Vanadium Catalyzed Synthesis of Cyclic Organic Carbonates

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Vanadium complexes bearing easily synthesized, differently functionalized salen and salphen ligands were prepared and tested for their ability to catalyze the cycloaddition of carbon dioxide to epoxides resulting in cyclic organic carbonates. The reactivity of the prepared catalysts dramatically increases when a coordinating hydroxyl group is present as a substituent in the organic epoxide. The commercially available [VO(acac)$_2$] complex was used as reference compound, and, in this case, we found that V$_{10}$O$_{26}$·(NBu$_4$)$_4$ was formed during the catalytic reactions. This compound, characterized by X-ray diffraction analysis, is likely the active catalyst, and it results in significantly better yields of cyclic carbonates compared to those obtained with Schiff base containing vanadyl complexes. The high activity of the mixed polyoxo vanadyl-vanadate complex marks it as a powerful catalyst within the context of CO$_2$ fixation chemistry.

Introduction

The synthesis of organic (poly)carbonates has attracted considerable attention because of the potential uses of this class of compound in various consumer-based products, such as batteries and aircraft windows.[1] From a sustainability point of view, current processes for the synthesis of cyclic carbonates suffer from several disadvantages. They often involve harsh reaction conditions and unfavorable reagents, such as the highly toxic reagent phosgene.[2] A much greener alternative synthesis for cyclic carbonates involves the highly atom-economical reaction of CO$_2$ with epoxides; for this reaction, transition metal catalysis has been extensively explored.[3] Typically, a Lewis acid metal complex is combined with a nucleophilic co-catalyst, which fulfills a number of important requirements such as mutual tolerance, high compatibility, and stability under a wide range of conditions. Despite the extensive studies of (transition) metal catalyzed cyclic carbonate synthesis, the discovery of catalysts able to operate under mild (ambient) conditions remains a major academic challenge.[4]

From a sustainability point of view, the choice of catalyst is extremely important; it has to be catalytically active under mild conditions, relatively non-toxic, and, ideally, accessible from renewable sources. A large number of studies have been reported regarding the use of Schiff base ligands, such as salen [1,2-bis-(salicylideneamino)-ethane] or salphen [1,2-bis-(salicylideneamino)-benzene] as ligands for metal complexes comprising Cr^{III}, Co^{III}, Al^{III}, Sn$^{II/IV}$, Cu^{II}, and Zn^{II} metal ions in the context of organic carbonate synthesis.[5] The use of Schiff base ligands presents a number of advantages among which are their ease of synthesis, the simple electronic and steric modulation, and the versatility in their complexation behaviors, which allow the generation of many metal complexes with a variety of properties.[6] The choice of metal, apart from economical reasons, is also dictated by its potential toxicity, affecting the overall sustainability of the process.[7]

Vanadium is an abundant and relatively non-toxic metal.[8] It is also known to act as a Lewis acid catalyst, especially in complexes with high-valent V^{IV} or V^{V} metal centers. Reports of vanadium-mediated oxidation of organic substrates such as olefins, thioethers, amines, and phosphines, using a number of oxidizing agents, have been published.[9] Lee and co-workers reported that a simple and commercially available vanadium trichloride catalyst was able to catalyze the reaction between a variety of terminal epoxides/cyclohexene oxide and carbon dioxide.[10] Unfortunately, though, this required elevated temperatures (90–120 °C) and pressures (1.5 MPa = 14.8 bar). Therefore, the search for a V catalyzed procedure (Scheme 1) providing good activity under mild reaction conditions continues to attract huge interest. A general system for preparing a wide range of functional cyclic carbonates has not yet been reported.

After considering the issues mentioned above, we focused our attention on vanadium compounds, such as the easily pre-
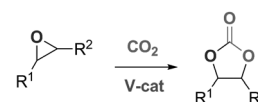
Scheme 1. Vanadium catalyzed synthesis of cyclic carbonates.

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pared vanadyl salphen and salen complexes, for the synthesis of cyclic organic carbonates from epoxides and CO_2 (Scheme 1). The catalytic results were compared with those gathered for the commercially available V^{IV} complex [VO(acac)$_2$] (acac = acetylacetonate). In the reactions carried out with these latter complexes, we observed the precipitation of a new species that is most likely responsible for the observed activity. The structure of this active component in the formation of five-membered carbonates was elucidated by various analytical techniques; formation a decavanadate complex was unambiguously demonstrated. The presence of mostly V^V centers in this polyoxometalate (POM) seems to illustrate the importance of this high oxidation state for achieving catalytic reactivity.

Results and Discussion

A series of differently substituted V^{IV}(O)salen and V^{IV}(O)salphen complexes bearing electron-donating and electron-withdrawing groups on the aromatic rings of the ligand scaffold (compounds **2a**–**2f** and **3a**–**3f**; Scheme 2) were prepared and
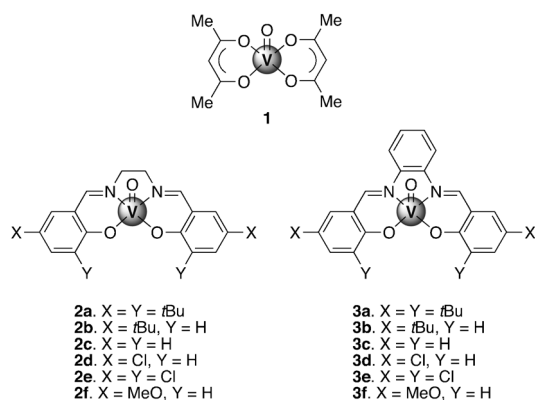
Scheme 2. Vanadium-based catalysts used for the investigation of the CO_2 addition reaction with 1,2-epoxyhexane.

screened as potential catalysts for the cycloaddition reaction of CO_2 and 1,2-epoxyhexane in the presence of NBu$_4$I (Bu = butyl) as co-catalyst, under mild conditions (45 °C, 1 MPa CO_2 pressure) and using mesitylene as an internal standard. The results obtained are shown in Table 1, as are those obtained with the reference compound [VO(acac)$_2$]. The reaction conditions were chosen on the basis of the best results obtained in previous work using other metal complexes as catalysts.[11] Methyl ethyl ketone (MEK) was used as the solvent, taking into account that it is one of the most efficient solvents for solubilization of CO_2.[12]

The electronic effect of the substituents on the vanadium centers in these VO(salen) and VO(salphens) compounds was investigated with cyclic voltammetry (Supporting Information). The redox potential E_p of the V^{IV}/V^V couple increased both in the salen and salphen series of vanadyl complexes in agreement with the variation of the electron density on the metal caused by the presence of the different substituents. The more positive redox potentials of the salphen complexes with re-

Table 1. Vanadium catalyzed conversion of various mono-substituted epoxides and CO_2 into the corresponding monocyclic carbonate under different reaction conditions.[a]

Substrate	Catalyst	Entry	T [°C]	p(CO₂) [MPa]	Yield [%]
*n*Bu	**1**	1[b]	45	1	75
		2	45	1	100
		3	35	1	87
		4	25	1	57
		5	25	0.2	63
		6[c]	25	0.2	91
		7[d]	35	1	72
		8[e]	45	1	39
	2d	9	45	1	3
	3c	10	45	1	3
	4b	11	45	1	6
HOCH₂	**1**	12	45	1	90
		13	35	1	75
		14	35	0.2	60
		15[c]	25	0.2	87
	3c	16	45	1	55
Ph	**1**	17	45	1	69
		18	25	0.2	48
PhCH₂	**1**	19	45	1	100
		20	25	0.2	96
MeOCH₂	**1**	21	45	1	72
ClCH₂	**1**	22	45	1	96
	1	23	45	1	58

[a] Reaction conditions: substrate (0.4 M); mesitylene (0.4 M); catalyst (0.01 M, 2.5 mol %); co-catalyst (NBu₄I, 0.01 M, 2.5 mol %); solvent (2-butanone = MEK, 5.0 mL); reaction time = 18 h, p(CO₂) = 1.0 MPa. [b] Catalyst loading is 1 mol %. [c] Co-catalyst concentration was 0.02 M (5 mol %). [d] NBu₄Br was used as co-catalyst. [e] MeCN was used as solvent.

spect to the salen ones indicates that the aromatic ring confers to vanadium a higher Lewis acidity.

For comparison, data for the reactions with V^{IV}(O)salen **2d** and V^{IV}(O)salphen **3c**, and triflate V^V salphen species **4c** (Scheme 3) are given in Table 1 (entries 9, 10, 11, and 16, respectively), but the yields of cyclic carbonates proved to be generally low throughout the entire range of catalysts, despite the variation in the nature of the vanadium center.[13] However, when 1,2-epoxy-3-hydroxypropane (glycidol) was used as the substrate, the reactivity of catalyst **3c** increased significantly, giving rise to 55 % yield for the corresponding cyclic
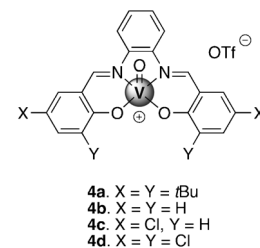
Scheme 3. V^V salphen complexes used as catalyst for the cycloaddition of CO_2 to 1,2-epoxyhexane.

carbonate (Table 1, entry 16). This is likely due to the coordination of the hydroxyl group to the salphen scaffold which increases the binding affinity between the substrate and the catalyst. Further support for this hypothesis was derived from X-ray diffraction studies carried out for **3b** (Figure 1) in which the V^{IV} complex has a methanol molecule hydrogen-bonded to one of the phenolic O atoms of the salphen ligand.
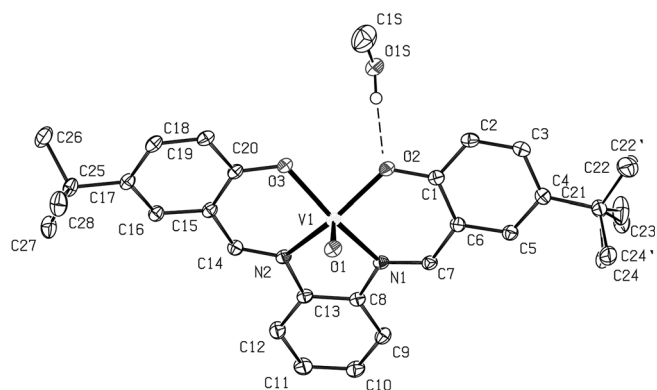
Figure 1. X-ray molecular structure for **3b**. Co-crystallized solvent molecules are omitted for clarity except for the hydrogen-bonded MeOH to **3b**. One of the *tert*-butyl (*t*Bu) groups shows a rotational disorder, and the disorder in the MeOH is not shown here. Selected bond distances/angles [Å/°]: V(1)–O(1) = 1.6011(9), V(1)–O(2) = 1.9452(9), V(1)–O(3) = 1.9250(8), V(1)–N(1) = 2.0611(10), V(1)–N(2) = 2.0722(10); N(1)-V(1)-O(1) = 103.34(4), N(1)-V(1)-O(3) = 148.68(4), N(2)-V(1)-O(2) = 143.75(4), O(2)-V(1)-O(1) = 108.91(4), O(3)-V(1)-O(1) = 107.36(4).

In addition to the salen and salphen vanadyl complexes, the commercially available [VO(acac)$_2$] was also tested to serve as a reference compound. Interestingly, it turned out to be much more active than the VO(salen) complexes. Previously, Darensbourg and co-workers reported that [VO(acac)$_2$] is a Lewis acid catalyst for the synthesis of trimethylene carbonates (TMC, six-membered cyclic carbonates) from (substituted) trimethylene oxides (oxetanes) and CO$_2$ under relatively mild conditions using tetrabutylammonium bromide as the co-catalyst.[14] Therefore, the catalytic activity observed for [VO(acac)$_2$] is not fully unexpected, and the previous results concerning the formation of TMC was explained by a *prior* formation of an oxetane-adduct from the starting vanadium complex. However, in our work focusing on five-membered cyclic carbonates and a slightly different co-catalyst (NBu$_4$I), we found evidence that the actual catalytic species likely involves a [VO(acac)$_2$] derivative (see below). In fact, a dark purple precipitate[15] was always present at the end of the reaction carried out with this metal precursor. This solid was recovered by filtration, used in a subsequent catalytic run and proved to be catalytically active. It is not possible to fully compare the observed yields with respect to the starting vanadium species [VO(acac)$_2$] because of the much lower solubility of the purple solid in MEK after being isolated.

Because [VO(acac)$_2$] appears to be a good pre-catalyst for the formation of organic carbonates, the scope of the reaction was investigated further. As shown in Table 1, mono-substituted epoxides can be converted to the corresponding cyclic car-

bonates by "VO(acac)$_2$" in good yields under mild reaction conditions. Using 1,2-epoxyhexane and 1,2-epoxy-3-hydroxypropane (Table 1, entries 1–16) as the substrates, the reaction was fully investigated by varying parameters, such as temperature, pressure and the amounts of catalyst and co-catalyst. The use of [VO(acac)$_2$] gave appreciable yields even when the reaction was performed at low pressure and ambient temperature (T = 25 °C, p(CO$_2$) = 0.2 MPa, Table 1, entries 5–6). The solvent MEK appears to play an important role in increasing the yields of the reaction because the use of CH$_3$CN as the medium for the conversion of 1,2-epoxyhexane (forming a purple solution, but no observable precipitate) caused the yield to drop to 39% (Table 1, entry 8). A plausible explanation may be that solvents such as acetonitrile can potentially coordinate to the vanadium metal center in [VO(acac)$_2$] and/or the purple precipitate and, thus, compete with epoxide coordination. The precipitate is linked with an active form of the vanadium complex as discussed above.

The catalytic activity of "VO(acac)$_2$" was also tested for di-substituted epoxides which are considered more difficult to activate owing to an increased steric hindrance in the ring-opening of the oxirane ring by the halide nucleophile. Consequently, higher pressures and temperatures are needed to realize conversion of these substrates to the corresponding organic carbonates, and generally low yields were observed (Table 2).

Table 2. Conversion of di-substituted epoxides and CO$_2$ to the corresponding monocyclic carbonate by [VO(acac)$_2$] using NBu$_4$X as the co-catalyst.[a]

| Entry	Substrate	T [°C]	Yield [%] X = I	Yield [%] X = Br
1	Me–△–Me (O)	75	6[b]	20[c]
2	Me–△–Me (O)	75	10[d]	33[e]
3	Me–△–''Me (O)	75	5[f]	26[g]
4	(cyclohexene oxide)	45	0	–
4		75	2	8
5	Me, Me–△ (O)	45	4	14
5		75	25	34

[a] Reaction conditions: substrate (0.4 M); mesitylene (0.4 M); catalyst (0.004 M, 1 mol%); co-catalyst (NBu$_4$X, 0.05 M, 2.5 mol%), solvent (2-butanone = MEK, 5 mL); reaction time = 18 h; p(CO$_2$) = 1 MPa. [b] > 99% *cis*: a mixture of 85:15 *trans/cis* substrate was used. [c] 15:85 *cis/trans*. [d] 4:6 *cis/trans*. [e] 91:9 *cis/trans*. [f] Only *trans* product was observed. [g] 12:88 *cis/trans*.

In general, the substitution of iodide with bromide in the co-catalyst slightly increased the yields. The compound *cis*-2,3-dimethyl-oxirane is more easily activated than its *trans* isomer, and the reaction appears to have a reasonable degree of retention of configuration in most cases (Table 2, entries 2 and 3).

To gain insight into the formation of the purple complex in the [VO(acac)$_2$] catalyzed reactions, the reaction was carried

out at 45 °C in the absence of CO_2 (in air), both with and without 1,2-epoxyhexane. It appears that the substrate is involved in the formation of the precipitate because only a small amount formed in the absence of the epoxide. Replacing the epoxide with water led to neither a color change nor precipitation, and the presence of a ten-fold increase in amount of the epoxide showed almost the same isolated yield for the precipitate (46 % after 18 h). We then performed a series of experiments to investigate the effect of the solvent on the formation of this purple precipitate (see Supporting Information). Generally, the medium had a pronounced effect because the reactions carried out in THF, acetone, toluene, and MEK all produced the precipitate in moderate to excellent yields (31–99 %, 18 h). The use of CH_3CN, $CHCl_3$ or ethanol (EtOH) as solvents did not lead to any observable precipitation whereas the two former media showed a color change from initial green to purple. The purple precipitate formed during the catalytic cycle was analyzed by electrospray ionization mass spectrometry (ESI-MS), elemental analysis, infrared (IR), UV/Vis and ^{51}V NMR spectroscopies, and X-ray diffraction.

The X-ray diffraction analysis of the crystallized purple precipitate provided useful information concerning the identity of this species (Figure 2). The structure comprises a tetraanionic
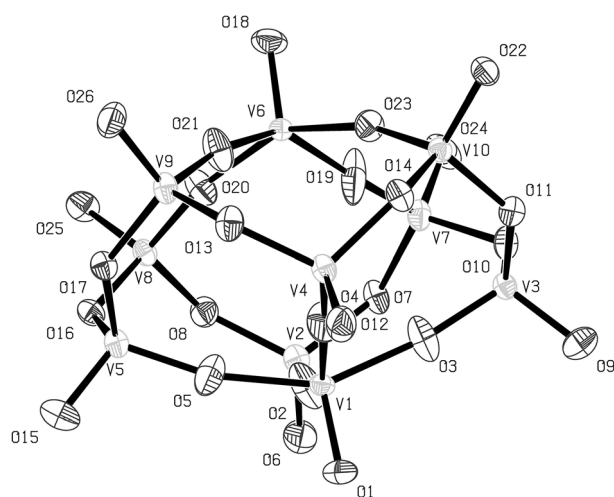

Figure 2. The tetraanionic portion of the X-ray molecular structure of the re-crystallized purple precipitate. Hydrogen atoms, NBu_4 cations (four), and co-crystallized solvent molecules are omitted for clarity. Selected bond distances [Å]: V(1)—O(1) = 1.565(3), V(1)—O(2) = 1.927(4), V(1)—O(3) = 1.943(4), V(1)—O(4) = 1.944(4), V(1)—O(5) = 1.928(4); V(3)—O(9) = 1.620(4), V(3)—O(10) = 1.800(3), V(3)—O(11) = 1.801(3), V(3)—O(3) = 1.668(4). Both V(1) and V(6) centers are V^{IV}, and the others are V^V.

decavanadate with four NBu_4 cations,[16] for which the molecular formula is $V_{10}O_{26}(NBu_4)_4$. The starting acetylacetonate V complex seems to lose the two bidentate ligands to form a polyoxometalate complex. In this compound, there are eight V^V and two V^{IV} centers, and because the highest oxidation state prevails, it seems that the catalytic activity originates from these metal centers. Note that the absence of iodide (the nucleophile used for the ring opening step in the catalytic studies reported in Tables 1 and 2) in the polyanionic structure

should reduce the reactivity upon reusing the precipitate in cyclic carbonate formation; indeed a lower yield was observed when using the purple precipitate as the catalyst without additional co-catalyst. The presence of two paramagnetic V^{IV} metals in the structure also explains why the complex does not show any peaks in the ^{51}V NMR spectra in CD_3CN or in CD_2Cl_2.

The ESI-MS of the purple precipitate presents two main peaks in the positive mode; the first peak at $m/z = 242$ confirms the presence of NBu_4^+ cations in the precipitate, and the second at $m/z = 629.5$ is ascribed to a fragmentation of the decavanadate anion to form a V_7O_{17} species (see Supporting Information). In the negative mode, one peak at $m/z = 744.7$ is present, and it was assigned to the fragment anion HV_8O_{21}. Although the purple complex is air stable at room temperature, it presents moderate stability in solution because the color changes from dark violet to yellow in organic solvents, such as CH_2Cl_2 or CH_3CN, over prolonged periods. This may be ascribed to the formation of the "all V^V" decavanadate with the formula $V_{10}O_{28}$ that is known to have a yellow color. Alternatively, the formation of a metavanadate species can be envisaged, which has been reported to be catalytically active in various reactions.[17]

The IR and UV/Vis spectroscopic data of the purple precipitate was compared with data from the literature[16] and further supported the formation of the decavanadate (Supporting Information). The elemental analyses (carried out multiple times with samples from different reactions) always showed data consistent with the proposed molecular formula of the decavanadate. The formation of the vanadate was accelerated by the epoxide in the presence of the co-catalyst (NBu_4I). The formation mechanism (Scheme 4) of this large decavanadate species
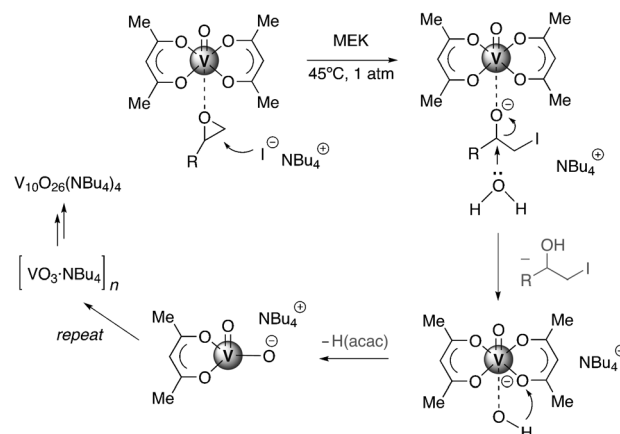
Scheme 4. Possible formation mechanism of the decavanadate species.

probably starts with the formation of the simple tetrahedral *meta*-vanadate from [VO(acac)₂] by acidic displacement of the two bidentate acetylacetonate ligands. The accelerating role of the epoxide may be explained by its potential to form an intermediate species with a V—alkoxide bond after iodide induced ring-opening. The fact that using oxetane as the substrate led

to much smaller amounts of vanadate[15] supports this view because the ring-opening of oxetanes is more difficult with halide nucleophiles. The basic alkoxide then could react with residual water to yield a V—OH species from which H—acac could be eliminated, forming a V—O bond that is charge neutralized by NBu$_4$. Subsequent elimination of the second acac ligand via a similar pathway could then lead to a V(O$_3$) (*meta*-vanadate, yellow) and other higher-order vanadates that precede the eventual *deca*-vanadate formation.

Conclusions

In summary, a series of substituted salen and salphen vanadyl complexes were prepared and used as catalysts in the formation of cyclic organic carbonates from epoxides and CO$_2$. The reactivities of the complexes were compared with commercially available [VO(acac)$_2$]. The results indeed showed that vanadium may be an attractive and active metal in the presence of a suitable nucleophile as co-catalyst in the context of CO$_2$ fixation chemistry. The presence of an alcohol group in the substrate (such as glycidol) allowed a possible ditopic binding to the metallosalen scaffold, thereby increasing the reactivity. Among all of the catalysts investigated, "VO(acac)$_2$" was by far the most active, and it can be used under very mild conditions (25 °C, p(CO$_2$) = 0.2–1.0 MPa). Note that the higher activity of [VO(acac)$_2$] can be ascribed to the formation of a new decavanadate (Bu$_4$N)$_4$V$_{10}$O$_{26}$ complex that was isolated and fully characterized. This polyoxometalate, mainly comprising vanadium centers in a high oxidation state (+5), may thus hold great promise for the development of new catalytic procedures that take advantage of the Lewis acidic nature of the V^V metal centers within the structure.

Experimental Section

Synthesis of the ligand precursors

The salen and salphen ligands were prepared from commercially available starting materials following literature procedures.[18] Two equivalents of the appropriate salicylaldehyde were dissolved in a minimal amount of boiling methanol (MeOH). One equivalent of ethylenediamine or *o*-phenylendiamine was added and the solutions were left to cool to ambient temperature under stirring. The orange or yellow precipitates were recovered by filtration, washed with cold methanol and further purified by crystallization from ethanol when required. The purity of the ligand precursors was established by ^{1}H NMR spectroscopy.

Synthesis of the vanadyl complexes

Complexes **2a**, **2c**–**2f**, **3a**, **3c**–**3f**, and **4a**–**4d** (Schemes 2 and 3) were prepared following the methods reported in the literature with slight modifications.[18] The respective ligand was dissolved in a minimal amount of boiling methanol. A methanol solution of 1 equivalent of [VO(acac)$_2$] or [V(acac)$_3$] was added. The mixture was then allowed to cool to room temperature and kept at this temperature while stirring for 18 h. The green or brown precipitate that formed was recovered by filtration and washed with methanol, triturated with diethyl ether, and dried. The known com-

pounds obtained were characterized by either matrix-assisted laser desorption/ionization (MALDI) or ESI-MS. To the best of our knowledge, catalysts **2b** and **3b** have not been previously published, and a detailed experimental part for these derivatives is found below. Synthesis of V^V complexes were obtained by dissolving the corresponding V^{IV} complex in a minimal volume of CH$_2$Cl$_2$ under stirring at 0 °C, and bubbling O$_2$ through the solution for 5 min. After the addition of 1.2 equivalents of trifluoromethanesulfonic acid, a dark precipitate formed, and the reaction mixture was allowed to stir overnight. The solid V^V complex was recovered by centrifugation (6000 rpm) of the reaction mixture and decantation of the supernatant solution.

[*VO(5-tBu-salen)*] **2b**: The ligand 5-*t*Bu-salen (250 mg, 0.66 mmol) was dissolved in 60 mL of boiling methanol and a solution of 1 equiv of [VO(acac)$_2$] dissolved in 5 mL of methanol was added. After cooling to room temperature, the mixture was stirred for an additional 18 h. The precipitate was recovered by filtration, washed with methanol, and dried. Yield: 195 mg (0.44 mmol), 66%. UV/Vis (acetonitrile): λ (ε_{max}) = 246 nm (56 000), 278 nm (27 000), 370 nm (9200); IR (neat): $\tilde{\nu}$ = 466, 476, 529, 558, 717, 806, 833, 983, 1182, 1257, 1303, 1332, 1383, 1470, 1535, 1620, 2865, 2955 cm^{-1}; ESI(+)-MS (MeOH): m/z = 468.2 (M+Na)$^+$ (calcd 468.2); elemental analysis calcd (%) for C$_{24}$H$_{30}$N$_2$O$_3$V·$^1/_3$H$_2$O (451.45): C 63.85, H 6.85, N 6.21; found: C 63.85, H 6.63, N 6.26.

[*VO(5-tBu-salphen)*] **3b**: The ligand 5-*t*Bu-salphen (200 mg, 0.47 mmol) was dissolved in 100 mL of boiling methanol, and then a solution of 1 equiv of [VO(acac)$_2$] dissolved in 5 mL of methanol was added. The solution was cooled to room temperature and allowed to stir for eight hours. A large part of the solvent was evaporated under reduced pressure at 35 °C, and the solution was kept in the freezer overnight. The green precipitate was recovered by filtration, washed with methanol and diethyl ether (20 mL), and dried. Yield: 191 mg (0.39 mmol), 82%. Crystals suitable for X-ray diffraction were obtained from methanol and the structure is shown in Figure 1. UV/Vis (acetonitrile): λ (ε_{max}) = 246 nm (40 900), 318 nm (22 700), 409 nm (15 400); IR (neat): $\tilde{\nu}$ = 402, 485, 508, 538, 565, 611, 673, 700, 731, 817, 834, 979, 1146, 1181, 1258, 1312, 1362, 1378, 1462, 1528, 1576, 1597, 1615, 2959 cm^{-1}; ESI(+)-MS (MeOH): m/z = 516.2 (M+Na)$^+$ (calcd 516.2); elemental analysis calcd (%) for C$_{28}$H$_{30}$N$_2$O$_3$V·MeOH (525.53): C 66.28, H 6.52, N 5.33; found: C 65.91, H 6.69, N 5.40.

General procedure for the catalytic reactions

All of the solutions were prepared in vials. The reagents were added in the order: catalyst, substrate, nucleophilic salt, mesitylene (the internal standard) and solvent (methyl ethyl ketone (MEK), 5 mL). The solutions were stirred, subjected to ultrasonication to maximize the dissolution of the catalyst and then transferred to a stainless steel reactor. Catalytic reactions with chloro-substituted salphen and salen vanadium complexes were carried out in the presence of the solid catalyst because those catalysts are only partially soluble in MEK. The CO$_2$ atmosphere was created by carrying out five cycles of pressurization at 0.5 MPa and depressurization, and then stabilizing the pressure at 0.2 MPa. When a lower pressure was used, the reaction was degassed until reaching the value desired. The solutions were stirred for 18 h and heated when required. Analysis of the solutions were done by means of ^{1}H NMR in [D$_6$]DMSO using mesitylene as an internal standard. The blank reaction was done without any metal complex in solution and showed no observable conversion at T = 45 °C and p(CO$_2$) = 1.0 MPa.

Decavanadate (Bu₄N)₄V₁₀O₂₆: A solution of [VO(acac)₂] (32.3 mg, 0.121 mmol), NBu₄I (46.6 mg, 0.126 mmol) and 1,2-epoxyhexane (30 μL, 0.249 mmol) was stirred for 18 h at 45 °C. The solid (9.8 mg) was isolated by filtration, washed with MEK, and dried. A second fraction of the product (4.9 mg) was also isolated. Yield: 14.7 mg, purple solid (0.00776 mmol), 64%, analyzed as the decavanadate. UV/Vis (acetonitrile): λ (ε_{max}) = 324 nm (14 500), 508 nm (1800). IR (neat): $\tilde{v}$ = 399, 656, 837, 881, 954, 994, 1379, 1482, 2872, 2954 cm^{-1}. ESI(+)-MS (MeOH): m/z = 629.5 (HV₇O₁₇)$^+$ (calcd 629.5) 242.3 (NBu₄)$^+$ (calcd 242.3). ESI(−)-MS (MeOH): m/z = 744.7 (HV₈O₂₁)$^+$ (calcd 744.6). Elemental analysis calcd for V₁₀O₂₆·(NBu₄)₄·2 H₂O (1931.28): C: 39.80, H 7.72, N 2.90; found: C 39.62, H 7.58, N 2.92.

Electrochemical measurements

The cyclic voltammetry was carried out in DMF using tetrabutylammonium perchlorate (TBAP, re-crystallized from ethanol) as the electrolyte salt (0.1 M). The vanadyl complexes were dissolved in the electrolyte solution. A Ag/AgCl electrode was used as the reference.

X-ray diffraction studies

The crystals were stable under atmospheric conditions; nevertheless they were prepared under inert conditions, and immersed in perfluoropolyether as the protecting oil for manipulation. Measurements were made on a Bruker–Nonius diffractometer equipped with an APPEX 2 4 K CCD area detector, a FR591 rotating anode with Mo$_{K\alpha}$ radiation, Montel mirrors and a Kryoflex low temperature device (T = 173 °C). Full sphere data collection was used with ω and ϕ scans. The programs used were: data collection Apex2 V2011.3 (Bruker-Nonius 2008), data reduction Saint+Version 7.60A (Bruker AXS 2008) and absorption correction SADABS V. 2008-1 (2008). The SHELXTL Version 6.10 (Sheldrick, 2000)[19] program was used for the structure solution. The structure was refined using SHELXTL-97-UNIX VERSION.

Crystal data for 3b: Formula: C₂₉H₃₄N₂O₄V ; M_r = 525.52; crystal size 0.15×0.15×0.03 mm; monoclinic; space group $P2_1/c$; a = 12.0214(8), b = 10.5465(7), c = 21.2871(14) Å; α = 90, β = 101.772(2), γ = 90°; V = 2642.1(3) Å^3; Z = 4; ρ_{calcd} = 1.321 mg M^{-3}; μ(Mo$_{K\alpha}$) = 0.412 mm^{-1}; T = 100(2) K; θ(min/max) = 1.73/30.04°; 7359 reflections collected; 6476 unique reflections (R_{int} = 0.0298); refinement method: full-matrix least-squares on F^2 ; data/restraints/parameters: 7359/22/383; GoF on F^2 = 1.046; R_1 = 0.0320 and wR_2 = 0.0865 [$I > 2\sigma(I)$]; R_1 = 0.0384 and wR_2 = 0.0915 (all data); largest diff. peak and hole: 0.791 and −0.380 e Å^3 (CCDC 852356 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.)

Crystal data for decavanadate (Bu₄N)₄V₁₀O₂₆: Formula: C₇₀H₁₅₆N₄O₂₈V₁₀; M_r = 1982.35; crystal size 0.20×0.10×0.03 mm; orthorhombic; space group $P2_12_12_1$; a = 16.8869(18), b = 17.0015(19), c = 33.697(3) Å; α = β = γ = 90°; V = 9674.6(18) Å^3; Z = 4; ρ_{calcd} = 1.361 mg M^{-3}; μ(Mo$_{K\alpha}$) = 0.986 mm^{-1}; T = 100(2) K; θ(min/max) = 1.34/25.44°; 17696 reflections collected; 13822 unique reflections (R_{int} = 0.0625); refinement method: full-matrix least-squares on F^2; data/restraints/parameters: 17696/269/1105; GoF on F^2 = 1.088; R_1 = 0.0593 and wR_2 = 0.1390 [$I > 2\sigma(I)$]; R_1 = 0.0851 and wR_2 = 0.1546 (all data); largest diff. peak and hole: 1.002 and −0.804 e Å^3 (CCDC 852355 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge

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