Co-polymerization of propylene oxide and CO_2 using early transition metal (groups IV and V) metallocalix[*n*]arenes (n = 4, 6, 8)

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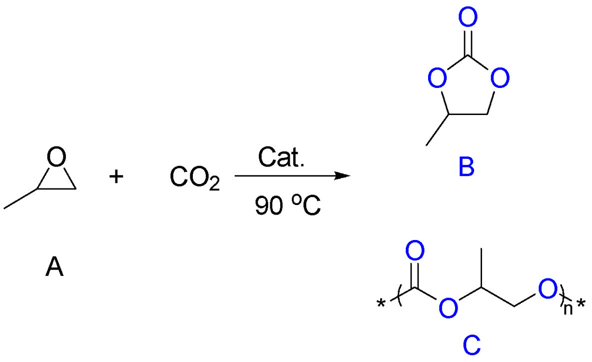
Abstract: A number of metallocalix[*n*]arenes, where n = 4, 6, or 8, of titanium and vanadium have been screened for their ability to act as catalysts for the co-polymerization of propylene oxide and CO_2 to form cyclic/polycarbonates. The vanadium-containing catalysts, namely [VO(L^1Me)] (**1**), [$(VO_2)L^2H_6$] (**2**),

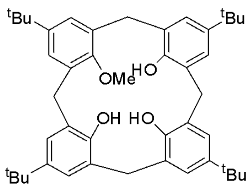
$[Na(NCMe)_6]_2[(Na(VO)_4L^2)(Na(NCMe))_3]_2$ (**3**), $[VO(\mu\text{-}OH)L^{3/}H_2]_2\cdot 6CH_2Cl_2$ (**4**), $\{[VO]_2(\mu\text{-}O)L^4[Na(NCMe)_2]_2\}$ (**5**), $\{[V(Np\text{-}tolyl)]_2L^4\}$ (**6**) and $[V(Np\text{-}RC_6H_4)Cl_3]$ (R = Cl (**7**), OMe (**8**), CF_3 (**9**)), where L^1H_3 = methylether-p-*tert*-butylcalix[4]areneH_3, L^2H_8 = p-*tert*-butylcalix[8]areneH_8, L^3H_4 = p-*tert*-butylthiacalix[4]areneH_4, L^4H_6 = p-*tert*-butyltetrahomodioxacalix[6]areneH_6, performed poorly, affording, in the majority of cases, TONs less than 1 at 90 ºC over 6 h and low molecular weight oligomeric products ($M_n \leq 1665$). In the case of the titanocalix[8]arenes, $\{(TiX)_2[TiX(NCMe)]_2(\mu_3\text{-}O)_2(L^2)\}$ (X = Cl (**10**), Br (**11**), I (**12**)), which all adopt a similar, ladder-type structure, the activity under the same conditions is somewhat higher (TONs > 6) and follows the trend Cl > Br > I; by comparison the non-calixarene species $[TiCl_4(THF)_2]$ was virtually inactive. In the case of **10**, it was observed that the use of PPNCl (bis(triphenylphosphine)iminium chloride) as co-catalyst significantly improved both the polymer yield and molecular weight (M_n 3515). The molecular structures of the complexes $[HNEt_3]_2[VO(\mu\text{-}O)L^3H_2]_2\cdot 3CH_2Cl_2$ (**4**$\cdot 3CH_2Cl_2$), $[VO(\mu\text{-}OH)L^{3/}H_2]_2\cdot 6CH_2Cl_2$ (**4**$^{/}$) (where $L^{3/}H_2$ is a partially oxidized form of L^3H_4) and $\{(TiCl)_2[TiCl(NCMe)]_2(\mu_3\text{-}O)_2(L^2)\}\cdot 6.5MeCN$ (**10**$\cdot$6.5MeCN) are reported.

1. | INTRODUCTION

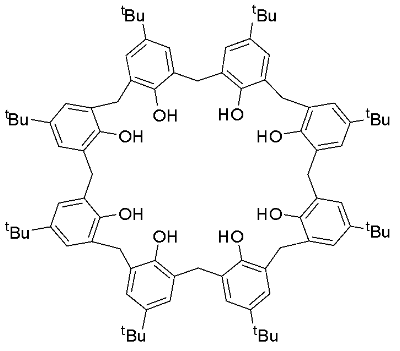
Given the current issues associated with CO_2 pollution and the environment, there is now a pressing need to develop processes which can utilize and transform CO_2 into other useful materials such as urea, formic acid, dimethyl ether, urethane, isocyanate, and polyurethane, etc.[1-3] One such process of interest converts CO_2 into polycarbonates via coupling with an epoxide.[4] To-date, this has met with some success,[5-11] although the resulting polycarbonates have found limited application.[12-13] We have previously investigated the use of salen complexes of the metals chromium and cobalt, and found that they can function as catalysts for the co-polymerization of CO_2 with propylene oxide under mild conditions (Scheme 1).[14] The product selectivity was good with > 99% head-to-tail linkages observed, and very little cyclic carbonate was present (see B, Scheme 1). The exploration of new catalysts for this process continues to attract much attention, and a range of metals have been employed from chromium through to zinc.[15-35] However, reports concerning the use of early transitions metals, specifically of groups IV and V are scant.[36-45] Herein, we investigate the use of metallocalix[*n*]arenes as catalysts for this co-polymerization process, given that calixarenes have been described as pseudo oxide surfaces,[46] and that they have exhibited promising catalytic potential in a number of other processes.[47] Calix[*n*]arenes are phenolic macrocycles in which the *n* phenols can be linked via a variety of bridges.[48] In the present study, we have utilized the calixarenes shown in Scheme 2, which differ in both size and bridge. We have focused herein on the use of the earth abundant metals titanium and vanadium, given that the derived calix[*n*]arene species are both relatively non-toxic[49-50] and readily accessible.[51] The complexes screened herein are shown in Scheme 3.



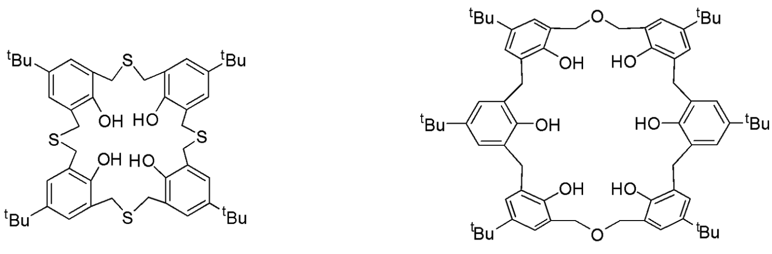
SCHEME 1. Co-polymerization of propylene oxide and CO_2.



L^1(Me)H$_3$

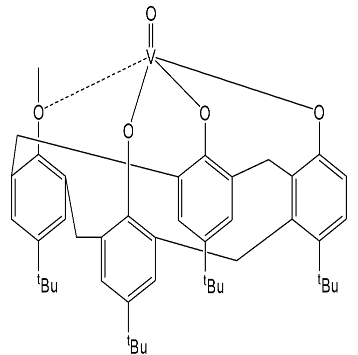


L^{2}H$_8$



L^3H_4 L^4H_6

SCHEME 2. Calixarenes employed in the present study.



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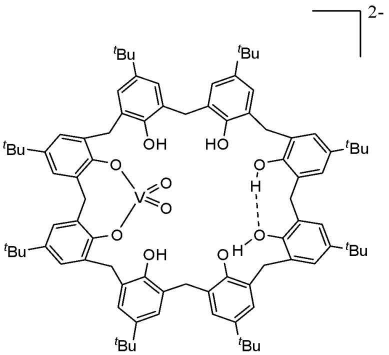

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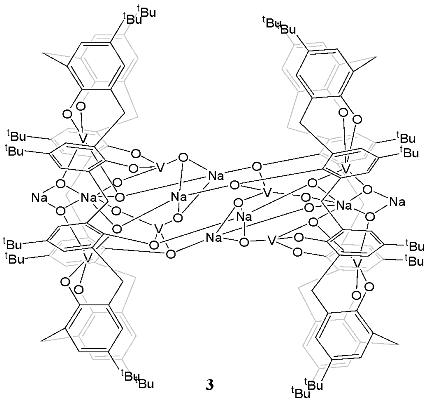

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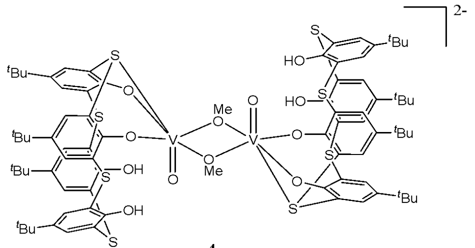

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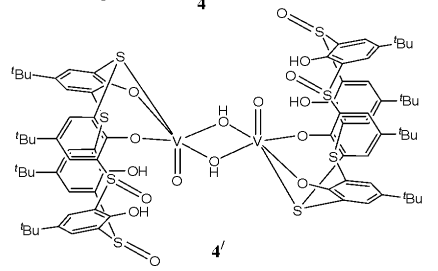
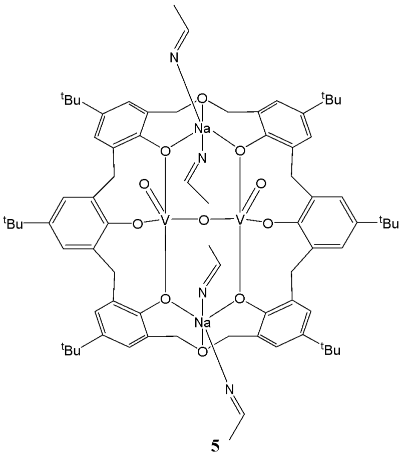


4′



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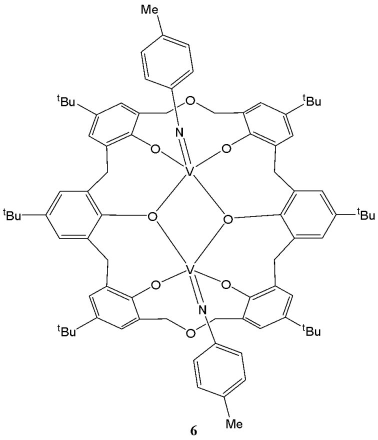

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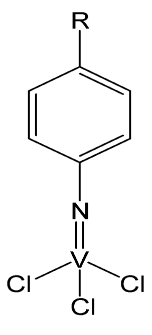
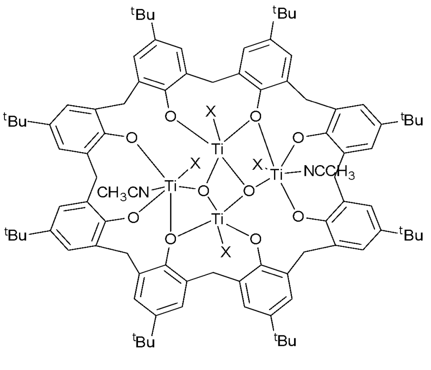
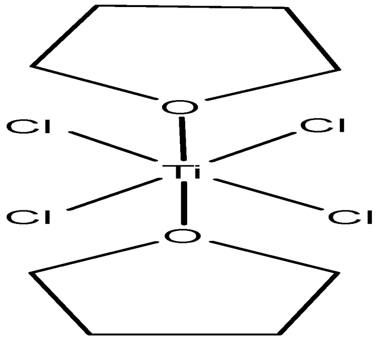


R=Cl(**7**), OMe(**8**), CF_3(**9**)



X = Cl(**10**), Br(**11**), I(**12**)



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SCHEME 3. The metallocalix[4, 6, and 8]arenes screened herein and the non-calixarene precursors used as benchmarks.

2. | EXPERIMENTAL

2.1 | Materials

2.1.1 | General

All complexes were prepared under nitrogen using standard Schlenk techniques and dried and degassed solvents. The precursors [$TiCl_4$] (99%), [$TiBr_4$] (99%), and [TiI_4] (99%) were purchased from Sigma Aldrich. The compounds p-*tert*-butylcalix[8]areneH_8 (98%) and p-tert-butylthiacalix[4]areneH_4 were obtained from TCI, UK. Tetrahydrofuran (99%), toluene (99%), and acetonitrile were purchased from Adamas-Beta. N_2 (99.99%) and CO_2 (99.995%) were purchased from Xi'an Teda Cryogenic Equipment Co., Ltd. Methylether-*p*-*tert*-butylcalix[4]areneH_3 and p-*tert*-butyltetrahomodioxacalix[6]areneH_6 were prepared according the methods reported in literature.[52,53] The complexes [$V(p\text{-}RC_6H_4N)Cl_3$] were prepared according the method reported by Maatta et al.[54] [$TiCl_4(THF)_2$] was prepared by the method of Schrock et al.[55] All other chemicals were purchased from commercial companies and used without further purification. The complexes **1**[56], **2**[57], **3** [58], **5**, **6**,[59] and **10** - **12**,[60] were prepared by the literature methods.

2.1.2 | Synthesis of $[HNEt_3]_2[VO(\mu\text{-}O)L^4H_2]_2\cdot3CH_2Cl_2$ ($4\cdot3CH_2Cl_2$)

p-*tert*-Butylthiacalix[4]areneH_4 (0.108 g, 0.15 mmol), [$VOSO_4$] (0.147 g, 0.90 mmol), and Et_3N (1.51 mL, 10.8 mmol) were refluxed for 12 h in methanol (10 mL) under a nitrogen atmosphere. On cooling, volatiles were removed *in-vacuo* and the residue was washed with acetonitrile (30 mL), and then extracted in CH_2Cl_2 (10 mL). A layer of hexane (10 mL) was carefully added and the solvent system left to diffuse for 7 days to afford yellow prisms of **4** (*ca*. 15% yield). Anal. $C_{97}H_{136}Cl_6N_2O_{12}S_8V_2$ requires C, 55.66; H, 6.55; N, 1.34 %. Found: C, 55.83; H, 6.59; N, 1.38 %. IR: 3545w, 3406bw, 1403m, 1260s, 1178m, 1096bs, 1018bs, 938m, 869m, 800s, 722m, 638m. For **4**$^{/}$: Yield: 21%. ^1H NMR ($CDCl_3$, 400

MHz, 298K) δ: 10.72 (s, 4H, O*H*), 7.63 – 7.21 (4x m, 16H, aryl*H*), 5.23 (s, 12H, CH_2Cl_2), 1.08, 1.06 (2x s, 72H, C(CH_3)$_3$); (μ-OH not observed). ^{51}V NMR ($CDCl_3$) δ: –475.1.

2.2 | Methods

2.2.1 | Catalytic reaction

The co-polymerization reaction of propylene oxide and CO_2 to cyclic polycarbonates was carried out in a 16 mL stainless steel autoclave with a Teflon inner container in a batch mode of operation. In a typical reaction, propylene oxide (5 mL) and catalyst (100 mg) were added into the inner container, which was transferred into the autoclave. The reactor was sealed and charged with 1 MPa of N_2 to remove the air three times. After that, it was charged with 5 MPa of CO_2 and heated to 90 °C and stirred for 5 h. Upon reaction, the solid catalyst was separated using an extra magnet, and the liquid was analyzed on a gas chromatograph (GC9720, Zhejiang Fuli Analytical Instruments Co., Ltd., China) equipped with a flame ionization and GC-MS (Agilent 6890N-5975) with an HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). The afforded products (cyclic/polycarbonates) were analyzed on a Gel Permeation Chromatography (Waters 1525 & Agilent PL-GPC220) at room temperature.

2.2.2 | Crystallography Experimental.

Diffraction data for **4**·3CH_2Cl_2 was collected using silicon 111 mono-chromated synchrotron radiation at the ALS station 11.3.1.[61] That for **4$'$**·6CH_2Cl_2 was collected using a conventional fine-focus sealed beam source on a CCD diffractometer with graphite mono-chromation,[61] while data for **10**·6.5MeCN were collected using a rotating anode X-ray tube and a hybrid pixel array detector. All data sets were corrected for absorption and Lp effects.[62] Structures were solved by direct methods or a dual space charge-flipping algorithm. [63] Refinement was on F^2 [64] and proceeded routinely except as described as follows: for **4**·3CH_2Cl_2 the crystals degraded rapidly when exposed to the air, most likely due to desolvation. Me groups on tBu groups at C(7) and C(17) were refined as two-fold disordered with major occupancy 72.6(12) and 71.2(17)% respectively. The CH_2Cl_2 containing C(49) was refined at half weight. For

4$^{/}$·6CH_2Cl_2 the data were non-merohedrally twinned with both twin components used in refinement with a twin ratio of 0.6053:0.3947(18). The twin law is a 180° rotation about reciprocal axis [1 0 0]. Three unique CH_2Cl_2 molecules per asymmetric unit. Those at C(41) and C(43) were refined as disordered over two sets of positions with major occupancies of 0.622(19) and 0.512(5)%, respectively, while that at C(42) was refined at exactly half weight due to it being very diffuse or low occupancy. In addition, another CH_2Cl_2 per unit cell or per dimer was modelled as an area of diffuse electron density by the Platon Squeeze method which recovered 48 electrons in one void on a centre of symmetry. [65-66] CH_2Cl_2 has 42 electrons, and this tallied with the point atom observations. The disordered CH_2Cl_2 at C(41) resides in the calixarene cavity. For **10**·6.5MeCN the data were also merohedrally twinned with twin law [–1 0 0, 0 –1 0, 0.777 0 1] with a twin ratio 0.8908:0.1092(11). Two-fold disorder was modelled for the entire ^{t}Bu group at C(51) with major component occupancy 70(2)%. Also, two-fold disorder of the Me groups in the ^{t}Bu groups at C(17A) and C(84A) was modelled with major occupancy 73(3) and 58(3)% respectively. MeCN of crystallisation at N(12) was modelled as disordered over two sets of positions with major component 71.3(18)%.

CCDC 2018276-78 contain the crystal data for structures **4**·3CH_2Cl_2, **4**$^{/}$·6CH_2Cl_2, and **10**·6.5MeCN, respectively.

3 | RESULTS AND DISCUSSION

3.1 | Vanadium

Given the high activity exhibited recently by vanadyl-containing chelating phenolate species, we have investigated herein a number of vanadyl or vanadium imido containing calixarene systems.[45] We initially screened the known vanadyl p-*tert*-butylcalix[4]arene [VO(L^1Me)] **1**, [56] however the results for the co-polymerization of propylene oxide with CO_2 using **1** were disappointing (Entry 1, Table 1). Similar results were obtained using a VO_2 motif bound to the lower rim of a p-*tert*-butylcalix[8]areneH_6 ligand (derived from L^2H_8), i.e. complex **2** (Entry 2, Table 1). We then examined a complex containing multiple vanadyl centres to ascertain if potential cooperativity between the metal centres would enhance the observed catalytic activity. In particular, complex **3** bearing eight vanadium centres sanswiched between two L^2-derived ligands was screened under the same conditions as for **1** and **2**, but again only small amounts of polycarbonate (Entry 3, Table 1) were isolated. We then targeted a thia [-S-] bridged calixarene species, since changing to this type of bridge has proved beneficial in other catalytic processes,[67] and the bridging sulfur can help to stabilize novel motifs.[68-69] A new vanadyl complex **4** was isolated by reacting p-*tert*-butylthiacalix[4]areneH$_4$ (L^3H_4) with [$VOSO_4$] in the presence of triethylamine in dry methanol under nitrogen. Following removal of the solvent, the residue was washed with acetonitrile to remove the known (blue) complex $[HNEt_3]_5[(VO)_5(\mu_3\text{-}O)_4(SO_4)_4]$.[57] Subsequent extraction of the remaining residue into dichloromethane afforded the methoxide-bridged salt $[HNEt_3]_2[VO(\mu\text{-}OMe)L^3H_2]_2\cdot 3CH_2Cl_2$ (**4**$\cdot 3CH_2Cl_2$) (*ca.* 15 %) as small, solvent dependent, yellow prisms. The crystals were subjected to a single crystal X-ray diffraction study using synchrotron radiation, and the molecular structure is shown in Figure 1, with selected bond lengths and angles given in the caption; crystallographic data are given in Table 2. The molecule lies on a centre of symmetry, with three molecules of CH_2Cl_2 present; two in thiacalixarene cavities, making C–H···π interactions of 2.57 Å and 2.65 Å with rings C(1) > C(6) and C(21) > C(26) respectively, and two half-occupied molecules *exo*. On each of the thiacalixarenes, two phenolic groups are not involved in bonding to the metal, but are involved in H-bonding to the two coordinated phenolate groups. The $[HNEt_3]^+$ cations are involved in H-bonding to the vanadyl oxygen atoms. Each thiacalix[4]arene cavity possesses a distorted elliptical conformation, with opposite centroid···centroid separations of 6.514 Å and 7.498 Å. This complex has geometrical parameters similar to the bridged hydroxide salt $[VO(\mu\text{-}OH)L^5]_2[PPh_4]_2$, where L^5H_2 = 2,2$'$-thiobis(2,4-di-*tert*-butylphenol), reported by Limberg *et al.*[70] The same group has also reported the structure of the oxo-bridged salt $[VO(\mu\text{-}O)L^3H_2]_2[PPh_4]_2$.[71] The V···V distance [3.060(2) Å] in **4** is non-bonding, (*cf* 3.1705(4) Å in the Limberg hydroxo-bridged complex),[70] with the d^1 centres exhibiting weak antiferromagnetic coupling at ambient temperature (μeff = 2.06).

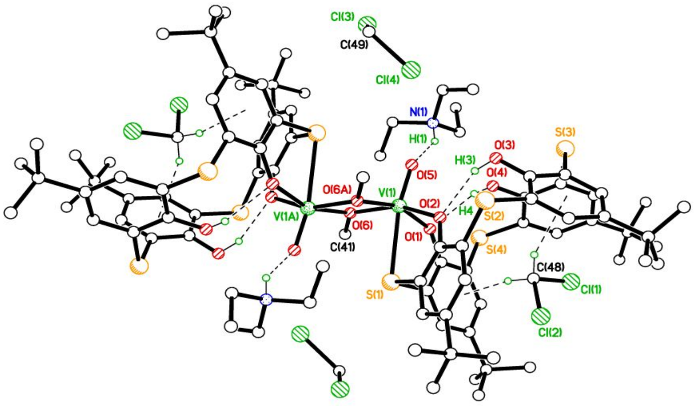


FIGURE 1. Molecular structure for the anion of **4**$\cdot 3CH_2Cl_2$. Non H-bonding H atoms removed for clarity. Selected bond lengths (Å) and angles (°): V(1)–O(1) 1.983(4), V(1)–O(2) 1.966(4), V(1)–O(5) 1.610(4), V(1)–O(6) 1.952(4), V(1)–O(6$'$) 1.970(4), V(1)–S(1) 2.801(2); O(1)–V(1)–O(2) 93.12(18), O(5)–V(1)–S(1) 169.41(16), V(1)–O(6)–V(1$'$) 102.55(18). Symmetry operator $'$ = –x+1, –y+2, –z+1.

Interestingly, on one occasion, following work-up as described above, we also isolated red/brown needles, which were found, by X-ray crystallography, to be the hydroxide-bridged dimeric structure $[VO(\mu\text{-}OH)L^{3'}H_2]_2\cdot 6CH_2Cl_2$ (**4$'$**$\cdot 6CH_2Cl_2$), where $L^{3'}H_2$ is a partially oxidized form of the parent thiacalixarene L^3H_4. This partially oxidized ligand bears bridges of the form $S_2SO_{0.163}SO_{0.382}$, and presumably arises via the presence of adventitious oxygen present during the preparation (the parent L^3H_4 appeared to contain no oxidized species). The molecular structure is shown in Figure 2, with selected bond lengths and angles given in the caption; crystallographic data are given in Table 2.

In **4$'$**, each vanadium(V) is distorted octahedral and is bounded by two calix phenoxide oxygens, one of the thia calix sulfur bridges, the two hydroxide bridges, and a vanadyl group. The molecule lies on a centre of symmetry. Two calixarene phenol groups remain protonated and form intramolecular H-bonds with metal-coordinated phenolate neighbours, as seen in **4**. The bridging hydroxide forms a H-bond with one of the CH_2Cl_2 molecules. The CH_2Cl_2 molecule in the calixarene cavity forms C–H···π interactions with two C atoms, C(13) and C(16), in one calixarene phenolate ring with distances of 2.94 Å and 2.86 Å respectively. The V···V distance [2.7809(11) Å] in **4**$^{/}$ is non-bonding (*cf* 2.7453(6) Å in the Limberg oxo-bridged complex).[71]

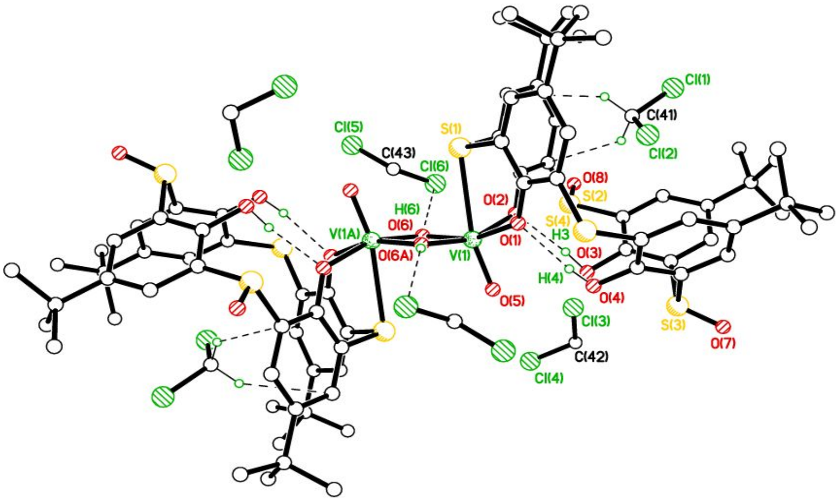


FIGURE 2. Molecular structure of **4**$^{/}$·$6CH_2Cl_2$. H atoms not involved in H-bonding omitted for clarity. Selected bond lengths (Å) and angles (°): V(1)–O(1) 1.967(3), V(1)–O(2) 1.975(3), V(1)–O(5) 1.606(3), V(1)–O(6) 1.828(3), V(1)–O(6$^{/}$) 1.849(4), V(1)–S(1) 2.7604(10); O(1)–V(1)–O(2) 91.91(10), O(5)–V(1)–S(1) 166.54(9), V(1)–O(6)–V(1$^{/}$) 98.30(11). Symmetry operator $^{/}$ = –x, –y+1, –z.

Dissappointingly, results from the screening utilizing this new thia-bridged species also proved to be poor (Entry 4, Table 1) affording only 0.6 g of polycarbonate per g of catalyst. Similarly, catalysts based on dimethyloxa (-CH_2OCH_2-) bridged calix[*n*]arenes have shown enhanced performance in other catalytic applications,[56] and so the known complexes **5** and **6** were prepared. Whilst the imido complex **6** was virtually inactive, slightly higher activity was observed for mixed-metal complex **5**, with a TON of 1.523 $g/g_{Cat.}$

To investigate whether the presence of the calixarene was detrimental to the process, we also targeted a series of vanadium imidotrichlorides, namely [V(p-RC$_6$H$_4$N)Cl$_3$] (R = Cl (**7**), OMe (**8**), CF$_3$ (**9**)). [17] All three of these imido trichlorides were either inactive or extremely poor catalysts.

3.2 | Titanium

For titanium, we focused on titanocalix[8]arenes, namely {(TiX)$_2$[TiX(NCMe)]$_2$(μ_3-O)$_2$(L^2)} (X = Cl (**10**), Br (**11**), I (**12**)) which were prepared, as reported elsewhere, by the interaction of [TiX$_4$] with the parent p-*tert*-butylcalix[8]areneH$_8$ (L^{2}H$_8$) in toluene and subsequent crystallization from acetonitrile.[60] In the case of X = Cl, the reaction afforded orange/red crystals suitable for a single crystal X-ray diffraction study. The molecular structure was found to be {(TiCl)$_2$[TiCl(NCMe)]$_2$(μ_3-O)$_2$(L^2)}·6.5(MeCN) **10**·6.5(MeCN), and is shown in Figure 3, with selected bond lengths and angles given in the caption; crystallographic data are given in Table 2. For **10**·6.5(MeCN), two Ti$_4$ complexes and 13 MeCNs of crystallization are found in the asymmetric unit (Figure 2). Each molecule comprises a Ti$_4$O$_4$ ladder, with end chlorides 'up', and middle two chlorides 'down'. We note that calix[8]arene titanium ladder complexes have recently been isolated and utilized for CO$_2$ photoreduction and photocatalytic H$_2$ production.[72-74] In **10**·6.5(MeCN), there are two triply-bridging oxo bridges, and terminal coordinated MeCNs on the two end Ti ions. Both independent molecules have the same basic arrangement of chlorides, oxos, and coordinated MeCNs. The diffraction data are twinned via twin law: [–1 0 0, 0 –1 0, 0.777 0 1] with a twin ratio 89.08:10.92(11)%. In the packing, MeCNs of crystallization lie in the clefts of the calixarene ligand and between molecules. Molecules form slightly off-set stacks parallel to *b*. The coordinated MeCN H atoms make weak contacts with the chloride ligands on the next molecule in the stack with H···Cl distances of approx. 3.0 Å – see Figure 4.

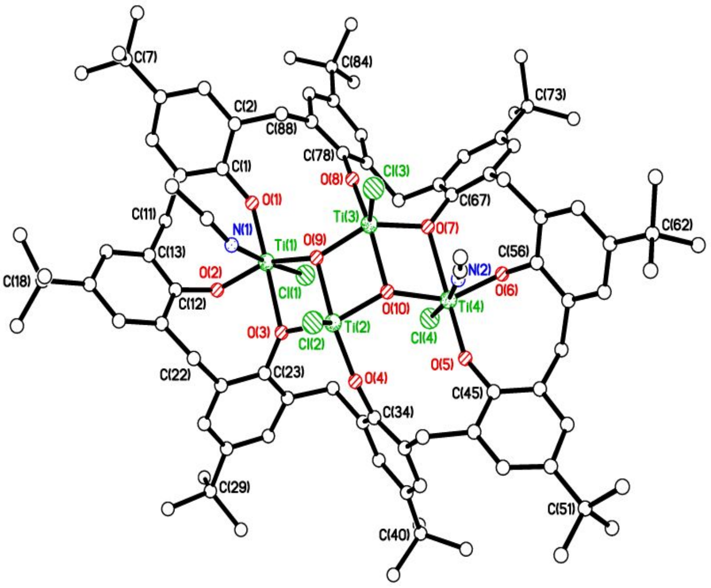


FIGURE 3. Molecular structure of $\{(\mathrm{TiCl})_2[\mathrm{TiCl(NCMe)}]_2(\mu_3\text{-O})_2(\mathrm{L}^2)\}\cdot 6.5\mathrm{MeCN}$ **10**·6.5MeCN. This is half of the asymmetric unit. There are two similar Ti$_4$ complexes and 13 MeCNs of crystallization in the asymmetric unit. H atoms and MeCNs of crystallization omitted for clarity. Selected bond lengths (Å) and angles (º): Ti(1)–O(1) 1.822(9), Ti(1)–O(2) 1.798(7), Ti(1)–O(3) 2.173(8), Ti(1)–O(9) 1.986(8), Ti(1)–Cl(1) 2.297(4), Ti(1)–N(1) 2.213(10), Ti(2)–O(3) 1.957(7), Ti(2)–O(4) 1.788(8), Ti(2)–O(9) 1.974(8), Ti(2)–O(10) 1.871(7), Ti(2)–Cl(2) 2.232(4); Ti(1)–O(1)–C(1) 146.6(7), Ti(1)–O(2)–C(12) 136.3(7), Ti(1)–O(3)–C(23) 124.7(6), Ti(2)–O(4)–C(34) 159.2(7), Ti(1)–O(3)–Ti(2) 103.0(3), Ti(1)–O(9)– Ti(3) 139.3(4), O(3)–Ti(2)–O(10) 137.4(3).

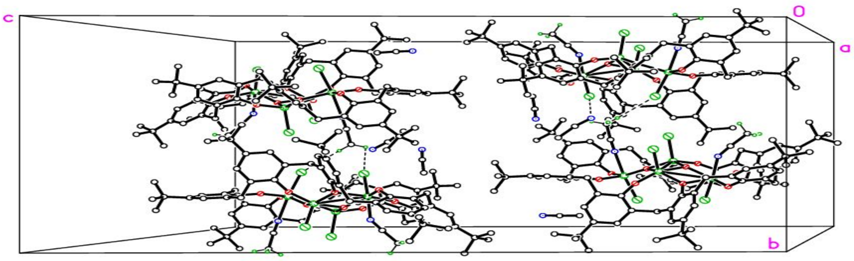
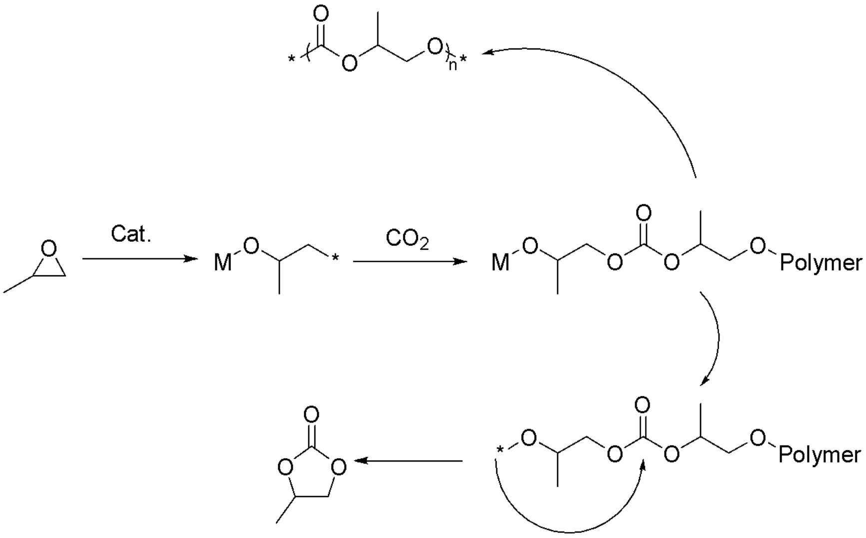


FIGURE 4. Stacking observed in **10**·6.5MeCN showing weak C–H···Cl interaction between a coordinated MeCN on one molecule and the two outer chlorides on the molecule above/below in the *b* direction.

3.3 | Co-polymerization of propylene oxide with CO_2

The effect of the catalysts on the co-polymerization of propylene oxide with CO_2 was investigated, and the results are summarized in Table 1. All 'polymers' obtained were of low polydispersity (PDI < 1.4), which suggested that these polymerizations occurred without significant side reactions. However, only low molecular weight oligomeric products ($M_n \leq 1665$) were obtained using the current systems. The absence of a co-catalyst herein such as PPNCl (bis(triphenylphosphine)iminium chloride) or n-Bu_4NCl may account for these low molecular weights. The screening of complexes **1–13** revealed that the complexes namely **5**, **10**, **11** and **12** herein, exhibited comparatively higher activities (TON > 1 g/g_{Cat}) under the conditions employed. For the vanadium catalysts, it was observed that the poly(propylene carbonate) oligomerization rate followed the order: **5**>**4**>**1**>**6**≈**2**>**7**>**9**>**3**>**8** and for titanium complex, the rate followed the order: **10**>**11**>**12**>**13**. ^{1}H NMR spectra of the poly(propylene carbonate) indicated that the selectivity is relatively higher when using catalyst **1** **(**Figure 5**)**. The generally accepted mechanism for the copolymerization of CO_2 and epoxides involves the alternate enchainment of CO_2 and the epoxide via insertion into either a metal alkoxide or carbonate bond (Scheme 1). A growing polymer dissociates from an electron-rich metal center leading to the formation of cyclic carbonate.[75,76]



SCHEME 4. Proposed mechanism for the copolymerization of propylene oxide and CO_2.

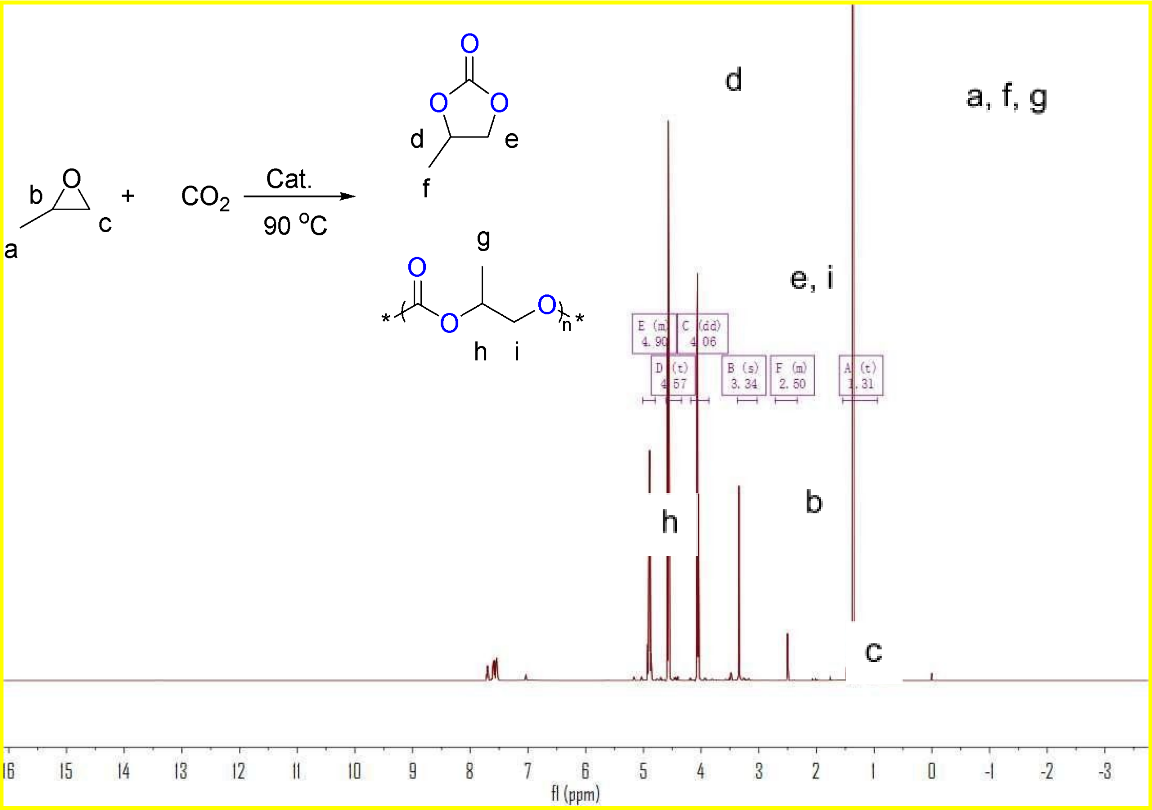


FIGURE 5. ^{1}H NMR of the spectrum ($CDCl_3$, 400 MHz, 298 K) of the cyclic/poly(propylene carbonate) synthesized with **11** (run 12, Table 1).

TABLE 1. Results from the catalytic screen of complexes **1** to **13**. [a]

Entry	Cat.[b]	S_B (10^5)[c]	m_B (mg)[d]	TON ($g/g_{Cat.}$)[d]	Selectivity (polymer, %)[e]	Yield (polymer, mg)[f]	M_n[g]	PDI[g]
1	$[VO(L^1Me)]$ (**1**)	7.13	12.24	0.122	62.5	7.62	420	1.05
2	$[(VO_2)L^2H_6]$ (**2**)	3.12	5.36	0.054	30.6	1.65	460	1.08
3	$[Na(NCMe)_6]_2[(Na(VO)_4L^2)(Na(NCMe))_3]_2$ (**3**)	0.18	0.31	0.003	55.7	0.17	415	1.34
4	$[VO(\mu\text{-}OH)L^{3'}H_2]_2$ (**4**)	13.55	23.29	0.233	44.6	10.39	1005	1.06
5	$\{[VO]_2(\mu\text{-}O)L^4[Na(NCMe)_2]_2\}$ (**5**)	88.65	152.33	1.523	57.6	87.72	1250	1.03
6	$\{[V(N\mathit{p}\text{-tolyl})]_2L^4\}$ (**6**)	3.22	5.53	0.055	32.8	1.80	700	1.20
7	$[V(\mathit{p}\text{-}NC_6H_4\text{-}Cl)Cl_3]$ (**7**)	1.05	1.80	0.018	20.5	0.37	710	1.11
8	$[V(\mathit{p}\text{-}NC_6H_4\text{-}OMe)Cl_3]$ (**8**)	0	0	0	-	-	-	-
9	$[V(\mathit{p}\text{-}NC_6H_4\text{-}CF_3)Cl_3]$ (**9**)	0.29	0.50	0.005	34.2	0.17	560	1.03
10	$\{(TiCl)_2[TiCl(NCMe)]_2(\mu_3\text{-}O)_2(L^2)\}$ (**10**)	332.37	571.07	5.711	39.2	223.85	1655	1.19
11	$\{(TiCl)_2[TiCl(NCMe)]_2(\mu_3\text{-}O)_2(L^2)\}$ (**10**)[h]	1120.00	1961.5	19.613	48.5	932.93	3515	1.12
12	$\{(TiBr)_2[TiBr(NCMe)]_2(\mu_3\text{-}O)_2(L^2)\}$ (**11**)	271.56	373.57	3.736	33.7	125.89	1025	1.22
13	$\{(TiI)_2[TiI(NCMe)]_2(\mu_3\text{-}O)_2(L^2)\}$ (**12**)	117.49	201.75	2.017	24.5	49.41	1020	1.25
14	$[TiCl_4(THF)_2]$ (**13**)	0.69	1.18	0.012	32.8	0.39	835	1.09

Reaction conditions: [a] Propylene oxide: 5 mL, Temperature: 90 ℃, Pressure of CO_2: 5 MPa, Reaction time: 6 h; [b] *Cat.*: 100 mg. [c] Measured by GC. [d] Derived from S_B. [e] Based on ^1H NMR spectroscopy. [f] Yield (oligomer/polymer) = $m_{product}$ ×Selectivity (oligomer/polymer). [g] Determined by gel permeation chromatography in THF, PDI = (M_w/M_n). [h] Reaction performed with PPNCl present as co-catalyst.

Duan *et al* have explored the influence of the co-catalyst bis(triphenylphosphine)iminium chloride (PPNCl) of the copolymerization of propyleneoxide with CO_2 when using a cobalt catalyst bearing a salen-like ligand.[77] In their studies, it was observed that the use of increasing amounts of PPNCl led to enhanced catalytic performance, including an increase in the polymer molecular weight. With this in mind, we employed PPNCl herein with the best of our catalysts, and also found significant increases in polymer yield and molecular weight (see run 11, table 1).

TABLE 2. Crystallographic data for **4**·$3CH_2Cl_2$, **4′**·$6CH_2Cl_2$ and **10**·6.5MeCN.

Compound	**4**·$3CH_2Cl_2$	**4′**·$6CH_2Cl_2$	**10**·6.5Me
Formula	$C_{97}H_{136}Cl_6N_2O_{12}S_8V_2$	$C_{86}H_{106}Cl_{12}O_{13.09}S_8V_2$	$C_{92}H_{110}Cl_4N_2O_{10}Ti_4$
Formula weight	2093.13	2132.90	2004.06
Crystal system	Monoclinic	Triclinic	Monoclin
Space group	$P2_1/n$	*P*□1	$P2_1/c$
a (Å)	15.5952(15)	11.8180(11)	29.8061(
b (Å)	14.9297(14)	12.0316(12)	18.5546(
c (Å)	24.581(2)	20.587(2)	40.3480(1
α (°)	90	96.263(2)	90
β (°)	98.458(7)	103.581(2)	106.680(
γ (°)	90	93.263(2)	90
V ($Å^3$)	5661.0(9)	2818.3(5)	21374.1(1
Z	2	1	8
Temperature (K)	150(2)	150(2)	100(2)
Wavelength (Å)	0.7749	0.71073	1.54178
Calculated density ($g·cm^{-3}$)	1.228	1.257	1.246
Absorption coefficient (mm^{-1})	0.64	0.65	3.84
Transmission factors (min./max.)	0.937, 0.975	0.717, 0.860	0.553, 1.0
Crystal size (mm^3)	0.13 × 0.08 × 0.05	0.55 × 0.33 × 0.24	0.26 × 0.07 ×
θ(max) (°)	27.5	28.3	68.3
Reflections measured	41136	53410	155537
Unique reflections	10028	13900	38456
R_{int}	0.119	0.042	0.204
Reflections with $F^2 > 2\sigma(F^2)$	5135	9834	22830
Number of parameters	662	632	2537
R_1 [$F^2 > 2\sigma(F^2)$]	0.082	0.070	0.142
wR_2 (all data)	0.281	0.222	0.426
GOOF, *S*	1.01	1.03	1.05
Largest difference peak and hole (e $Å^{-3}$)	0.83 and –0.96	1.07 and –0.80	1.52 and –

4 | CONCLUSIONS

In summary, we have developed a number of metallocalix[*n*]arenes, where n = 4, 6, or 8, of titanium and vanadium which act as catalysts for the co-polymerization of propylene oxide and CO_2 to cyclic polycarbonates. The vanadium-containing catalysts performed poorly affording, in the majority of cases, TONs less than 1 at 90 °C within 5 h. In the case of the titanocalix[8]arenes, which all adopt a similar ladder-type structure, the activity under the same conditions is somewhat higher (TONs > 6) and follows the trend Cl > Br > I. In the absence of a co-catalyst, the products obtained in these systems were low molecular weight oligomeric products ($M_n \leq 1665$). However, the use of PPNCl as a co-catalyst with the titanocalix[8]arene system **10** led to a significant improvement in both the polymer yield and molecular weight.

CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

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