Vanadium(V) Catalysts with High Activity for the Coupling of Epoxides and CO$_2$: Characterization of a Putative Catalytic Intermediate

Claudia Miceli,[§] Jeroen Rintjema,[†] Eddy Martin,[†] Eduardo C. Escudero-Adán,[†] Cristiano Zonta,[§] Giulia Licini,*[§] and Arjan W. Kleij*[†,‡]

[§]Dipartimento di Scienze Chimiche and CIRCC, Università di Padova, Via Marzolo 1, 35131 – Padova, Italy

[†]Institute of Chemical Research of Catalonia (ICIQ), the Barcelona Institute of Science and Technology (BIST), Av. Països Catalans 16, 43007 – Tarragona, Spain.

[‡]Catalan Institute of Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 – Barcelona, Spain.

ABSTRACT: Vanadium(V) complexes derived from aminotriphenolate ligands are demonstrated to be highly active catalysts for the coupling of various terminal and internal epoxides with carbon dioxide to afford a series of substituted organic carbonates in good yields. Intriguingly, a V(V) complex bearing peripheral chloride groups on the ligand framework allowed for the formation and isolation of a rare complex that incorporates a ring-opened epoxide with one of the phenolate–O atoms acting as a nucleophile and the metal center as a Lewis acidic site. This unusual structure was characterized by X-ray diffraction and ^{51}V-NMR, and was shown to exhibit catalytic activity for the coupling of propylene oxide and CO_2 when combined post-synthetically with these substrates. The results obtained herein clearly show that vanadium complexes in a high oxidation state are powerful catalysts for the activation of challenging internal epoxides, and their conversion into cyclic organic carbonates.

◼ INTRODUCTION

Small molecule activation, and particularly carbon dioxide (CO_2) capture and conversion,[1] continues to challenge the synthetic communities to devise more efficient and sustainable catalysis protocols for classically low-reactive molecules. In the realm of sustainable development, it is essential to design new catalyst systems that are characterized by an easy, modular and cost-effective construction while addressing the requisite of general availability of the raw materials and using thus abundant and preferably renewable chemical building blocks.[2] Carbon dioxide represents an interesting source of carbon in synthetic chemistry, but its successful conversion relies on the use of catalysts and high-energy co-reactants that can mediate its conversion, since the latter is challenged both from a kinetic and thermodynamic point of view.[3] Over the last decade, the growth of new catalytic technologies for CO_2 conversion has been spectacular with progress reported for a wide series of transformations.[4] Metal catalysis has been prominent in most of the synthetic efforts directed towards CO_2 "fixation" activating either this carbon feedstock directly or a co−reactant able to induce a coupling reaction.[5] An often applied strategy in this regard has been the Lewis acid activation of small heterocyclic ethers in the presence of a nucleophilic additive giving rise to alkoxide intermediates that smoothly react with CO_2 to form carbonate structures: these linear carbonate species eventually evolve into either cyclic[6] or polycarbonates[7] and the observed chemoselectivity typically depends on the reaction conditions, the type of nucleophile and Lewis acidic metal complex.

Successful catalysts for cyclic organic carbonate (COC) formation include the use of abundant main group metals such as aluminum,[8] iron,[9] and zinc,[10] and transition metals (Co, Cr)[11] most often in combination with N_x,O_y-coordinating ligands such as salens ($x = y = 2$)[12] and aminotriphenolates

(x = 1, y =3).[13] We have been interested in the use of O_3N-chelating aminotriphenolate ligands and their complexes for catalytic applications, and have reported on the use of Ti(IV) derivatives for the oxidation of sulfides and secondary amines into nitrones,[14] Mo(VI) and W(VI) complexes for the oxidation of sulfides, olefins and chloro– and bromoperoxidation,[15] and more recently the Fe(III) mediated formation of cyclic carbonates and the preparation of Catechol Oxidase and Catalase mimics.[16] The use of aminophenolate type ligands is beneficial towards the stabilization of different (higher) oxidation states such as V(III) and V(V),[17] and the V(V) complexes have previously been successfully used in the context of haloperoxidase models in sulfoxidation chemistry.[18] Inspired by the presence of high-oxidation state V centers in these complexes representing strongly Lewis acidic sites, we envisioned that such compounds would also be highly efficient in epoxide activation/ring-opening in the presence of a suitable nucleophile, and give rise to COC formation in the presence of CO_2. As far as we know, the use of vanadium in the formation of COCs and related compounds remains rare, and with limited application potential.[19]
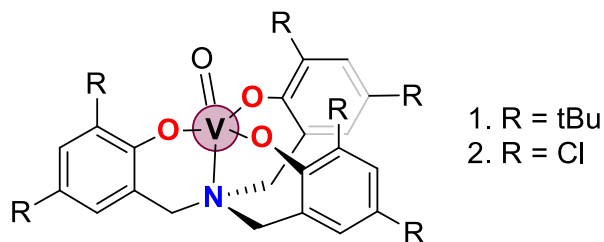

Figure 1. V(V) aminotriphenolate complexes **1** and **2** used in this work as catalyst components for COC formation.

Therefore, we set out to explore the potential of V(V) aminotriphenolate complexes (Figure 1) in the formation of COC and have specifically focused on the conversion of more challenging sub-

series of internal epoxide partners. The use of this class of substrates is currently attracting more attention as efficient catalysts have become available for their conversion,[20] and therefore new catalyst systems should be comparatively evaluated against this advanced state of the art in COC formation. In this work we will demonstrate that V(V) aminotriphenolate complexes combined with suitable halide nucleophiles offer highly efficient binary catalysts for COC formation from a wide series of internal epoxides. Further to this, the unexpected low activity for the conversion of some terminal epoxides by the strongest Lewis acidic V(V) complex was investigated in more detail. This has resulted in the formation and structural characterization of a unique and unprecedented catalytic intermediate where the V(V) center and one of the phenolate donors had cooperatively activated the epoxide substrate to form a six-coordinate V(V) complex comprising of a bidentate aryloxo-alkylether fragment. This new epoxide activation mode was confirmed by X-ray analysis, and further use of this intermediate in COC formation was also demonstrated. Our results thus demonstrate the use of a powerful new binary catalyst system for challenging coupling reactions between internal epoxides and CO_2, and mark the use of abundant vanadium as a useful and sustainable alternative in COC formation.

■ RESULTS AND DISCUSSION

2.1 Screening Phase. The V(V) complexes **1** and **2** were combined with NBu$_4$I and used as binary catalysts for the formation of COCs **D−F** from terminal epoxides **A−C** (Table 1). As a reference catalyst, we used the previously reported and highly active binary catalyst **3**/NBu$_4$I[21] under similar conditions to examine the catalytic potential of the V(V) complexes.

Table 1. Screening Experiments carried out with V(V) Complexes 1 and 2 using various Terminal Epoxides (A−C) and one Internal Epoxide (D).[a]
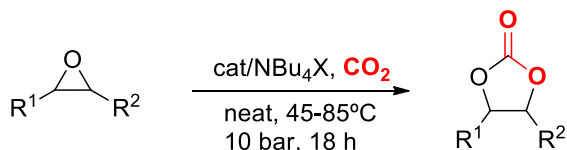
A: R^1 = *n*Bu, R^2 = H
B: R^1 = -CH_2Cl, R^2 = H
C: R^1 = Ph, R^2 = H
D: R^1 = Ph, R^2 = Me

E: R^1 = *n*Bu, R^2 = H
F: R^1 = -CH_2Cl, R^2 = H
G: R^1 = Ph, R^2 = H
H: R^1 = Ph, R^2 = Me
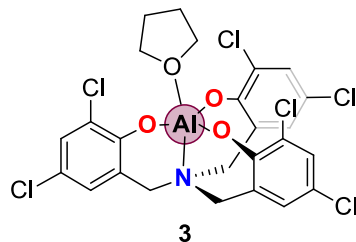
Entry	substrate	Cat. (%)	Nu (%)	T (ºC)	Yield (%)[b]
1	**A**	**1**, 0.50	1.25	45	>99
2	**A**	**1**, 0.50	–	45	0
3	**A**	**2**, 0.50	–	45	0
4	**A**	–	1.25	45	64
5	**A**	**1**, 0.20	0.50	45	94
6	**A**	**1**, 0.10	0.25	45	58
7	**A**	**1**, 0.10	–	45	0
8	**A**	–	0.25	45	23
9	**A**	**2**, 0.10	0.25	45	73
10	**A**	**3**, 0.10	0.25	45	>99
11	**B**	**1**, 0.10	0.25	45	70
12	**B**	**2**, 0.10	0.25	45	19
13	**B**	**3**, 0.10	0.25	45	74
14	**B**	–	0.25	45	7
15	**C**	**1**, 0.10	0.25	45	67
16	**C**	**2**, 0.10	0.25	45	18
17	**C**	**3**, 0.10	0.25	45	60
18	**C**	–	0.25	45	26
19[c]	**D**	**2**, 0.50	1.25	85	70[d]
20[c]	**D**	**2**, 0.50	5.0	85	>99 (68)[e]
21[c]	**D**	**1**, 0.50	5.0	85	93 (41)[e]
22[c]	**D**	**2**, 0.25	5.0	85	>99
23[c]	**D**	–	5.0	85	26
24[c]	**D**	**3**, 0.50	5.0	85	>99 (55)[e]

[a]Reaction conditions: 2.0 mmol of epoxide, temperature indicated, NBu$_4$**I** (amount indicated), 10 bar, 18 h, neat. Nu stands for nucleophilic additive, and catalyst and nucleophile loadings are in mol%. [b]NMR yield using mesitylene as internal standard; selectivity towards the COC product >99%. [c]Conditions used: 1.0 mmol **D**, NBu$_4$**Br** (amount indicated), 10 bar, 18 h, neat. [d]Conversion was 98%, with benzaldehyde (28%) being formed as a by-product. [e]In parentheses the NMR yield after 6 h.

The conversion of 1,2-epoxyhexane **A** was first evaluated and a combination of complex **1** (0.50 mol%) with NBu$_4$I (1.25 mol%) provided quantitative yield for the COC product **D** (entry 1). The complexes **1** and **2** themselves proved to be unproductive (entries 2 and 3) whereas NBu$_4$I alone gave a 64% yield of **D**. This prompted us to further lower the loading of **1** and NBu$_4$I (entries 5–7) and we were pleased to find that a combination of **1** (0.10 mol%) and NBu$_4$I (0.25–0.50 mol%) still provided appreciable to high yield of the COC **E** whereas the yield in the presence of only NBu$_4$I was significantly lower (entry 8). Upon using the more Lewis acidic V(V) complex **2** (*cf.*, entries 6 and 9, 58% *vs.* 73%) a higher yield of **E** was noted compared to the binary system **1**/NBu$_4$I. Comparison with the previously reported and highly active binary catalysts **3**/NBu$_4$I (entry 10),[5f,21] shows that for 1,2-epoxyhexane conversion the binary systems based on V-complexes 1 and 2 have lower, though still appreciable activity. Other terminal epoxides were then also examined (styrene oxide **B** and epichlorohydrin **C**; entries 11–18), and surprisingly in these cases the binary catalyst based on **1** proved to be significantly more active than the one derived from **2**. Catalyst **1**/NBu$_4$I showed again a considerably higher yield for COCs **F** and **G** compared to the background reaction mediated by the nucleophile only but, more importantly, similar order magnitude COC yields as determined for the Al-based binary system **3**/NBu$_4$I (*cf.*, entries 11 *vs.* 13 and 15 *vs.* 17). Since binary **3**/NBu$_4$I catalysts have been reported among the most active for COC formation using terminal epoxides,[5f,21] it therefore seems that aminotriphenolate V(V) complexes have also high catalytic potential.

In order to challenge the binary couples consisting of **1** or **2** and a suitable ammonium halide nucleophile towards COC formation, an internal epoxide (*trans* **D**) was then probed as a reaction partner (entries 19–24). Interestingly, in the formation of COC **H** the use of complex **2** was more beneficial showing higher yield of the desired product (*cf.*, entries 20 and 21). At a loading of 1.25

mol% of NBu$_4$Br,[22] however, substantial formation of benzaldehyde (entry 19, 28%) was noted as a likely result of the V(V) complex acting as a catalyst for oxidative cleavage after initial formation of a diol intermediate.[18c] An increase in the nucleophile loading up to 5.0 mol% solved this problem with the chemo-selectivity, and under these conditions (entry 20) quantitative formation of COC **H** was obtained, and for this substrate upon using Al-complex **3** (entry 24) a slightly lower yield was obtained after a 6 h reaction time. When comparing the V-based catalysts of this work with a recently reported diphenolate V(V) based complex (0.20 mol%) combined with NBu$_4$Br (0.20 mol%) for the conversion of PO at 80ºC and 40 bar CO_2 pressure (18 h; conversion 79%),[19c] it seems that the complexes of this study show relative good potential. However, since some disparity exists between our conditions (Table 1) and the ones reported previously, some caution is needed to quantitatively compare these data.[23] The conditions reported for the successful formation of disubstituted COC **H** using V-complex **2** were then taken as a starting point for the coupling of various internal epoxides with CO_2.

2.2 Scope in Disubstituted COC products. Motivated by the results summarized in Table 1, a series of internal epoxides was then converted into their disubstituted COCs **4–19** (see Figure 2) using the binary catalyst **2**/NBu$_4$Br. The product diversity proved to be wide, and various (functional) epoxides (either commercial ones or prepared in few steps from easily accessible starting materials, see the Supporting Information; SI) could be converted in their cyclic carbonates typically in good yields. Different ring-size epoxides are suitable substrate partners including five-, six- and eight-membered ones (**4–9**, **17-19**), though in the preparation of **7** and **9** we observed that longer reaction times (up to 3 days) and/or increasing the binary catalyst loading did not improve the results. COC **7** is a rather interesting structure that comprises an epoxide unit that was unaffected during the catalytic trials, and thus remains available for post-synthetic modification.

The binary catalyst **2**/NBu₄Br also proved to be useful to convert a trimethoxysilylalkyl derived epoxide without observable degradation (*cf.*, formation of **10**). COC product **11** was obtained from a biomass-derived fatty acid precursor (oleic acid) and represents an interesting contextual case towards biomass valorization.[24] The COCs **13–16** were prepared from their stereo-pure *cis* or *trans* precursors: whereas the coupling of *trans* 2,3-dimethyloxirane with CO_2 proceeded with high retention of configuration (**13**: *cis*/*trans* = 4:96), the use of the diastereo-isomerically pure *cis* epoxide led to substantial loss of stereo-information
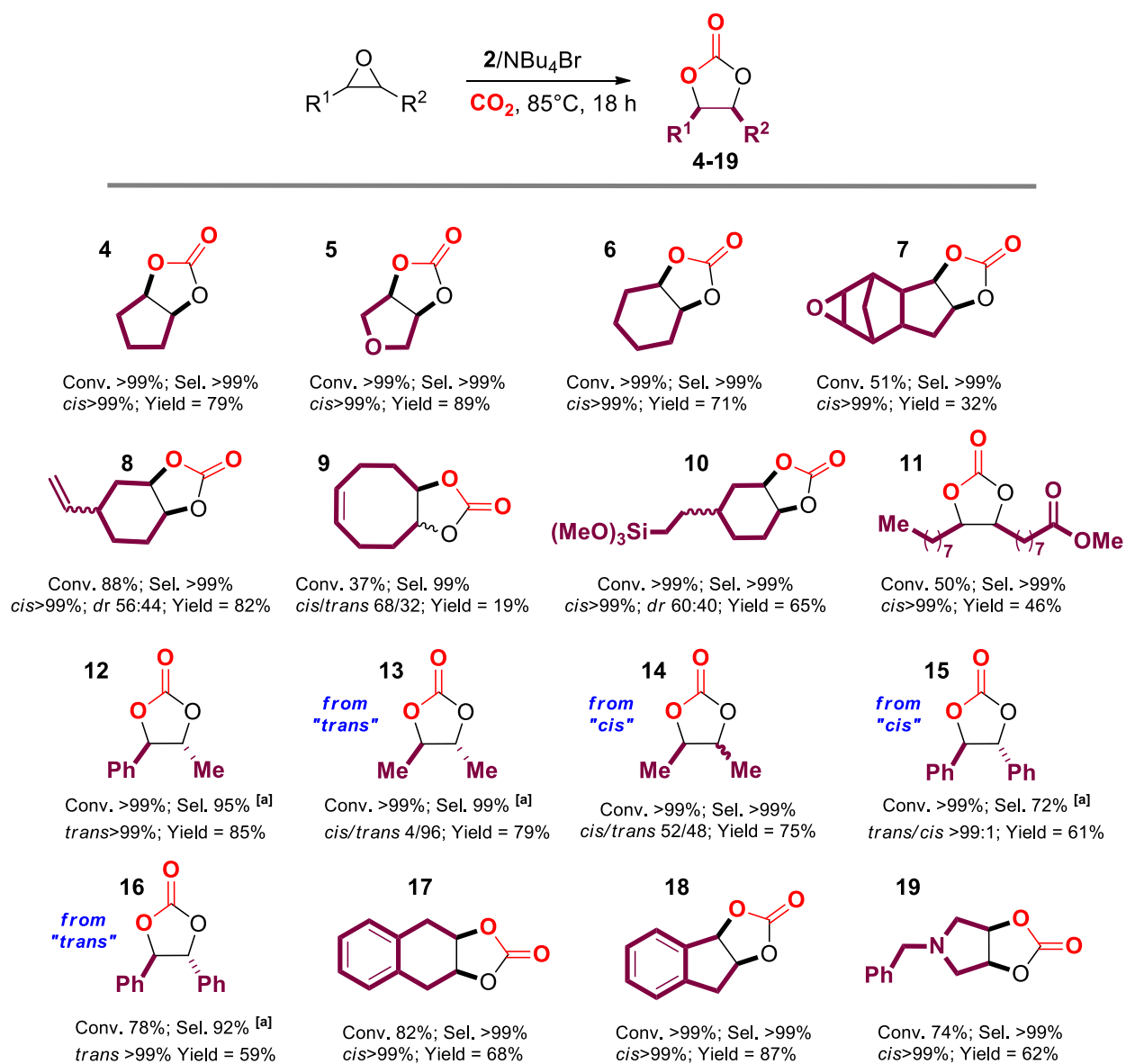

Reaction scheme: R¹, R² substituted oxirane with **2**/NBu₄Br, CO_2, 85°C, 18 h → cyclic carbonate **4-19**

4
Conv. >99%; Sel. >99%
cis>99%; Yield = 79%

5
Conv. >99%; Sel. >99%
cis>99%; Yield = 89%

6
Conv. >99%; Sel. >99%
cis>99%; Yield = 71%

7
Conv. 51%; Sel. >99%
cis>99%; Yield = 32%

8
Conv. 88%; Sel. >99%
cis>99%; *dr* 56:44; Yield = 82%

9
Conv. 37%; Sel. 99%
cis/*trans* 68/32; Yield = 19%

10
(MeO)₃Si—
Conv. >99%; Sel. >99%
cis>99%; *dr* 60:40; Yield = 65%

11
Me
OMe
Conv. 50%; Sel. >99%
cis>99%; Yield = 46%

12
Ph Me
Conv. >99%; Sel. 95% [a]
trans>99%; Yield = 85%

13
from "trans"
Me Me
Conv. >99%; Sel. 99% [a]
cis/*trans* 4/96; Yield = 79%

14
from "cis"
Me Me
Conv. >99%; Sel. >99%
cis/*trans* 52/48; Yield = 75%

15
from "cis"
Ph Ph
Conv. >99%; Sel. 72% [a]
trans/*cis* >99:1; Yield = 61%

16
from "trans"
Ph Ph
Conv. 78%; Sel. 92% [a]
trans >99% Yield = 59%

17
Conv. 82%; Sel. >99%
cis>99%; Yield = 68%

18
Conv. >99%; Sel. >99%
cis>99%; Yield = 87%

19
Ph
N
Conv. 74%; Sel. >99%
cis>99%; Yield = 62%

Figure 2. Synthesis of disubstituted COCs **4–19** from internal epoxides and CO_2 using the binary catalyst **2**/NBu$_4$Br. General conditions: epoxide (4 mmol), **2** (0.5 mol%), NBu$_4$Br (5 mol%), neat, 85 °C, $p(CO_2)^o$ = 10 bar, 18 h. The *dr* values were determined by ^{13}C NMR spectroscopy using inverse-gated decoupling, and reported yields are isolated ones after column purification. Reported relative configurations of the drawn structures refer to the major/expected product. [a] In these reactions an aldehyde by-product was formed as shown by ^1H NMR.

(**14**: *cis*/*trans* = 52:48). Such loss of stereo-information was reported before and is generally explained by the occurrence of both S$_N$1 and S$_N$2 based ring closing mechanisms.[20e,24d] The use of a sterically more congested substrate (*cis*/*trans* 2,3-diphenyloxirane), however, led to exclusive isolation of the *trans*-configured products (**15** and **16**) regardless the initial configuration of the epoxide substrate. The combined results clearly show the high catalytic potential of V(V) complex **2** in the formation of these challenging conversions, and the scope of COC products reported in Figure 2 is among the widest reported to date.

2.3 Mechanistic Investigations. Based on the remarkable and relatively low activity found for the activation of styrene oxide and epichlorohydrin (Table 1) by the more Lewis acidic V(V) complex **2** compared to **1**, we decided to investigate the origin of this behavior. Since previous work on related Al(III) aminotriphenolate complexes showed that cyclic ether coordination[5f,21] precedes the ring-opening process by an external nucleophile, we first combined complex **2** and the simplest terminal epoxide (propylene oxide, PO) and focused on the formation of a similar epoxide-coordinated structure and its analysis by X–ray diffraction. Fortunately, crystalline material obtained from a mixture of **2** and excess PO in CH$_3$CN could be easily obtained and the determined structure (**2**–PO) is presented in Figure 3. Much to our surprise, instead of the expected

PO-coordinated V(V) complex,[25] unprecedented formation of a V(V) complex comprising of a ring-opened PO had occurred mediated by one of the phenolate O–atoms that acted as an internal nucleophile.

The V-center in **2**–PO is asymmetrically positioned in a rather distorted octahedral coordination structure, with the vanadyl fragment (V(1)–O(1) = 1.5877 Å) occupying one of the equatorial positions. The three O–donors of the aminophenolate ligand occupy the remaining positions of the equatorial plane, with the V(1)–O(3) distance (2.3413 Å) being significantly longer than the other V–O bonds (V(1)–O(2) and V(1)–O(5) of 1.8912 and 1.8701 Å, respectively). The axial O–donor originating from the activated epoxide shows a relatively short bond length of 1.7871 Å (V(1)–O(4)) pointing at negative charge localization at this O–center, and thus the organic fragment connected through O(3) and O(4) should be regarded as a mono-anionic arylethanolate fragment with V(1)–O(3) being a dative bond involving an arylalkyl ether donor.
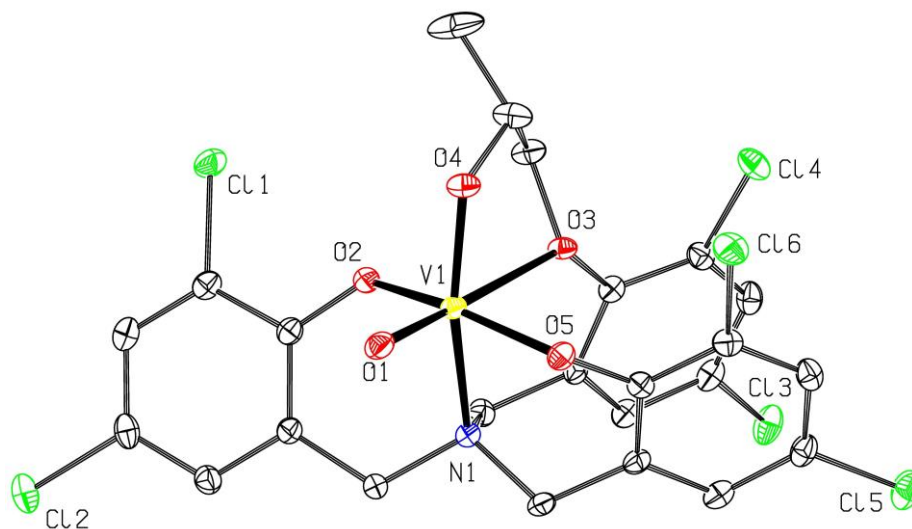
Figure 3. X-ray molecular structure of the unusual PO–adduct **2**–PO based on V(V) complex **2**. Selected bond lengths (Å) and angles (º), with esd´s in parentheses: V(1)-O(1) = 1.5877(17), V(1)-O(2) = 1.8912(16), V(1)-O(3) = 2.3413(17), V(1)-O(4) = 1.7871(17), V(1)-O(5) = 1.8701(16), V(1)-N(1) = 2.244(2); O(4)-V(1)-N(1) = 155.88(8), O(1)-V(1)-O(3) = 178.71(8), O(2)-V(1)-O(5) = 158.95(7).

Thus, it seems reasonable to suggest that after initial coordination of the PO molecule, both the Lewis acidic V center and one of the Lewis basic phenolate cooperatively activate the epoxide and form a stable, six-coordinate V(V) complex. Interestingly, such a process shows parallels with the ring-opening of the epoxide by an external nucleophile (often proposed to be the first step in COC formation using binary catalysts), though in the present case the phenolate acts as an internal nucleophile. The structure of **2**–PO was further analyzed/confirmed by MALDI-TOF mass analysis and ^{51}V-NMR spectroscopy.

To gain further insight in the formation of **2**–PO, ^{51}V NMR titration studies were carried out using **2** and different amounts of PO (Figure 4). The respective NMR traces were recorded 5 h after initial mixing (traces **b–f**), and a comparison was made with the ^{51}V resonances for **2** (trace **a**) and isolated **2**–PO (trace **g**). Upon addition of PO, a multifold of resonances appeared that seem to converge to two major resonances located at −457 and −470 ppm. The latter peak assignment was facilitated by the ^{51}V NMR analysis of an isolated crystalline sample of **2**–PO and could thus be assigned to this unusual structure. Furthermore, the reaction of **2** and PO to induce the formation of **2**–PO depends on the excess of PO present in solution; interestingly, at a lower excess of PO (33 equiv, **d**) the spectrum evolves in time (*i.e.*, a few days) to the same final trace observed under (**f**) suggesting that *full* conversion of **2** into **2**–PO under these conditions (25ºC, 33–fold excess of PO) is relatively slow.

It is likely that the formation of **2**–PO is preceded by simple PO coordination which may occur both in an equatorial and axial fashion. Also the final *in situ* prepared product **2**–PO could have the vanadyl fragment occupying either an axial or equatorial position in the octahedral complex, which could explain the presence of the two main peaks. Such behavior was also demonstrated for other V(V) complexes comprising of *O₂,N,N′*-coordinated tetradentate ligands showing V-

resonances in the same region as noted for **2**–PO.[17b,18b] Alternatively, in solution Lewis acidic

2–PO may be part of larger clusters such as dimers that can affect the [51]V resonance and account

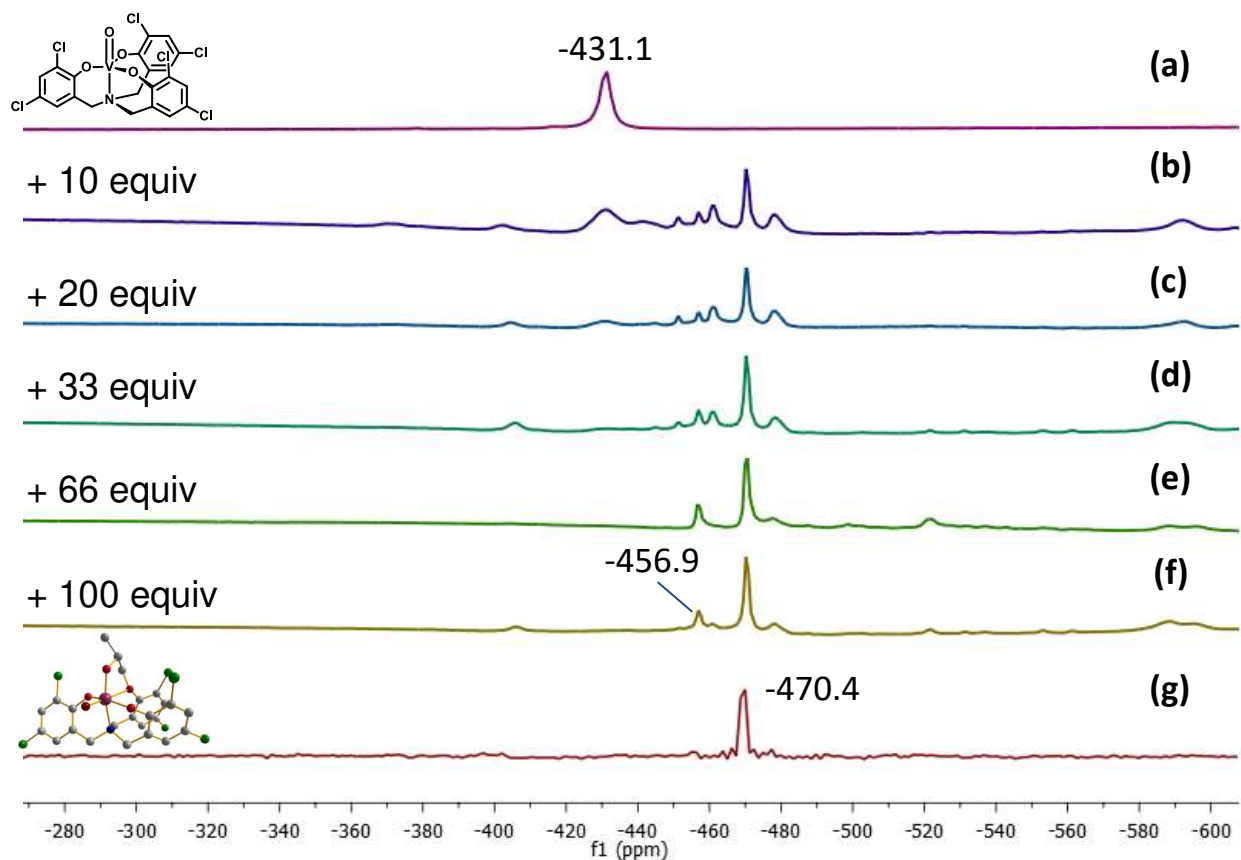for the presence of some other minor species (*cf.*, trace **f**).

Figure 4. [51]V-NMR titration of complex **2** with various amounts of PO. Conditions used: [**2**] = 0.01 M in CD$_3$CN, NMR spectrum was recorded 5 h after initial mixing of **2** and PO. See the SI for further details.

In order to test whether the pre-isolated complex **2**–PO acts as a functional model for the epoxide

ring-opening stage, we performed some further catalytic tests with a pre-isolated sample of **2**–PO

and combined it with NBu$_4$Br[26] and fresh PO, and used it as a binary system for the formation of propylene carbonate (see Table 2). The catalysis data was compared against the background reaction (use of NBu$_4$Br only, entry 1), and the activity of **2**/NBu$_4$Br and **1**/NBu$_4$Br (entries 2 and 3) under similar reaction conditions and catalyst loadings. From the data in Table 2 it is clear that the complex **2**–PO still exhibits catalytic activity toward COC formation as it delivers propylene carbonate in a significantly higher yield than the background reaction. Remarkably, the combination of parent V(V) complex **2** with NBu$_4$Br under the reported conditions and (low) catalyst loading seems to possess similar activity as the binary combination **2**–PO/NBu$_4$Br pointing towards a relatively fast *in situ* formation of **2**–PO at 50ºC and >800 equiv of PO (Table 2).

Table 2. Comparison of the Activity of the Binary Systems 2-PO/NBu$_4$Br, 1/NBu$_4$Br and 2/NBu$_4$Br in the Formation of Propylene Carbonate.^{a}
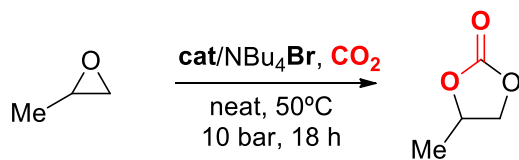
Entry	V-complex (mol %)	Nu (mol%)	Yield (%)^b
1	–	NBu$_4$Br, 0.048	3
2	**1**, 0.024	NBu$_4$Br, 0.048	96
3	**2**, 0.024	NBu$_4$Br, 0.048	9
4	**2-PO**, 0.024	NBu$_4$Br, 0.048	9

^{a}Reaction conditions: 20.0 mmol propylene oxide, 50ºC, 10 bar, 18 h, neat. Nu stands for nucleophilic additive. ^{b}NMR yield determined using mesitylene as internal standard; selectivity towards the COC product >99%. The average of two runs is reported.

As noted for the conversion of styrene oxide **B** and epichlorohydrin **C** (Table 1), a much lower activity for COC formation is noted when compared with the results obtained with the binary system **1**/NBu$_4$Br, suggesting that terminal epoxides with a modest steric impediment likely have a higher tendency to (partially) form an epoxide adduct of type **2**–PO. Further evidence for this hypothesis was gathered by analysis of the resultant complex when combining **2** with 100 equiv of epichlorohydrin (ECH) and analyzing the product by ^{51}V NMR and MALDI-TOF mass spectrometry (see SI), and X–ray diffraction (Figure 5).
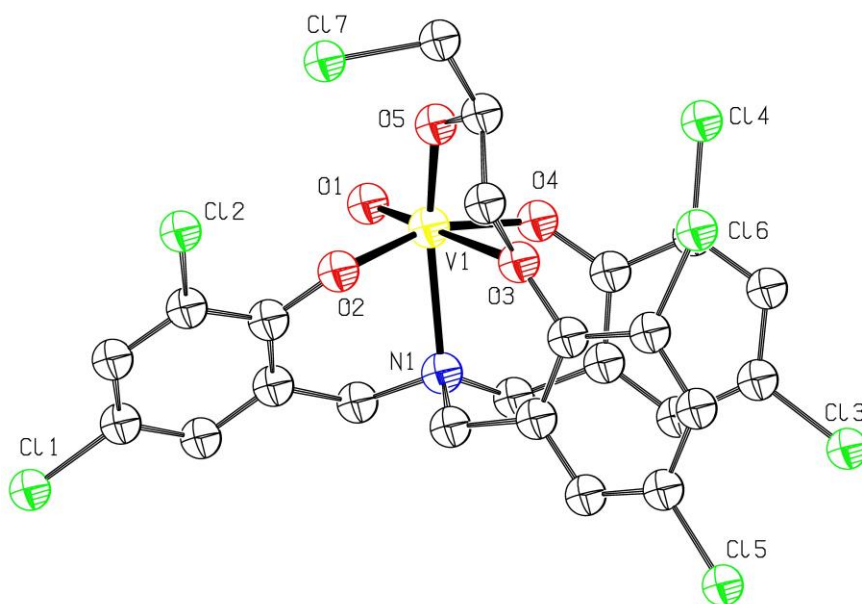

Figure 5. X-ray molecular structure of **2**–ECH based on V(V) complex **2**, ECH = epichlorohydrin. Selected bond lengths (Å) and angles (º), with esd´s in parentheses: V(1)-O(1) = 1.585(4), V(1)-O(2) = 1.893(4), V(1)-O(3) = 2.327(4), V(1)-O(4) = 1.879(4), V(1)-O(5) = 1.808(4), V(1)-N(1) = 2.233(5); O(4)-V(1)-N(1) = 84.25(17), O(1)-V(1)-O(3) = 179.8(2), O(2)-V(1)-O(5) = 92.21(19), O(2)-V(1)-O(4) = 159.53(18), N(1)-V(1)-O(5) = 156.53(19).

Similar formation of an unusual epoxide adduct was noted (*cf.*, formation of **2**–ECH), and therefore the combined analytical data clearly show a more general tendency to form intermediates of type **2**–PO when using terminal epoxide substrates with relatively small substituents.

In order to further test this hypothesis, crystallization of the sterically more crowded V(V) complex **1** was carried out in the presence of PO: X–ray diffraction studies revealed that the crystals corresponded to the starting complex **1** with no additional ligand being present in the coordination sphere (X–ray structure determined, see SI).[27] This seems to suggest that the coordination of PO and its subsequent incorporation into the V(V) aminotriphenolate complex as noted in **2**–PO is sterically modulated, but electronic effects cannot be ruled out as the V center may be involved in activating the epoxide towards intramolecular nucleophilic attack by one of the phenolate O-atoms. Furthermore, upon using sterically more hindered/demanding epoxides such as 1,2-epoxyhexane **A** and *trans* 2-phenyl-3-methyloxirane **D**, the expected reactivity order is restored. The more Lewis acidic complex **2** shows in these cases higher activity upon combining with NBu$_4$X (X = I, Br; Table 1) than noted for **1** under comparable conditions. These latter observations thus justify the use of the more Lewis acidic complex **2** in the conversion of internal, sterically more congested epoxides and the formation of COCs **4**–**19** (Figure 2).

Based on our observations and analyses, we propose that the formation of COCs using **2** starts off with coordination of the epoxide giving rise to a hexa-coordinated V(V) complex (Figure 6). Such coordination chemistry has been previously observed for various V(V) complexes ligated by tetradentate ligands in the literature[17a-b,18b] and recently also a H$_2$O-ligated V(V) aminotriphenolate was crystallographically characterized.[17a] In the presence of terminal epoxides, the formation of a complex of type **2**–PO can occur with a higher tendency if the epoxide substituent is relatively small.[28] It should be noted that the epoxide-based structures themselves (**2**–PO and **2**–ECH) do not

show any catalytic turnover and require the addition of an external nucleophile for reactivation. Upon reactivation, complex **2** can reenter the catalytic cycle in the presence of NBu₄**X** (**X** = Br, I), suggesting the subsequent formation of V(V) alkoxide intermediate species with the halide nucleophile **X** incorporated. Such a species can be formed through a nucleophilic attack of the bromide onto the arylalkyl ether part of the unusual intermediate, and allows for a nucleophilic displacement of the original phenolate. It is likely that this step is turnover-limiting in those cases where such a stable intermediate (*cf.*, **2**–PO and **2**–
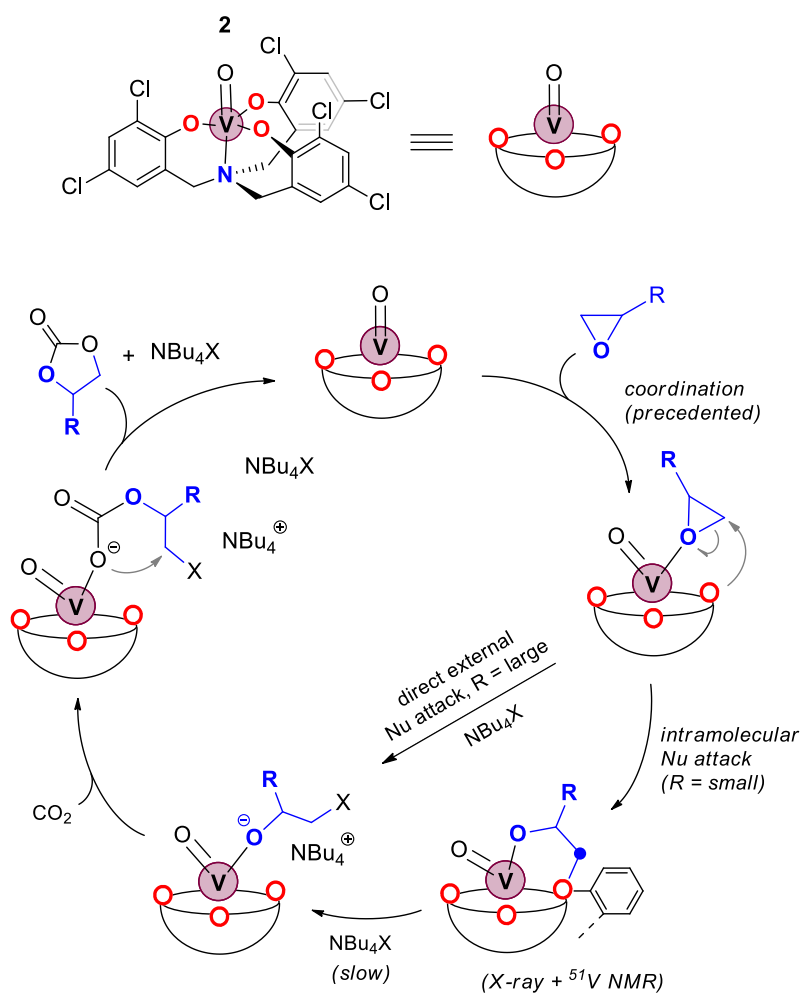

Figure 6. Proposed mechanistic manifold for the formation of COCs using the binary catalyst **2**/NBu₄**X** (X = Br, I).

ECH) can be formed, and therefore explains the lower relative reactivity for **2**/NBu$_4$**I** in the conversion of terminal epoxides with smaller substituents. Once the halide-containing alkoxide intermediate is formed, the formation of the COC follows a standard CO_2 insertion and ring-closing sequence delivering the final product and regenerating the five-coordinated V(V) complex **2** and NBu$_4$**X** for further catalytic turnover.

■ CONCLUSION

In this contribution we show that vanadium (V) complexes derived from aminotriphenolate ligands form powerful binary catalysts with ammonium salts and allow for the conversion of generally more challenging internal epoxides and CO_2 into their respective COCs with ample scope in epoxide reaction partners that display functional group diversity. Furthermore, the screening data and mechanistic control reactions together with the X–ray molecular structures determined for **2**–PO and **2**–ECH have revealed a new manifold towards the activation of the epoxide substrate leading to the formation of a functional model of an alkoxide-related (epoxide–activated) intermediate. The complexes **2**–PO and **2**–ECH can reengage in COC formation after combining with an ammonium salt. The unprecedented formation of these unusual compounds is sterically regulated, and has been confirmed to be operative for epoxides with limited steric impediment (propylene oxide, epichlorohydrin), whereas for sterically more encumbered substrates it can be assumed that initial coordination of the epoxide to the V(V) center is followed by epoxide ring-opening mediated by an external (halide) nucleophile. Therefore this work does not only show the high potential of high oxidation state V-complexes as binary catalyst components in COC formation, but the use of a V(V) aminophenolate species has also allowed for

the first time to identify a unique epoxide-activation mode reminiscent of a generally proposed intermediate in COC formation following epoxide activation by a Lewis acid and an external nucleophile.

AUTHOR INFORMATION

Corresponding Authors

*E-mail for G.L: giulia.licini@unipd.it.

*E-mail for A.W.K.: akleij@iciq.es.

Orchid

Arjan W. Kleij: **0000-0002-7402-4764**

Notes

The authors declare no competing financial interest.

■ ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal. ####.

Characterization data for all the organic carbonates and complexes, and crystallographic details in cif format (PDF).

■ ACKNOWLEDGMENTS

REFERENCES

(1) For some general reviews: (a) Aresta, M.; Dibenedetto, A.; Angelini, A. *Chem. Rev.* **2014**, *114*, 1709–1742. (b) Peters, M.; Köhler, B.; Kuckshinrichs, W.; Leitner, W.; Markewitz, P.; Müller, T. E. *ChemSusChem* **2011**, *4*, 1216–1240. (c) Sanz-Pérez, E. S.; Murdock, C. R.; Didas, S. A.; Jones, C. W. *Chem. Rev.* **2016**, *116*, 11840–11876. (d) Kondratenko, E. V.; Mul, G.; Baltrusaitis, J.; Larrazábal, G. O.; Pérez-Ramírez, J. *Energy Environ. Sci.* **2013**, *6*, 3112–3135.

(2) (a) *Renewable Raw Materials – New Feedstocks for the Chemical Industry*; Ulber, R.; Sell, D.; Hirth, T.; Eds.; Wiley-VCH: Weinheim, 2011, p 1-244. (b) Ciriminna, R.; Lomeli-Rodriguez, M.; Demma Carà, P.; Lopez-Sanchez, J. A.; Pagliaro, M. *Chem. Commun.* **2014**, *50*, 15288-15296. (c) Williams, C. K.; Hillmyer, M. A. *Polym. Rev.* **2008**, *48*, 1-10. (d) Winkler, M.; Romain, C.; Meier, M. A. R.; Williams, C. K. *Green Chem.* **2015**, *17*, 300-306.

(3) (a) *Carbon Dioxide as Chemical Feedstock*; Aresta, M.; Ed.; Wiley-VCH: Weinheim, 2010, p. 1-414. (b) Sakakura, T.; Choi, J. C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365-2387. (c) Perathoner, S.; Centi, G. *ChemSusChem* **2014**, *7*, 1274-1282.

(4) General reviews on CO_2 transformations: (a) Klankermayer, J.; Wesselbaum, S.; Beydoun, K.; Leitner, W. *Angew. Chem. Int. Ed.* **2016**, *55*, 7296-7343. (b) Liu, Q.; Wu, L.; Jackstell, R.;

Beller, M. *Nat. Commun*. **2015**, *6*, 5933. (c) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kühn, F. E. *Angew. Chem. Int. Ed*. **2011**, *50*, 8510-8537. (d) Yu, B.; He, L.-N. *ChemSusChem* **2015**, *8*, 52-62. (e) Kielland, N.; Whiteoak, C. J.; Kleij, A. W. *Adv. Synth. Catal.* **2013**, *355*, 2115-2138.

(5) For selected, seminal examples of direct CO_2 activation: (a) Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M *J. Chem. Soc. Chem. Commun*. **1975**, 636-637. (b) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc*. **1978**, *100*, 7405-7407. (c) Castro-Rodriguez, I.; Nakai, H.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *Science* **2004**, *305*, 1757-1759. For a small selection of generally applicable approaches of co-reactant (H_2, epoxide, propargylic systems) activation, see: (d) Tanaka, R.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc*. **2009**, *131*, 14168-14169. (e) Wesselbaum, S.; vom Stein, T.; Klankermayer, J.; Leitner, W. *Angew. Chem. Int. Ed*. **2012**, *51*, 7499-7502. (f) Whiteoak, C. J.; Kielland, N.; Laserna, V.; Escudero-Adán, E. C.; Martin, E.; Kleij, A. W. *J. Am. Chem. Soc.* **2013**, *135*, 1228-1231. (g) Yu, B.; He, L.-N. *ChemSusChem* **2015**, *8*, 52-62.

(6) (a) Martín, C.; Fiorani, G.; Kleij, A. W. *ACS Catal*. **2015**, *5*, 1353-1370. (b) Comerford, J. W.; Ingram, I. D. V.; North, M.; Wu, X. *Green Chem*. **2015**, *17*, 1966–1987. (c) Fiorani, G.; Guo, W.; Kleij, A. W. *Green Chem*. **2015**, *17*, 1375–1389. (d) Schäffner, B.; Schäffner, F.; Verevkin, S. P.; Börner, A. *Chem. Rev*. **2010**, *110*, 4554–4581.

(7) (a) Nozaki, K. *Pure Appl. Chem*. **2004**, *76*, 541−546. (b) Darensbourg, D. *Chem. Rev*. **2007**, *107*, 2388−2410. (c) Lu, X.-B.; Darensbourg, D. J. *Chem. Soc. Rev*. **2012**, *41*, 1462−1484. (d) Childers, M. I.; Longo, J. M.; Van Zee, N. J.; LaPointe, A. M.; Coates, G. W. *Chem. Rev*. **2014**, *114*, 8129−8152.

(8) (a) Rintjema, J.; Epping, R.; Fiorani, G.; Martín, E.; Escudero-Adán, E. C.; Kleij, A. W. *Angew. Chem. Int. Ed*. **2016**, *55*, 3972-3976. (b) Cozzolino, M.; Press, K.; Mazzeo, M.; Lamberti, M. *ChemCatChem* **2015**, *8*, 455-460. (c) North, M.; Quek, S. C. Z.; Pridmore, N. E.; Whitwood, A. C.; Wu, X. *ACS Catal*. **2015**, *5*, 3398-3402. (d) Tian, D.; Liu, B.; Gan, Q.; Li, H.; Darensbourg, D. J. *ACS Catal.* **2012**, *2*, 2029-2035. (e) Rintjema, J.; Guo, W.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. *Chem. Eur. J.* **2015**, *21*, 10754-10762. (f) Qin, Y.; Guo, H.; Sheng, X.; Wang, X.; Wang, F. *Green Chem*. **2015**, *17*, 2853-2858. (g) Fuchs, M. A.; Altesleben, C.; Zevaco, T. A.; Dinjus, E. *Eur. J. Inorg. Chem*. **2013**, 4541-4545.

(9) (a) Whiteoak, C. J.; Martin, E.; Martínez Belmonte, M.; Benet-Buchholz, J.; Kleij, A. W. *Adv. Synth. Catal*. **2012**, *354*, 469-476. (b) Buchard, A.; Kember, M. R.; Sandeman, K. G.; Williams, C. K. *Chem. Commun.* **2011**, *47*, 212-214. (c) Della Monica, F.; Vummaleti, S. V. C.; Buonerba, A.; De Nisi, A.; Monari, M.; Milione, S.; Grassi, A.; Cavallo, L.; Capacchione, C. *Adv. Synth. Catal.* **2016**, *358*, 3231-3243. (d) Buonerba, A.; De Nisi, A.; Grassi, A.; Milione, S.; Capacchione, C.; Vagin, S.; Rieger, B. *Catal. Sci. Technol.* **2015**, *5*, 118-123.

(10) (a) A. Decortes, A. W. Kleij, *ChemCatChem***2011**, *3*, 831-834. (b) M. A. Fuchs, C. Altesleben, S. C. Staudt, O. Walter, T. A. Zevaco, E. Dinjus, *Catal. Sci. Technol*. **2014**, *4*, 1658-1673. (c) J. Hu, J. Ma, Q. Zhu, Q. Qian, H. Han, Q. Mei, B. Han, *Green Chem*. **2016**, *18*, 382-385. (d) Y. Ren, J. Chen, C. Qi, H. Jiang, *ChemCatChem* **2015**, *7*, 1535-1538. (e) Mercadé, E.; Zangrando, E.; Claver, C.; Godard, C. *ChemCatChem* **2016**, *8*, 234-243. (f) Ren, Y.; Chen, J.; Qi, C.; Jiang, H. *ChemCatChem***2015**, *7*, 1535-1538.

(11) For some examples: (a) Lu, X.-B.; Liang, B.; Zhang, Y.-J.; Tian, Y.-Z.; Wang, Y.-M.; Bai, C.-X.; Wang, H.; Zhang, R. *J. Am. Chem. Soc*. **2004**, *126*, 3732–3733. (b) Paddock, R. L.; Nguyen,

S. T. *Chem. Commun*. **2004**, 1622-1623. (c) Paddock, R. L.; Nguyen, S. T. *J. Am. Chem. Soc*. **2001**, *123*, 11498–11499. (d) Chang, T.; Jin, L.; Jing, H. *ChemCatChem* **2009**, *1*, 379-383. (e) Ren, W.-M.; Wu, G.-P.; Lin, F.; Jiang, J.-Y.; Liu, C.; Luo, Y.; Lu, X.-B. *Chem. Sci.* **2012**, *3*, 2094–2102.

(12) Decortes, A.; Castilla, A. M.; Kleij, A. W. *Angew. Chem. Int. Ed*. **2010**, *49*, 9822-9837.

(13) Licini, G.; Mba, M.; Zonta, C. *Dalton Trans*. **2009**, 5265-5277.

(14) (a) Mba, M.; Prins, L. J.; Licini, G. *Org. Lett*. **2007**, *9*, 21-24. (b) Mba, M.; Prins, L. J.; Zonta, C.; Cametti, M.; Valkonen, A.; Rissanen, K.; Licini, G. *Dalton Trans*. **2010**, *39*, 7384-7392. (c) Zonta, C.; Cazzola, E.; Mba, M.; Licini, G. *Adv. Synth. Catal*. **2008**, *350*, 2503-2506.

(15) (a) Badetti, E.; Romano, F.; Marchiò, L.; Taşkesenlioğlu, S.; Daştan, A.; Zonta, C.; Licini, G. *Dalton Trans*. **2016**, *45*, 14603-14608. (b) Romano, F.; Linden, A.; Mba, M.; Zonta, C.; Licini, G. *Adv. Synth. Catal*. **2010**, *352*, 2937-2942.

(16) (a) Whiteoak, C. J.; Gjoka, B.; Martin, E.; Martínez Belmonte, M.; Escudero-Adán, E. C.; Zonta, C.; Licini, G.; Kleij, A. W. *Inorg. Chem*. **2012**, *51*, 10639-10649. (b) Badetti, E.; Gjoka, B.; Nagy, E. M.; Bernardinelli, G.; Kündig, P. E.; Zonta, C.; Licini, G. *Eur. J. Inorg. Chem*. **2015**, 3478–3484.

(17) (a) Groysman, S.; Goldberg, I.; Goldschmidt, Z.; Kol, M. *Inorg. Chem*. **2005**, *44*, 5073-5080. (b) Wolff, F.; Lorber, C.; Choukroun, R.; Donnadieu, B. *Inorg. Chem*. **2003**, *42*, 7839-7845.

(18) (a) Mba, M.; Pontini, M.; Lovat, S.; Zonta, C.; Bernardinelli, G.; Kündig, P. E.; Licini, G. *Inorg. Chem*. **2008**, *47*, 8616-8618. (b) Barroso, S.; Adão, P.; Madeira, F.; Teresa Duarte, M.; Costa Pessoa, J.; Martins, A. M. *Inorg. Chem*. **2010**, *49*, 7452-7463. For an extensive review on

this topic: (c) Amadio, E.; di Lorenzo, R.; Zonta, C.; Licini, G. *Coord. Chem. Rev*. **2015**, *301–302*, 147–162.

(19) (a) Coletti, A.; Whiteoak, C. J.; Conte, V.; Kleij, A. W. *ChemCatChem* **2012**, *4*, 1190-1196. Recently North and coworkers used V(V) salen complexes as catalysts for the formation of cyclic carbamates, see: (b) Beattie, C.; North, M. *RSC Adv*. **2014**, *4*, 31345-31352. Note a highly recent contribution from Kerton and coworkers that describes the use of V(V) bisphenolate complexes for cyclic carbonate synthesis: (c) Elkurtehi, A. I.; Kerton, F. M. *ChemSusChem* **2017**, DOI: 10.1002/cssc.201601548.

(20) Selected examples: (a) Laserna, V.; Fiorani, G.; Whiteoak, C. J.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. *Angew. Chem. Int. Ed*. **2014**, *53*, 10416-10419. (b) Qin, J.; Wang, P.; Li, Q.; Zhang, Y.; Yuan, D.; Yao, Y. *Chem. Commun*. **2014**, 50, 10952-10955. (c) Castro-Osma, J. A.; Lamb, K. J.; North, M. *ACS Catal*. **2016**, *6*, 5012–5025. (d) Martínez-Rodríguez, L.; Otalora Garmilla, J.; Kleij, A. W. *ChemSusChem* **2016**, *9*, 749-755. (e) Whiteoak, C. J.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. *Adv. Synth. Catal*. **2013**, *355*, 2233-2239. (f) Martínez, J.; Castro-Osma, J. A.; Earlam, A.; Alonso-Moreno, C.; Otero, A.; Lara-Sánchez, A.; North, M.; Rodríguez-Diéguez, A. *Chem. Eur. J*. **2015**, *21*, 9850–9862.

(21) Whiteoak, C. J.; Kielland, N.; Laserna, V.; Castro-Gómez, F.; Martin, E.; Escudero-Adán, E. C.; Bo, C.; Kleij, A. W. *Chem. Eur. J*. **2014**, *20*, 2264-2275.

(22) Note that typically a bromide based nucleophile such as NBu$_4$Br is used for the conversion of internal epoxides. For exemplary use of bromide based nucleophiles for these types of transformations see references 5f, 8e, 9a, 20a and 20d.

(23) For a highly recent and detailed benchmarking studies involving various Al(III) based binary catalysts see: Rintjema, J.; Kleij, A. W. *ChemSusChem* **2017**, DOI: 10.1002/cssc.201601712.

(24) For recent examples of catalytic bio-based cyclic carbonate synthesis see: (a) Tenhumberg, N.; Büttner, H.; Schäffner, B.; Kruse, D.; Blumenstein, M.; Werner, T. *Green Chem*. **2016**, *18*, 3775-3788. (b) Fiorani, G.; Stuck, M.; Martín, C.; Martínez-Belmonte, M.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. *ChemSusChem* **2016**, *9*, 1304-1311. (c) Maisonneuve, L.; More, A. S.; Foltran, S.; Alfos, C.; Robert, F.; Landais, Y.; Tassaing, T.; Grau, E.; Cramail, H. *RSC Adv*. **2014**, *4*, 25795-25803. (d) Langanke, J.; Greiner, L.; Leitner, W. *Green Chem*. **2013**, *15*, 1173-1182.

(25) Recently a H_2O-ligated hexa-coordinated V(V) aminotriphenolate complex was crystallographically and spectroscopically characterized showing that a coordination site is indeed available for O–donor ligands, see reference 17a.

(26) Since the **2**–PO complex is sterically more congested than complex **2** itself, we decided to use NBu_4Br rather than NBu_4I for further catalytic tests as bromide is a smaller sized nucleophile. Note that for Al(III) based binary catalysts we found that the use bromide and iodide based nucleophiles induced similar type of activity in terminal epoxide conversions, see reference 5f and 21.

(27) The X–ray molecular structure for complex **1** was reported before, see reference 17a.

(28) In order to support the fast formation of **2**–PO from 2 and PO, we carried out a time-dependent ^{51}V NMR experiment (50ºC) combining the V-complex **2** and a large excess of 200 molar equiv of PO in CD_3CN. Despite the fact that the dilution is much higher than reported in Table 2 (reactions carried out "neat"), smaller excess of PO was used (200 versus 833 equiv) and

the lack of efficient stirring during the NMR experiment, we found that the formation of **2**–PO is relatively fast with around 50% of the V-complex being present as **2**–PO after 1.5 h. For details see the SI.

Insert Table of Contents Graphic and Synopsis Here

intermediate

X-ray + MS
^{51}V *NMR*

NBu$_4$**X**

CO_2

- wide scope for R^1 + R^2
- 16 examples, yield up to 89%
- functional group diversity