DOI: 10.1002/adsc.201000496

Molybdenum(VI) Amino Triphenolate Complexes as Catalysts for Sulfoxidation, Epoxidation and Haloperoxidation

Francesco Romano,[a] Anthony Linden,[b] Miriam Mba,[a] Cristiano Zonta,[a,*] and Giulia Licini[a,*]

[a] Università di Padova, Dipartimento di Scienze Chimiche, via Marzolo 1, 35131 Padova, Italy
Fax: (+34)-049-827-5239; e-mail: cristiano.zonta@unipd.itgiulia.licini@unipd.it
[b] Institute of Organic Chemistry University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

Received: June 25, 2010; Revised: September 10, 2010; Published online: November 17, 2010

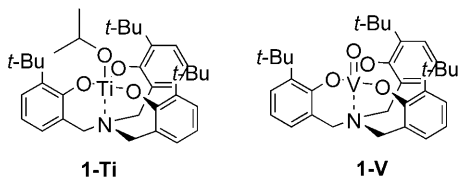
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000496.

Abstract: Two molybdenum(VI) complexes bearing a C_3 symmetrical amino tris-*tert*-butylphenolate ligand have proved to be air- and water-tolerant catalysts that efficiently catalyse, in high yields and selectivity, the oxidation of sulfides, olefins and halides. In particular high turnover frequencies and turnover numbers (TOF and TON) have been obtained for the cyclooctene epoxidation (catalyst loading down to 0.05%, TONs up to 88,000 and TOFs up to 7500 h^{-1}).

Keywords: epoxidation; haloperoxidation; homogeneous catalysis; molybdenum; sulfoxidation

In transition metal chemistry, ligands are used to control the environment of the metal. In particular, ligands can modulate the electronic and steric properties around the metal centre, thereby controlling its catalytic properties. While a considerable number of ligands are known, few of them are able to express their reactivity across different metals. These ligands, which have been defined as "privileged", are BINOls, BINAPs, Josiphos, Salens and *Cinchona* alkaloids and outstanding applications are known in stereoselective catalysis.[1] The possibility of developing "unique" classes of ligands able to form stable complexes with a variety of metals, while also being catalytically active towards a variety of reactions is of considerable interest. In this scenario, amino triphenolate ligands have attracted attention due to their ability to form stable metal complexes with a wide variety of transition metals and main group elements.[2] However, while a substantial number of publications regarding their synthesis and coordination chemistry are available, the catalytic performances of the corresponding metal complexes have only recently been reported. Catalytic studies have focused mainly on polymerization reactions,[3] Diels–Alder reactions[4] and oxygen transfer processes.[5] Regarding the latter, we have recently shown that the amino tris-*tert*-butylphenolate titanium(IV) complex **1-Ti** (Scheme 1) has noteworthy catalytic properties in the oxidations of sulfides and secondary amines,[5a,b] while the corresponding vanadium(V) complex **1-V** effectively catalyses the oxidation of sulfides and halides, and has proved to be a structural and functional model of vanadium-dependent haloperoxidases.[5c] What emerged from these studies is that while the tetradentate nature of the ligand is important for the stability and geometry of the complex, the presence of *tert*-butyl substitutions *ortho* to the phenol group has an impressive influence on its stability under turnover conditions. During the catalytic cycle, the *tert*-butyl groups shield the metal from the formation of multinuclear species and they prevent the hydrolytic degradation, thus increasing the catalyst life.

More recently, we extended our investigation into the catalytic properties of amino tris-*tert*-butylphenolate metal complexes to molybdenum(VI). In fact, Mo(VI) complexes are in general known to be effective catalysts in oxygen transfer reactions.[6] In particular, a wide interest in these catalysts arose in the 1960s when ARCO and Halcon reported on the

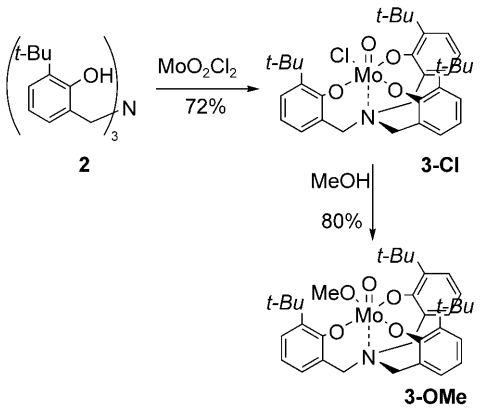


Scheme 1. Ti(IV) and V(V) amino tris-*tert*-butylphenolate complexes.

olefin epoxidation catalysed by Mo(VI) compounds in the homogenous phase.[7] However, a major drawback for the existing Mo(VI)-based catalysts is the formation, under turnover conditions, of polymeric species, which are much less active catalysts.[8] An optimal candidate for overcoming this problem is an amino tris-*tert*-butylphenolate metal complex of Mo(VI). This complex should be able to maintain the mononuclear nature of the catalyst, while the stability towards hydrolysis should allow for low catalyst loadings. Herein we report on the synthesis and characterisation of two new amino tris-*tert*-butylphenolate molybdenum(VI) complexes and their catalytic performance in the oxidation of sulfides, olefins and halides using hydrogen peroxide or alkyl peroxides as terminal oxidants.

Tris-*tert*-butylphenolamine **2** was prepared using a synthetic strategy developed in our group which is based on a three-fold reductive amination of the corresponding substituted salicyl aldehyde.[9] The molybdenum complexes were synthesised using a methodology recently reported by Lehtonen for similar systems which uses MoO_2Cl_2 as the metal source.[10] After dissolving solid MoO_2Cl_2 with stoichiometric amounts of **2** in toluene, the resulting mixture was kept at reflux temperature to obtain an intense purple solution (Scheme 2). Molybdenum complex **3-Cl** was purified by flash chromatography on SiO_2 using toluene as eluent. Displacement of the chloro ligand in favour of a methoxy group can easily be achieved by refluxing complex **3-Cl** in methanol in the presence of one equivalent of triethylamine. Compound **3-OMe** was also purified using flash chromatography.

The formation of mononuclear, six-coordinated complexes was confirmed by ESI-MS and ^{1}H NMR studies. In particular, an octahedral coordination geometry can be established by symmetry considerations on the basis of VT ^{1}H NMR spectra.[11] At room temperature, both **3-Cl** and **3-OMe** show a ^{1}H NMR spectrum with three set of signals for the diastereotopic benzylic protons, consistent with a C_S average symmetry of the system caused by fluxional processes.[2] At lower temperatures (−60 °C) the benzylic proton resonances resolve into five sets of signals, consistent with a C_1 symmetry of the complexes. The octahedral coordination geometry has been confirmed by the X-ray crystal structure of **3-Cl** (Figure 1). In the mononuclear complex, the nitrogen atom donor is located *trans* to the terminal oxo group.



Scheme 2. Synthesis of the molybdenum(VI) complexes **3-Cl** and **3-OMe**.

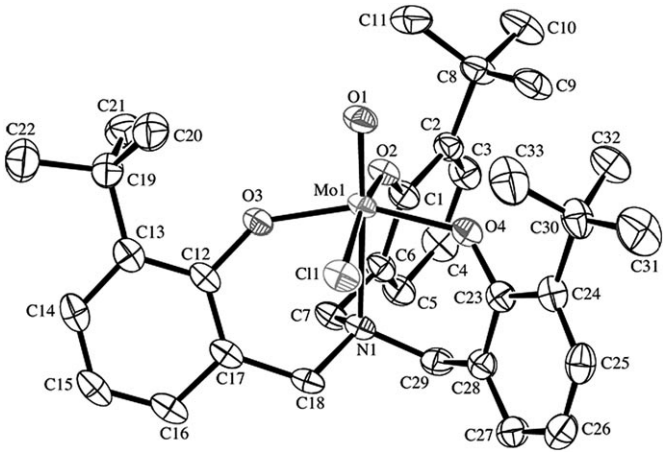


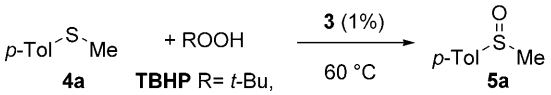
Figure 1. Displacement ellipsoid representation of the molecular structure of **3-Cl**.

The reactivity of complexes **3-Cl** and **3-OMe** has been investigated in a series of reactions, namely the oxidation of sulfides, olefins and halides. The oxidations were performed using as terminal oxidants alkyl peroxides (cumyl hydroperoxide **CHP** or *tert*-butyl hydroperoxide **TBHP**) and the more environmentally friendly hydrogen peroxide.

Sulfide oxidations were performed under homogeneous conditions and the reaction course was followed by ^{1}H NMR. *p*-Tolyl methyl sulfide **4a** was used as test substrate and 1% of complexes **3-Cl** and **3-OMe** as catalysts (Table 1). In the presence of both complexes sulfide **4a** was oxidized selectively to the corresponding sulfoxide **5a** in high yields and with complete consumption of the oxidant. The best results, in terms of reactivity, were obtained using the **3-Cl**/H_2O_2 system (Table 1, entry 5).

However, the results obtained are not comparable with the ones obtained with **1-Ti** and **1-V** as far as the reaction rates are concerned. Furthermore, the major application of molybdenum(VI)-based catalysts is the epoxidation of alkenes, oxidations that neither **1-Ti** nor **1-V** catalysts are able to perform.[12] Epoxidation reactions were carried out using cyclooctene **6a** as a test substrate, in $CDCl_3$ or CD_3OD depending on the oxidant employed, and the reaction courses were followed *via* ^{1}H NMR and GC analysis (Table 2). Both **3-OMe** and **3-Cl** complexes catalyse the oxygen transfer to cyclooctene in the presence of alkyl peroxides,

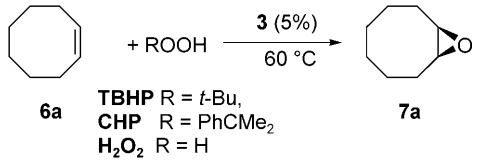
Table 1. Oxidation of *p*-tolyl methyl sulfide **4a** at 60 °C. Effect of the catalyst and oxidant.[a]



Entry	ROOH	Solvent	Catalyst	$t_{1/2}$ [min][b]	**5a** Yield [%][c]
1	**CHP**	$CDCl_3$	**3-Cl**	47	90
2	**CHP**	$CDCl_3$	**3-OMe**	60	91
3	**TBHP**	$CDCl_3$	**3-Cl**	30	83
4	**TBHP**	$CDCl_3$	**3-OMe**	135	65
5	H_2O_2	CD_3OD	**3-Cl**	12	99
6	H_2O_2	CD_3OD	**3-OMe**	20	99

[a] *Reaction conditions:* 60 °C, $[\mathbf{4a}]_0 = [ROOH]_0 = 0.1$ M, [**3**] = 0.001 M.
[b] Time required for a 50% decrease of the initial concentration of sulfide.
[c] Determined by ^{1}H NMR analysis on the crude reaction mixture after complete oxidant consumption (iodometric test).

Table 2. Oxidation of cyclooctene **6a** at 60 °C catalysed by **3**. Effect of the catalyst and oxidant.[a]



Entry	ROOH	Solvent	Catalyst	$t_{1/2}$[b] [min]	**7a** Yield [%][c]
1	**CHP**	$CDCl_3$	**3-Cl**	80	95
2	**CHP**	$CDCl_3$	**3-OMe**	130	80
3	**TBHP**	$CDCl_3$	**3-Cl**	52	99
4	**TBHP**	$CDCl_3$	**3-OMe**	105	83
5	H_2O_2	CD_3OD	**3-Cl**	–	–
6	H_2O_2	CD_3OD	**3-OMe**	–	–

[a] *Reaction conditions:* 60 °C, $[\mathbf{6a}]_0 = [oxidant]_0 = 0.1$ M, [**3**] = 0.005 M.
[b] Time required for a 50% decrease of the initial concentration of olefin.[c] Yield determined by ^{1}H NMR analysis on the crude reaction mixture after complete oxidant consumption (iodometric test). Complete selectivity towards the epoxide was observed.

while they failed when hydrogen peroxide was used in methanol solution. The best results, as far as reactivity and chemical yields are concerned, were obtained using the **3-Cl/TBHP** system, and the catalytic activity for this system has been explored more in detail (Table 3).

The catalyst loading could be reduced down to 0.01% without affecting the efficiency of the system.

Table 3. Oxidation of cyclooctene **6a** at 60 °C. Effect of the catalyst loading.[a]

Entry	$[\mathbf{6a}]_0$	**TBHP** (1 equiv.)		**TBHP** (2 equiv.)	
		% cat	Yield [%][b]	% cat	Yield [%][b]
1	0.1	5	99	5	99
2	1	0.5	99	0.5	99
3	1	0.05	94	0.05	99
4	1	0.01	94	0.01	97
5	1	0.001	67	0.001	88

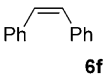
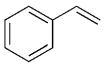
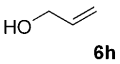
[a] Reactions were carried out at 60 °C in $CDCl_3$. In the absence of catalyst conversions lower than 10% are observed after 24 h.
[b] Yield determined by ^{1}H NMR analysis on the crude reaction mixture after 24 h. Complete selectivity towards the epoxide was observed.

A further lowering to 0.001% led to lower yields with one equivalent of **TBHP**, however high yields can be restored using two equivalents of oxidant. Under the best conditions (Table 3, entry 5), a TON of 88,000, with a TOF around 7500 h^{-1} were obtained. These values are significantly high, especially if compared to other epoxidation catalysts,[6] confirming an exceptional stability and reactivity of the catalyst under turnover conditions.

The scope of the reaction was explored towards different olefins using one and two equivalents of **TBHP** (Table 4). The different olefins are generally oxidised in fairly high yields. While complete conversion to the corresponding epoxide is observed for cyclooctene **6a** and methylcyclohexene **6b** (Table 4, entries 1 and 2), lower conversions, even if with very good selectivities, are observed for linear olefins such as 1-hexene **6c** and 1-octene **6d** (Table 4, entries 3 and 4). In these cases, the use of oxidant in excess (2 equivalents) allows the conversions to be increased up to 75%, maintaining high selectivities (Table 4, entries 3 and 4). Comparable conversions are obtained for *trans*-stilbene **6e**, *cis*-stilbene **6f**, allyl alcohol **6h** and styrene **6g**, even if, in these cases, the corresponding epoxides are more reactive and unstable under the reaction conditions and they generally undergo consecutive ring opening, thereby decreasing the selectivity of the process. Furthermore, *trans*- and *cis*-stilbene (**6e** and **6f**) afford only the *trans*- and *cis*-epoxide, respectively, indicating that this is a stereospecific concerted oxygen transfer process.

Due to the remarkable stability shown by complexes **3** under turnover conditions, we also tested their catalytic performances in haloperoxidation reactions, where the catalyst requires to be stable under aqueous highly acidic conditions.[13] Catalyst **3-OMe** was examined in order to avoid contamination with the chloride ligand present in **3-Cl**. Reactions were performed under Butler's standard reaction conditions.[14] This translates into the use of tetrabutylam-

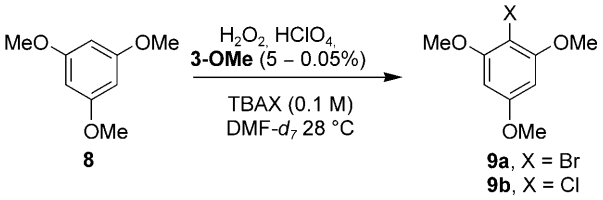
Table 4. Oxidation of olefins at 60 °C using **3-Cl/TBHP**.[a]

Entry	Substrate	**TBPH** (1 equiv.) Conv. [%]	Sel. [%]	**TBPH** (2 equiv.) Conv, [%]	Sel. [%]
1	 **6a**	99	99	99	99
2	 **6b**	99	99	99	99
3	 **6c**	50	95	77	95
4	 **6e**	45	97	73	96
5	 **6e**	78	52	86	75
6	 **6f**	73	54	75	98
7	 **6g**	75	44	72	26
8	 **6h**	58	70	76	80

[a] *Reaction conditions:* 60 °C, $[\mathbf{6a–h}]_0 = 0.1$ M, $[\mathbf{TBHP}]_0 = 0.1$ or 0.2 M, $[\mathbf{3\text{-}Cl}] = 0.005$ M.

[b] Conversion and selectivity determined by ^{1}H NMR analysis on the crude reaction mixture (DCE as internal standard).

Table 5. Formation of **9a** or **9b** as a function of $[H^+]$, $[H_2O_2]$, and of Mo(VI) catalysts (**3-OMe** or MoO_2Cl_2).[a]



Entry	X	**Cat** (%)	$[H_2O_2]_0$ [mM]	$[H^+]_0$ [mM]	$t_{1/2}$[b] [min]	Yield[c] [%]
1	Br	**3-OMe** (5)	8	3	<5	90
2	Br	**3-OMe** (5)	20	20	57	88
3	Br	**3-OMe** (5)	40	20	24	99
4	Br	**MoO_2Cl_2** (5)	40	20	24	99
5	Br	–	20	20	–	11
6	Br	**3-OMe** (0.5)	20	20	80	90
7	Br	**3-OMe** (0.05)	20	20	1440	50
8	Br	**MoO_2Cl_2** (0.05)	20	20	–	38
9	Cl	**3-OMe** (5)	40	20	–	20

[a] *Reaction conditions:* DMF-d_7, 28 °C using $[\mathbf{8}]_0 = 20$ mM, $[\mathbf{TBAX}]_0 = 0.1$ M, X = Br or Cl.

[b] Time for a 50% decrease of $[H_2O_2]_0$.

[c] Based on the limiting agent $HClO_4$ and determined by ^{1}H NMR (DCE as internal standard) on the crude reaction mixture after total oxidant consumption (iodometric test).

monium bromide (**TBABr**) and tetrabutylammonium chloride (**TBACl**) as halogen sources in the presence of 1,3,5-trimethoxybenzene **8** as test substrate. These reaction conditions allow for a comparison with previously developed catalysts.

The bromination reaction proceeds with high yields based on the limiting reagent (H^+) when a 5% loading of **3-MeO** was used (Table 5, entries 1–3). While the time required for the reaction is longer than that with the corresponding vanadium complex **1-V**, yields are generally higher. Catalyst loading could be decreased down to 0.05% (Table 5x, entry 7) and the product **9a** could be obtained in 50% yield with TON = 1000. The metal complex MoO_2Cl_2 is also an active catalyst, but it displays much lower reactivity than **3-OMe** (Table 5, entries 4 and 8), especially when used at low catalyst loadings. Reactions were also carried out in the presence of chloride ions. Slow chlorination of **8** could be achieved (**3-OMe** = 5%) obtaining **9b** in 20% yields after two days (Table 5, entry 9). The obtained yields indicate that the system is catalytically active and can perform four catalytic cycles. Our previous results on **1-V** showed that this system could also oxidise chloride ions, but only a single catalytic cycle was obtained.[5c] This result represents the first example of oxidative chlorination catalysed by a molybdenum(VI) complex.

In conclusion, tris-*tert*-butylphenolate molybdenum complexes **3-Cl** and **3-OMe** have proven to be active catalysts in the oxidation of sulfides, olefins and halides using alkyl hydroperoxides or hydrogen peroxide as primary oxidants. Conversion of the primary oxidant is, in most of the cases, quantitative and the optimisation of the reaction conditions allows the attainment of the products in good yields and with high turnover numbers, especially in the case of olefin epoxidation (TON up to 88,000 and TOF up to 7500 h^{-1} for cyclooctene).

These results, in combination with the results reported previously for the corresponding Ti(IV) and V(V) complexes, reinforce the knowledge that amino tris-*tert*-butylphenolate is a versatile ligand for the formation of very stable and active metal catalysts. Moreover, the same ligand, in combination with three different metals Ti(IV), V(V) and Mo(VI), offers the

possibility of preparing complexes which are able to oxidise efficiently a large range of functional groups.

Experimental Section

Synthesis of Mo(VI) Complex 3-Cl

Milled MoO_2Cl_2 (200 mg, 1 mmol) and the ligand precursor **2** (503 mg, 1 mmol) were mixed with toluene (50 mL) and the stirred suspension was heated to reflux for 18 h. The resulting intense purple solution was filtered through a short pad of silica and evaporated to afford complex **3-Cl** as a violet solid; yield: 500 mg (80%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.40$ (dd, 1H, $J = 7.8$ and 1.4 Hz, ArH), 7.34 (dd, 2H, $J = 7.8$ and 1.8 Hz, ArH), 7.15 (dd, 3H, $J = 9.2$ and 1.4 Hz, ArH), 6.98 (m, 3H, ArH), 3.99 (d, 2H, $J = 11.5$, NCH_2), 3.6 (d, 2H, $J = 21.1$ Hz, NCH_2), 3.49 (s, 2H, NCH_2), 1.59 (s, 9H), 1.47 (s, 18H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 159.84$ (C), 141.40 (C), 140.4 (CH), 128.71 (CH), 128.11 (C), 125.61 (CH), 60.23 (CH) 35.45 (CH), 35.43 (CH), 30.54 (C), 30.40 (C); ESI-MS: $m/z = 672.2$ ($M + Na^+$), 650.2 ($M + H^+$), 614.3 ($M - Cl^-$); elemental analysis (CHN): calculated for $C_{33}H_{42}NO_4ClMo$: C 61.16%, H 7.00%, N = 2.16%; found: C 61.64%, H 6.93%, N 2.18%.

Synthesis of Mo^{VI} Complex 3-OMe

Complex **3-Cl** (100 mg, 0.15 mmol) was dissolved in methanol and triethylamine (42 μL, 0.30 mmol) was added. The solution was stirred for three hours at reflux temperature. The resulting dark red solution was filtered through a short pad of silica and evaporated to afford complex **3-OMe** as a dark red solid; yield: 70 mg (72%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.34$ (dd, 1H, $J = 7.8$ and 1.4 Hz, ArH), 7.27 (dd, 2H, $J = 7.8$ and 1.4 Hz, ArH), 7.03 (dd, 2H, $J = 7.8$ and 1.4 Hz, ArH), 6.98 (dd, 3H, $J = 7.4$ and 1.8 Hz, ArH), 6.86 (m, 3H, ArH), 4.07 [s, 3H, $O(CH_3)$], 3.82 (d, 2H, $J = 13.3$ Hz, NCH_2), 3.58 (s, 2H, NCH_2), 3.47 (d, 2H, $J = 13.3$ Hz NCH_2), 1.59 [s, 9H, $C(CH)_3$], 1.43 [s, 18H, $C(CH)_3$]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 158.85$ (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: $m/z = 646.2$ ($M + H^+$), 614.3 ($M - MeO^-$); elemental analysis (CHN): calculated for $C_{34}H_{45}NO_5Mo$: C 63.45%, H 7.04%, N 2.18%; found: C 63.92%, H 6.96%, N 2.21%.

General Procedure for Monitoring the Oxidation Reactions Catalyzed by 3-Cl/3-OMe

A screw-cap NMR tube was charged with a solution of the Mo(VI) catalyst **3** (in $CDCl_3$, CD_3OD or DMF-d_6), the internal standard (1,2-dichloroethane, DCE), the oxidant (35% aqueous H_2O_2, 80% cumene hydroperoxide or 80% *tert*-butyl hydroperoxide) and the substrate were added up to a final volume of 0.6 mL. The NMR tube was maintained at 60 °C. Concentrations of reagents and products, were monitored by integration of ^{1}H NMR resonances in respect of the internal standard DCE (3.78 ppm).

Typical Epoxidation Procedure with 3-Cl/TBHP

In a 25-mL screw-cap vial, under nitrogen, complex **3-Cl** (0.05 mmol) was dissolved in 10 mL of DCE followed by TBHP (1.0 or 2.0 mmol) and, after 30 min, by the substrate (1.0 mmol). The solution was heated at 60 °C and the reaction course was monitored *via* TLC and GC-MS. After the disappearance of the oxidant (iodometric test), the solvent was removed under vacuum and the reaction mixture was purified directly *via* radial chromatography over silica gel (gradient: ethyl ether/petroleum ether). Products were identified by comparison of ^{1}H NMR and mass spectral data with those reported in the literature (**6a**,[15a] **6b**,[15a] **6c**,[15a] **6d**,[15a] **6e**,[15b] **6f**,[15b] **6g**,[15a] **6h**[15c]).

Single Crystal X-Ray Structure Determination

Compound **3-Cl·CHCl$_3$** (obtained from $CHCl_3$): $C_{33}H_{42}ClMoNO_4 \cdot CHCl_3$, $M = 767.43$, space group: $P2_1/n$ (monoclinic), $a = 9.4045(1)$ Å, $b = 19.1507(2)$ Å, $c = 19.9729(1)$ Å, $\beta = 98.7715(5)°$, $V = 3555.10(6)$ Å^3, $Z = 4$, μ(Mo $K\alpha$) = 0.705 mm^{-1}, $D_x = 1.434$ g cm^{-3}, $2\theta_{(max)} = 55°$, $T = 160$ K, 88965 measured reflections, 8148 independent reflections, 6837 reflections with $I > 2\sigma(I)$, refinement on F^2 with SHELXL97, 407 parameters, $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0439, $wR(F^2)$ [all data] = 0.1155, goodness of fit = 1.059, $\Delta\rho_{max} = 1.88$ e Å^{-3}. All measurements were made on a Nonius KappaCCD area-detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and an Oxford Cryosystems Cryostream 700 cooler. The asymmetric unit contains one molecule of **3-Cl** and one molecule of chloroform. The crystals tend to lose solvent in the air and collapse to a powder. The non-hydrogen atoms were refined anisotropically. All of the H atoms were placed in geometrically calculated positions and refined by using a riding model. The largest peak and hole of residual electron density are in the vicinity of a solvent Cl atom and is attributed to crystal quality deterioration caused by partial loss of solvent. CCDC 772695 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We acknowledge support of Fondazione Cassa di Risparmio di Padova e Rovigo (F.R.), Assegni di ricerca 2006 (M.M.) (Università di Padova), PRIN 2008 (MIUR), PRAT 2009 (Università di Padova) and COST, Action D40 'Innovative Catalysis – New Processes and Selectivities'.

References

[1] a) M. Bandini, P. G. Cozzi, A. Umani-Ronchi, *Pure. Appl. Chem.* **2001**, *73*, 325–329; b) T. P. Yoon, E. N. Jacobsen, *Science* **2003**, *299*, 1691–1693.
[2] G. Licini, M. Mba, C. Zonta, *Dalton Trans.* **2009**, 5265–5277.
[3] a) Y. Kim, G. K. Jnaneshwara, J. G. Verkade, *Inorg. Chem.* **2003**, *42*, 1437- 1447; b) S. Gendler, S. Segal, I.

Goldberg, Z. Goldschmidt, M. Kol, *Inorg. Chem.* **2006**, *45*, 4783–4790; c) A. J. Chmura, C. J. Chuck, M. G. Davidson, M. D. Jones, M. D. Lunn, S. D. Bull, M. F. Mahon, *Angew. Chem.* **2007**, *119*, 2330–2333; *Angew. Chem. Int. Ed.* **2007**, *46*, 2280–2283; d) A. J. Chmura, M. G. Davidson, C. J. Frankis, M. D. Jones, M. D. Lunn, *Chem. Commun.* **2008**, *11*, 1293–1295; e) A. J. Chmura, D. M. Cousins, M. G. Davidson, M. D. Jones, M. D. Lunn, M. F. Mahon, *Dalton Trans.* **2008**, *11*, 1437–1443.

[4] a) S. D. Bull, M. G. Davidson, A. L. Johnson, D. E. J. E. Robinson, M. F. Mahon, *Chem. Commun.* **2003**, 1750–1751; b) S. D. Bull, M. G. Davidson, A. L. Johnson, M. F. Mahon, D. E. J. E. Robinson, *Chem. Asian J.* **2010**, *5*, 612–620.

[5] a) M. Mba, L. J. Prins, G. Licini, *Org. Lett.* **2007**, *9*, 21–24; b) C. Zonta, E. Cazzola, M. Mba, G. Licini, *Adv. Synth. Catal.* **2008**, *350*, 2503–2506; c) M. Mba, M. Pontini, S. Lovat, C. Zonta, G. Bernardinelli, E. P. Kündig, G. Licini, *Inorg. Chem.* **2008**, *47*, 8616–8618; d) P. Axe, S. D. Bull, M. G. Davidson, M. D. Jones, D. E. J. E. Robinson, W. L. Mitchell, J. E. Warren, *Dalton Trans.* **2009**, *46*,10169–10171; e) M. Mba, L. J. Prins, C. Zonta, M. Cametti, A. Valkonen, K. Rissanen, G. Licini, *Dalton Trans.* **2010**, *39*, 7384–7392.

[6] a) C. D. Nunes, M. Pillinger, A. A. Valente, J. Rocha, A. D. Lopes, I. S. Gonçalves, *Eur. J. Inorg. Chem.* **2003**, 3870–3877; b) J. C. Alonso, P. Neves, M. J. P. da Silva, S. Quintal, P. D. Vaz, C. Silva, A. A. Valente, P. Ferreira, M. J. Calhorda, V. Felix, M. G. B. Drew, *Organometallics* **2007**, *26*, 5548–5556; c) S. Gao, P. Neves, B. Monteiro S. M. Bruno, S. S. Balula, A. A. Valente, F. A. Almeida Paz, M. Pillinger, C. Sousa, J. Klinowski, C. Freire, P. Ribeiro-Claro, I. S. Gonçalves, *J. Mol. Catal. A:* **2007**, *270*, 185–194; d) C. C. L. Pereira, S. S. Balula, F. A. A. Paz, A. A. Valente, M. Pillinger, J. Klinowski, I. S. Gonçalves, *Inorg. Chem.* **2007**, *46*, 8508–8510; e) S. Gago, P. Neves, B. Monteiro, M. Pessêgo, A. D. Lopes, A. A. Valente, F. A. Almeida Paz, M. Pillinger, J. Moreira, C. M. Silva, I. S. Gonçalves, *Eur. J. Inorg. Chem.* **2009**, 4528–4537; f) P. Neves, S. Gago, C. C. L. Pereira, S. Figueiredo, A. Lemos, A. D. Lopes, I. S. Gonçalves, M. Pillinger, C. M. Silva, A. A. Valente, *Catal. Lett.* **2009**, *132*, 94–103; g) F.-L. Chai, H.-L. Su, X.-Y. Wang, J.-C. Tao, *Inorg. Chim. Acta* **2009**, *362*, 3840–3844; h) A. Capapè, A. Raith, F. E. Kühn, *Adv. Synth. Catal.* **2009**, *351*, 66–70; i) A. Capapè, A. Raith, E. Herdtweck, M. Cokoja F. E. Kühn, *Adv. Synth. Catal.* **2010**, *352*, 547–556; j) A. Günyar, F. E. Kühn, *J. Mol. Catal. A:* **2010**, *319*, 108–113.

[7] a) F. E. Kühn, M. Groarke, É. Bencze, E. Herdtweck, A. Prazeres, A. M. Santos, M. J. Calhorda, C. C. Romão, I. S. Gonçalves, A. D. Lopes, M. Pillinger, *Chem. Eur. J.* **2002**, *8*, 2370–2383; b) D. V. Deubel, G. Frenking, P. Gisdakis, W. A. Herrmann, N. Rösch, J. Sundermeyer, *Acc. Chem. Res.* **2004**, *37*, 645–652.

[8] F. E. Kühn, A. M. Santos, I. S. Gonçalves, C. C. Romão, A. D. Lopes, *Appl. Organomet. Chem.* **2001**, *15*, 43–50.

[9] L. J. Prins, M. Mba Blázquez, A. Kolarović, G. Licini, *Tetrahedron Lett.* **2006**, *47*, 2735–2738.

[10] a) A. Lehtonen, R. Sillanpää, *Polyhedron* **2007**, *26*, 5293–5300; b) E. Lauréna, H. Kiveläa, M. Hänninenb, A. Lehtonen, *Polyhedron* **2009**, *28*, 4051–4055.

[11] See Supporting Information.

[12] Amino tris-*tert*-butylphenolate vanadium(V) complexes have shown poor styrene epoxidation activity (4–5 turnovers/day): S. Groysman, I. Goldberg, Z. Goldschmidt, M. Kol, *Inorg. Chem.* **2005**, *44*, 5073–5080.

[13] a) V. Conte, B. Floris, P. Galloni, A. Silvagni, *Adv. Synth. Catal.* **2005**, *347*, 1341–1344; b) A. Podgoršek, M. Zupan, J. Iskra, *Angew. Chem.* **2009**, *121*, 8576–8603; *Angew. Chem. Int. Ed.* **2009**, *48*, 8424–8450.

[14] a) R. de La Rosa, M. J. Clague, A. Butler, *J. Am. Chem. Soc.* **1992**, *114*, 760–761; b) M. J. Clague, N. L. Keder, A. Butler, *Inorg. Chem.* **1993**, *32*, 4754–4761.

[15] a) E. G. Ankudey, H. F. Olivo, T. L. Peeples, *Green Chem.* **2006**, *8*, 923–926; b) M. W. C. Robinson, A. M. Davies, R. Buckle, I. Mabbett, S. H. Taylor, A. E. Graham, *Org. Biomol. Chem.* **2009**, *7*, 2559–2564; c) J. M. Palomo, R. L. Segura, C. Mateo, M. Terreni, J. M. Guisan, R. Fernández-Lafuente, *Tetrahedron: Asymmetry* **2005**, *16*, 869–874.

