

Synthesis, Characterization and Catalytic Activity of a Tungsten(VI) Amino Triphenolate Complex

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Abstract Synthesis, characterization and catalytic activity of a novel tungsten(VI) amino triphenolate complex have been investigated. In particular, a tungsten(VI) amino triphenolate complex has been synthesized and tested in the oxidation of sulfides and cyclooctene, using hydrogen peroxide as terminal oxidant. The catalyst has proved to be air and water tolerant, also showing a good efficiency in terms of yields and selectivity. Moreover, an upgrade of our previous ligand synthesis is herein reported. The new developed procedure allows to obtain the triphenolamine in large scale without the use of chromatography for the intermediates purification.

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Graphical Abstract



Keywords Tungsten · Epoxidation · Sulfoxidation · Polydentate ligand · Hydrogen Peroxide

1 Introduction

The use of W(VI) based catalysts for the epoxidations of olefin dates back to the late 1940s and since that time has proved to be useful for the oxidation of a variety of carbon–carbon double bonds [1–4]. Heterogeneous W(VI) compounds, W-oxido cluster complexes, and tungstate WO₄^{2–} derivatives gained significant interest in oxidation catalysis, mainly with H₂O₂ as oxidizing agent [5–8]. In this specific case, it is assumed that the actual oxidant specie is a η^2 -peroxotungsten complex. Pertungstic acid and pertungstates are known to give highly stable aqueous solutions, and the tungstate ion itself has been shown to be quite superior to molybdate and vanadate in epoxidation reactions with H₂O₂, since the 'transition metal ion-induced decomposition' of hydrogen peroxide is much slower. Moreover, many Mo(VI)-based catalysts reported in the literature have shown to be inactive in the activation of H_2O_2 [9, 10]. To date, tungsten(VI) complexes are probably the best transition-metal catalysts for epoxidation reactions of alkenes with hydrogen peroxide, even if sometimes the epoxides formed tend to hydrolyze to the corresponding diols.

One of the most known system for epoxidation, using W(VI) and H₂O₂, was reported by Venturello [11]. His work showed that a mixture of tungstate and phosphate, in the presence of a tetraalkylammonium salt as phase transfer agent, catalyzed olefin epoxidation with H₂O₂ in a biphasic 1,2-dichloroethane/water medium. Since its discovery in 1983, several evolutions of tungsten catalysts have been reported [12-22]. Indeed, the literature regarding homogeneous mononuclear tungsten(VI) complexes as oxidation catalysts is constantly increasing. Among the different molecular catalysts, metal complexes bearing amine and diamine bis-phenolate ligands have attracted considerable attention over past decades in olefin polymerization and ring-opening polymerization of lactones and lactides [23, 24]. There are few reports on tungsten complexes with this family of ligands, and their application in epoxidation catalysis has been only recently investigated [25].

In our group there is a longstanding interest in the use of polydentate ligands such as trialkanolamines, [26-31] tripicolylamines (TMPA) [32-37] and triphenolamines (TPA) [38–49]. The latter have been extensively used by us with d_0 metals. In detail, we have been interested in the use of Ti(IV), V(V) and Mo(VI) complexes in oxidation reactions. More recently, we have extended the study also to W(VI) for the study of haloperoxidation reactivity [47]. The W(VI) complex showed a remarkable stability under the harsh reaction conditions required for the haloperoxidation, namely large excess of hydrogen peroxide and acid. Here we report the synthesis of a similar complex, which was tested in sulfoxidation and epoxidation reactions, which affords significant results using hydrogen peroxide as terminal oxidant. Within the course of this study, we also optimize our previously reported [48] synthetic methodology for the triphenolamine synthesis via reductive amination, avoiding chromatographic purifications within the different steps. This novel procedure has allowed the preparation of tris-(2-hydroxy-3-t-butylbenzyl)amine 5 in multigram scale.

2 Results and Discussion

2.1 Gram scale Synthesis of the Ligand

In our previous study, the haloperoxidation reactivity catalyzed by a W(VI) aminotriphenolate complex, was

investigated using *tris*-(2-hydroxy-3,5-di-*t*-butylbenzyl) amine as ligand [47]. This ligand was chosen in order to avoid a possible halogenation of the ligand aromatic ring positions during the haloperoxidation process. However, the required "protection" of the para position resulted in a complex characterized by high molecular weight and by a low solubility in polar solvents. For these reasons, in order to explore the oxidation of other substrates, we decided to use a catalyst bearing a ligand with a single *ortho-t*-butyl substituent on each aromatic ring.

Ligand 5 was prepared using the synthetic strategy developed in our group, based on a threefold reductive amination of the corresponding substituted salicylic aldehyde 2 [48]. The reductive amination needs to be performed on the protected aldehyde 2, which is obtained from the corresponding phenol 1 in good yield after ortho-formylation and O-benzylation. This synthetic route, which has been used successfully in the past years, offers the possibility to access to a large class of functionalized ligand in high yields. However, this method requires flash chromatographic purification steps and therefore the overall process can be carried out on only a few grams' scale. To overcome this problem, we improved the purification steps of the intermediates in order to avoid the use of chromatography (Scheme 1). The most critical purification step is the isolation of the aldehyde 2, which is obtained as an oil after O-benzylation. To overcome the chromatographic purification, aldehyde 2 was transformed into the corresponding bisulfite adduct 3, by mixing it with a solution of NaHSO₃ and ethanol. The bisulfite adduct 3 is water soluble and can be easily separated from the reaction mixture. Basification of the aqueous phase allows the re-obtaining of aldehyde 2 which was back-extracted with CH₂Cl₂. Via this method, it was possible to obtain 74 g (0.29 mol, 60% yield) of aldehyde 2, which was then used for the subsequent two steps. The following steps, reductive amination and deprotection of phenol group via Pd/C catalysed hydrogenolysis, can be carried out in multigram scale without problem and the product purifications can be performed by crystallization.

2.2 Synthesis of the Tungsten Complex

Tungsten(VI) complex **6** can be synthesized by reaction of WOCl₄ with *tris*-(2-hydroxy-3-*tert*-butylbenzyl)amine **5** (Scheme 2). The methodology, originally developed by Lehtonen for similar systems, [49–52] was slightly modified using an excess of triethylamine as base for deprotonation of the three phenol moieties. For this purpose, in a glove-box, the solid WOCl₄ was dissolved in methanol in the presence of stoichiometric amounts of **5** and five equivalents of triethylamine. The resulting mixture was stirred at room temperature overnight obtaining an intense yellow colored solution. After addition of 4 N HCl solution,



Scheme 2 Synthesis of complex 6 starting from ligand 5

extraction with dichloromethane, and purification by flash chromatography (dichloromethane/methanol) gave complex **6** as a yellow orange solid (65% yield). The formation of the mononuclear six coordinated complex **6**, was confirmed by ESI-MS and ¹H NMR studies. The ESI-MS spectrum, in negative mode, shows an isotopic pattern consistent with a W-dioxido complex bearing an amino triphenolate ligand (m/z=716). Tungsten complex **6** ¹H NMR spectrum is coherent with an octahedral, six coordinated species. In fact, three different set of signals can be detected for the diastereotopic benzylic protons: two doublets and one singlet, as expected for an octahedral geometry.

2.3 X-ray Crystal Structure of Complex 6

Suitable crystals for X-ray diffraction were obtained by crystallization of complex 6 in acetonitrile. The molecular structure is reported in Fig. 1. The metal center exhibits a distorted octahedral geometry achieved by the oxygen atoms of three phenoxy groups, a hydroxyl group, the central nitrogen atom of the ligand and an oxido moiety. The bond distances between the metal and oxygen atoms



Fig. 1 Molecular structure of 6 together with crystallization solvents $(H_2O \text{ and } CH_3CN)$. Thermal ellipsoids reported at the 30% probability level

in the equatorial plane are in the narrow range among 1.888(3)–1.923(3) Å. As expected, the W– O_{oxido} bond distance is the shortest (1.707(3) Å) and it is consistent with a W=O double bond. The longest distance is the W–N (2.438(4) Å) in agreement with the *trans* influence exerted by the oxido group [53]. Indeed, the W atom lies out of the equatorial plane by 0.31 Å and it is directed toward the oxido group.

The presence of water molecules of crystallization favors the formation of a supramolecular dimer in the solid state, due to the presence of four hydrogen bonds between the hydroxido groups and the water molecules (Fig. 2).



Fig. 2 Supramolecular dimer formed by two 6 complexes and two water molecules of crystallization. Only the hydrogen atoms involved into the HBs are shown. Symmetry code = 1-x; -y; 1-z

2.4 Catalytic Activity of 6: Sulfoxidation and Epoxidation

The use of multidentate amino triphenolate ligands has already shown to lead high stable metal complexes, allowing lower catalyst concentrations (without losing catalyst integrity) and high TONs and TOFs in the oxidation of different substrates. Starting from this background, W(VI) complex 6 was tested as catalysts for oxidation. Even though no significant catalytic activity was observed in the oxidation of secondary and tertiary amines, alcohols, and hydroxylation of ethyl benzene, very good results were achieved in the oxidation of sulfides using H_2O_2 as the terminal oxidant. In fact, complex 6 can activate hydrogen peroxide already at room temperature, affording quantitative yields of the corresponding sulfoxides with catalyst loading down to 1% (Table 1). This behavior is rather diverse from what we reported for the corresponding Mo(VI) based system, for which a reasonable reactivity was observed only at 60 °C [42]. In Fig. 3a comparison between the activity of complex 6 (1 mol%) with *tert*-butyl hydroperoxide (TBHP) and hydrogen peroxide toward oxidation of methyl-p-tolyl sulfide (sulfoxide formation) is reported. Higher yields in much shorter reaction time were obtained using hydrogen peroxide, as reported already with other W-based catalysts [54-58].

The scope of the reaction was explored with a series of sulfides and data are reported in Table 1. High yields and high sulfoxide/sulfone selectivity were obtained for all the tested substrates bearing either aromatic or aliphatic substituents. The sulfoxides have been obtained as main products with very high sulfoxide/sulfone (SO:SO₂) selectivity in the majority of the cases (Table 1).

The epoxidation reaction using *cis*-cyclooctene 8 with hydrogen peroxide/TBHP as oxidant in different solvents was also explored (Table 2). In all the cases, the formation



Fig. 3 Oxidation of methyl-*p*-tolyl sulfide with H_2O_2 (filled circle) and TBHP (filled square). Reaction conditions: 25 °C; [sulfide]₀ = [oxidant]₀ = 0.1 M; [**6**] =0.001 M; solvent=CD₃CN (with H_2O_2) or CD₃Cl (with TBHP)

of cyclooctene oxide was observed but much faster and higher chemical yields were obtained using acetonitrile as solvent and hydrogen peroxide as primary oxidant.

While substrate conversion up to 45% was obtained using TBHP, with hydrogen peroxide in acetonitrile epoxide yields up to 94% were obtained using a two-fold excess of oxidant. However, under these reaction conditions, we observed discoloration of the reaction mixture at the end of the reaction, that we associated to catalyst decomposition. Catalyst instability, under turn over conditions, could derive by a partial oxidation of the ligand followed by hydrolytic/oxidative decomposition of the metal complex itself.

3 Conclusions

In this communication, we have reported the synthesis of a novel W(VI) aminotriphenolate complex and its characterization. Catalytic studies showed that W(VI) TPA complex **6** can act as effective catalyst for oxygen transfer reactions using hydrogen peroxide as terminal oxidant. In particular, high yields and selectivities were observed for sulfoxidation of a series of sulfides and also *cis*-cyclooctene was oxidized to the corresponding epoxide with yields up to 94%. Further studies are needed to elucidate the nature of the active species in the oxidation process and the real origin of the catalyst decomposition in order to increase its performances.

Table 1	Oxidation of sulfides	7 a–g by 1	35% aqueo	ous hydrogen	perox-
ide cataly	(sed by 6 (1 mol%)				

Substrate		Yield (%) ^a	SO:SO ₂ ^a
1	Ta S	98	99:1
2	O ₂ N 7b	99	86:14
3	MeO 7c	89	99:1
4	C S C 7d	72	99:1
5	N N H 7e	99	90:10
6	C o Tf	99	75:25

Reaction conditions: $25 \,^{\circ}$ C; $[sulfide]_0 = [H_2O_2]_0 = 0.1 \text{ M}$ [6] = 0.001 M in CD₃OD

^aTotal yield determined by ¹H NMR analysis on the crude reaction mixture after complete oxidant consumption (iodometric test)

Table 2 Oxidation of *cis*-cyclooctene 8 at 60 °C catalysed by 6 (5 mol%)

ROOH	[ROOH] M	Solvent	t _{1/2} (min)	9 Yield (%) ^a
ТВНР	0.1	CDCl ₃	_	45
H_2O_2	0.1	CD ₃ OD	240	57
H_2O_2	0.1	CD ₃ CN	33	63
H_2O_2	0.2	CD ₃ CN	15	94

Effect of the oxidant and solvent, Reaction conditions: $60 \,^{\circ}\text{C}$; [8]=0.1 M; [6]=0.005 M

^aDetermined by ¹H NMR analysis on the crude reaction mixture after complete oxidant consumption (iodometric test)

3.1 Experimental Section

3.1.1 X-ray Crystallography

A summary of data collection and structure refinement for **6** is reported in the Supporting Info. Single crystal data were collected with a *Bruker Smart Breeze* area detector diffractometer, Mo K α : $\lambda = 0.71073$ Å. The unit cell parameters were obtained using 60 ω -frames of 0.5° width and scanned from three different zone of reciprocal lattice. The intensity data were integrated from several series of exposures frames (0.3° width) covering the sphere of reciprocal space. CCDC 1531503 contain the supplementary crystal-lographic data for this paper. A crystallographic table summarizing the structural refinement is reported in the supporting information.

Synthesis of Tungsten(VI) complex (6). In a glove-box under nitrogen atmosphere, $WOCl_4$ (136 mg, 0.40 mmol), NEt₃ (260 μ l, 2 mmol) and the ligand precursor 5 (200 mg, 0.39 mmol) were mixed in dry and degassed methanol (50 mL). The solution was left stirring at room temperature for 18 h and the resulting intense orange-red solution was filtered through a short pad of silica (or in a very short silica column) using dichloromethane/methanol (95:5) as eluent. The fractions collected were evaporated, 20 mL of HCl (1 N) were added and the mixture was stirred at room temperature for 20 min. An extraction with 20 mL of CH₂Cl₂ was then performed and the organic fraction was evaporated to afford complex 6 as an intense orange-yellow solid; yield: 65%. Crystals suitable for X-ray diffraction were obtained by recrystallization of the solid in CH₃CN. ¹H NMR (300 MHz, CD₃CN) δ 7.17 (m, 3 H, ArH), 6.97 (d, J=7.42 Hz, 2 H, ArH), 6.86 (d, J=7.43 Hz, 1 H, ArH), 6.64 (t, J=7.59 Hz, 2 H, ArH), 6.53 (t, J=7.58 Hz, 1 H, ArH), 3.97 (d, J=13.3 Hz, 2 H, NCH₂), 3.67 (s, 2 H, NCH₂), 3.57 (d, J=13.3 Hz, 2 H, NCH₂), 1.50 (s, 9 H), 1.28 (s, 18 H). ¹³C NMR (62.9 MHz, CDCl₃): $\delta = 158.85$ (C), 141.57 (C), 140.56 (CH), 128.67 (CH), 128.14 (C), 126.87 (CH), 60.65 (CH) 35.66 (CH), 35.20 (CH), 30.60 (C), 30.31 (C); ESI-MS: m/z = 716.2 (M⁻); elemental analysis (CHN): calculated for $C_{33}H_{43}NO_5W + CH_3CN$: C=55.42%, H=6.11%, N=3.69%; found: C 55.18%, H 6.43%, N 3.55%.

3.1.2 General Procedure for Catalytic Oxidations

In a screw-cap NMR tube, a solution of catalyst **6** (1 or 5 mol % in CDCl₃, CD₃OD or CD₃CN), internal standard (1,2-dichloroethane, DCE, 0.1 M), substrate (0.1 M) and oxidant (35% aqueous H_2O_2 , or 80% *tert*-butyl hydroperoxide in water, 0.1 M) were mixed up to a final volume of 0.6 mL. The experimental conditions of each catalytic oxidation are reported in Fig. 3 and Tables 1 and 2.

Concentrations of reagents and products, were monitored by integration of ¹H NMR resonances in respect of the internal standard DCE (3.78 ppm).

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