

In summary, we have reported that the C_3-symmetric Ti(IV) complexes **2** are effective catalysts for the sulfoxidation reactions without the need of isolation of the complex and prior activation. Thanks to the high stability of the complex **2c** the inexpensive and nontoxic aqueous hydrogen peroxide can be used as primary oxidant, with catalyst loadings down to 0.01% and TONs up to 8000 and high selectivity in the sulfoxide production. More detailed studies on the use of different oxidants and on the mechanism of the reaction and the characterization of the species involved in the process are currently under investigation and will be reported elsewhere.

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Supporting Information Available: Procedures and spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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