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Research paper

Bis(phenolate)-functionalized *N*-heterocyclic carbene complexes of oxo- and imido-vanadium(V)

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Dedicated to Maurizio Peruzzini on the occasion of his 65th birthday

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ABSTRACT

Oxo- and imido-vanadium(V) metal complexes supported by bis(phenolate)-functionalized *N*-heterocyclic carbene (NHC) ligands were synthesized and structurally identified. In the presence of $[(Ph_3P{=})_2N]Cl$ ([PPN]Cl), saturated NHC oxo-vanadium complexes showed activity in the coupling of CO_2 and cyclohexene oxide (CHO) into *cis*-cyclohexene carbonate (*cis*-CHC). More importantly, the oxo-vanadium complex bearing the less electron-donating benzannulated NHC ligand was found to be more active in CHO conversion to poly(cyclohexene carbonate) (PCHC) in addition to the *cis*-CHC, highlighting the beneficial effect of the weak electron-donating ability of the latter vs. saturated NHC ligands within such vanadium catalysts. Evaluation of the saturated NHC imido-vanadium catalyst performance led to the same activity and selectivity as the analogous oxo-vanadium catalysts owing to its reactivity with CO_2 via a [2 + 2] cycloaddition reaction forming an oxo-vanadium species.

1. Introduction

N-heterocyclic carbenes (NHCs) is an important class of ancillary ligands for the development of homogeneous catalysts based on transition metals [1–13]. Over the past decades, NHC ligands are remarkably well investigated within catalysis, notably employing late transition-metal complexes, whereas main group, early transition-metal and lanthanide carbene complexes have been far less explored in this respect [1–13]. Part of the grounding reasons for the latter of being less studied, mainly lies in the NHCs ease to dissociate from high oxidation-state metal [5,9,14–18]. To limit this disadvantage, several series of tailor-made multidentate NHC-donor ligands incorporating neutral or anionic donor ligands were designed to enhance their stability when bonded to such high oxidation-state metals [9,19–22]. Such high oxidation-state metal NHC-based chelate complexes are now subject to a growing interest for building up new robust catalysts for the oligomerization and (co)-polymerization of α-olefins and non-conjugated dienes, polymerization of methylene butyrolactone, ring-opening metathesis polymerization of cyclic olefins, hydroamination-cyclization of primary aminoalkenes, ring-opening polymerization of *rac*-lactide, and in the selective coupling of epoxides and CO_2 towards either cyclic carbonates or polycarbonates [11,15–18,21–26]. Although the number of active high oxidation-state metal catalysts in the copolymerization of epoxide with CO_2 forming selectively polycarbonates are still less investigated compared to the low-valent late transition metals (bearing mostly salen-type, β-diketiminate and porphyrin ligands) [24,26–33], we recently demonstrated classes of tridentate *O*-functionalized NHC ligands to be effective for stabilizing high-valent group 4 catalysts which in turn are active and highly selective catalysts for the copolymerization of epoxides with CO_2 [34–39]. Prompted by the recent disclosure of highly active group 4-carbene-based copolymerization systems, we were interested to further extend the use of tridentate *O*-functionalized NHC ligands to high-valent vanadium. So far, only few monodentate NHC-vanadium were reported in the literature [40–52], and even fewer multidentate functionalized NHC ligands stabilizing vanadium have successfully been synthesized (Scheme 1) [53–57].

Similarly catalysis involving NHC-vanadium complexes is scarce as exemplified by their applications in ethylene polymerization [47,48,51,53], propylene- or norbornene-ethylene copolymerization [46,48,52], whilst none has been reported to date in the coupling of epoxides with CO_2 that gives rise to polycarbonates. Only very few vanadium catalyst systems were reported to be active in the coupling of epoxides-CO_2 forming cyclic carbonates. Among the systems investigated, most of them are based on (di)oxo-vanadium(V) complexes bearing various type of multidentate ligands such as salen [58], salphen [58], acetylacetonate [58], porphyrin [59], aminotriphenolate [60,61],

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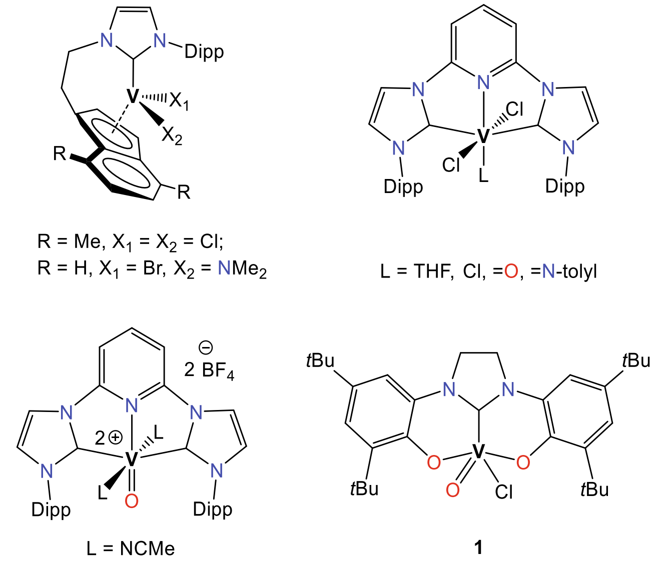


Scheme 1. Rare examples of multidentate bi-functionalized NHC ligands of vanadium(II), (III), (IV) and (V) (Dipp = 2,6-diisopropylphenyl).

and salicylidene hydrazide [62] combined with an excess of nucleophilic additives often under harsh reaction conditions. Intrigued by the catalytic performances of the previous *O*-functionalized NHC-group 4 catalysts, we were interested in evaluating whether NHC complexes of vanadium ($κ^3$-O,C,O-^{Is}NHC)V(═O)Cl **1** [57] and their derivatives could be potential catalysts for the copolymerization of epoxides with CO_2.

2. Results and discussion

2.1. Bis(phenolate) NHC oxo-vanadium complexes

Starting from the precursor ([$κ^3$-O,C,O]-^{Is}NHC)V(═O)Cl **1** (Scheme 1), several other complexes ([$κ^3$-O,C,O]- ^{Is}NHC)V(═O)X bearing various type of co-ligands (with X = O*i*Pr (**2**), N_3 (**3**), OAc (**4**) and OAc^F (**5**)), proven to enhance the catalyst performances in the copolymerization of CO_2-epoxides, were also synthesized as depicted in Scheme 2. While complexes **2**, **4** and **5** can straightforwardly be obtained in high yield from the salt metathesis reaction between complex **1** with a stoichiometric equivalent of LiO*i*Pr, NaOAc and NaOAc^F, respectively, in THF at room temperature, complex **3** could not be obtained using NaN_3 under similar reaction conditions, leading to an intractable reaction mixture. In contrast, the reaction of **1** with an excess of Me_3SiN_3 at 80 °C for 4 h leads via a metathetic exchange to the pure complex **3** in moderate yield (Scheme 2).

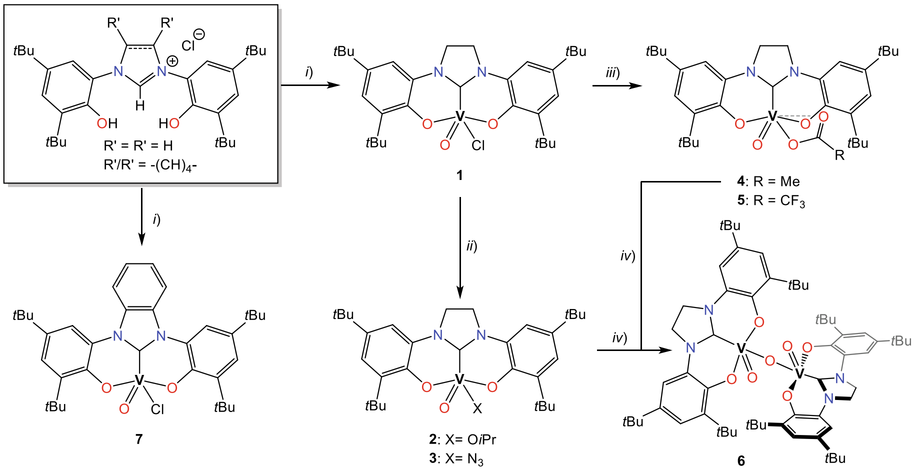
Table 1
Comparison of principal infrared frequencies, ^{51}V NMR chemical resonances and half-line width of oxo- and imido-vanadium(V) compounds in benzene-d_6.

Compounds	$ν_{(V=O)}$ or $ν_{(V=N)}$[a] (cm^{-1})	$ν_{(COO)}$ or $ν_{(N3)}$[a] (cm^{-1})	δ ^{51}V NMR[b] (ppm)	$Δν_{1/2}$[c] (Hz)
$V(=O)Cl_3$	995[d]		−5	23
$V(=O)(OiPr)_3$	1004	–	−641	9
1	980	–	−528	380
2	984	–	−613	304
3	982	2080	−540	247
4	987	1621	−533	243
5	996	1718	−585	421
6	984	–	− 635	698
7	1003	–	−513	324
8	1040	–	−432	187

[a] Resolution: ±4 cm^{-1}.
[b] Reference standard: neat $V(=O)Cl_3$ ($δ = 0$ ppm).
[c] Determined with line broadening fixed at 10 Hz and 128 scans.
[d] From ref. [66].

All ^{1}H NMR data for **2**–**5** are consistent with C_s-symmetric structures in solution showing characteristic resonance patterns for monomeric complexes of ([$κ^3$-O,C,O]-^{Is}NHC)V(═O)X as indicated by the appearance of a doublet of multiplets for the NCH_2 protons [35–37]. Although the V-$C_{carbene}$ signals were not detected in the ^{13}C NMR spectra of **2**–**5** (likewise to **1**), all other chemical resonances are consistent with the proposed structures for **2**–**5** (Scheme 2). The DRIFT spectra of these complexes show two strong absorption bands between 1490 and 1440 cm^{-1} and one absorption band between 979 and 996 cm^{-1} (Table 1, Fig. S1–3), attributable to C═N and V═O vibrations, respectively. For complex **3** an extra strong absorption band at 2080 cm^{-1} were observed corresponding to the azide asymmetric stretching vibration [63–65]. For complexes **4** and **5**, additional bands were observed at 1621 cm^{-1} and 1718 cm^{-1}, respectively, assigned to carboxylato stretching frequencies, along with three additional medium-to-strong bands at 1205, 1181 and 1154 cm^{-1} assigned to C-F stretching vibrations from the trifluoro acetate ligand in complex **5**.

Frequently, the large range of chemical shifts usually found for ^{51}V NMR spectroscopy provides a really sensitive characterization tool for probing electronic and steric features within a series of oxo-vanadium complexes [66–68]. The ^{51}V NMR data for **1**–**5** in benzene-d_6, along with both precursors $V(=O)(OiPr)_3$ and $V(=O)Cl_3$ are presented in Table 1. All ^{51}V chemical resonances of NHC oxo-vanadium complexes



Scheme 2. Synthesis of *mer*-tridentate bis(phenolate) saturated and benzannulated NHC vanadium(V) complexes **1**–**7**: *i)* $V(=O)(OiPr)_3$ in THF at RT [57]; *ii)* LiO*i*Pr in THF or Me_3SiN_3 in toluene, at RT; *iii)* NaOAc or NaOAc^F in THF at RT; *iv)* adventitious moisture at RT.

Table 2
Crystal structures and refinement data for **5** and **6**.

Compounds	5	6
Chemical formula	$C_{33}H_{44}F_3N_2O_5V$	$C_{62}H_{88}N_4O_7V_2$
Formula weight	656.64	1103.24
Temperature/K	123(2)	120(2)
Wavelength/Å	0.71073	0.82495
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{1/c}$ (No.14)	$P2_{1/n}$ (No.14)
a/Å	15.3728(7)	15.6163(2)
b/Å	17.2974(7)	27.57870(10)
c/Å	12.1482(5)	20.3189(2)
β/°	90.0480(10)	110.2310(10)
V/Å^3	3230.3(2)	8211.01(14)
Z	4	4
ρ_{calcd}/g cm^{-3}	1.350	0.892
Absorption coeff./mm^{-1}	0.367	0.396
F(0 0 0)	1384	2360
Range for data collection/ Θ°	1.772–29.974	2.354–33.003
Reflections collected	40,414	43,661
Independent reflections	9396 [R(int) = 0.0641]	12,119 [R(int) = 0.0207]
Completeness to Θ/%	100	71
Data/restraints/ parameters	9396/66/419	12119/66/731
Goodness-of-fit on F^2	1.044	1.059
Final R_1 indices [$I > 2\sigma(I)$]	R1 = 0.0510, wR2 = 0.1295	R1 = 0.0588, wR2 = 0.1780
R indices (all data)	R1 = 0.0686, wR2 = 0.1384	R1 = 0.0632, wR2 = 0.1829
Largest diff. peak; hole/e Å^{-3}	0.945 and −0.536	0.872 and −0.423

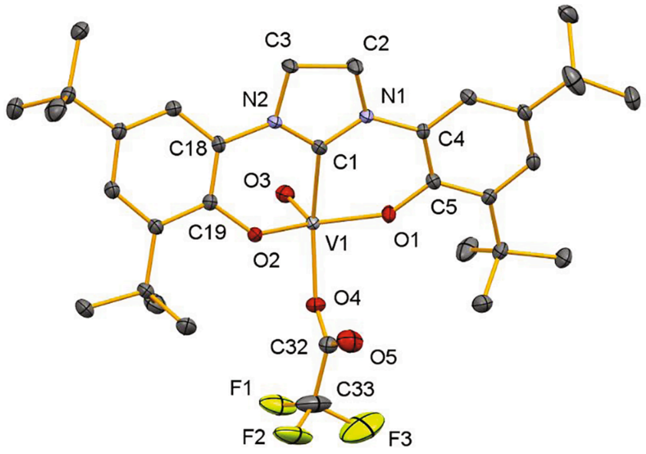


Fig. 1. Crystal structure of **5**. Hydrogen atoms are omitted for clarity.

Table 3
Comparison of Selected Bond Distances, Bond and Torsion Angles for complexes (^{Is}NHC)V(═O)X with X = Cl (**1**), and X = OAc^F (**5**).

Compounds	1[a]	5
Bond lengths (Å)		
V—C$_{carbene}$	2.095(3)	2.09223(17)
V═O	1.589(2)	1.5852(13)
V—O$_{Ar}$	1.810(2)/1.817(2)	1.7995/1.8063(12)
V—X	2.3077(10)	1.9604(13)
Bond Angles (deg)		
O$_{phenolate}$—V—O$_{phenolate}$	150.96(10)	144.36(6)
X—V—C$_{carbene}$	154.05(10)	159.32(6)
O$_{Ar}$—V═O	103.73(11)/101.60(11)	106.67(7)/106.05(6)
Torsion Angle (deg)		
C$_{Ar}$—O$_{phenolate}$—O$_{phenolate}$—C$_{Ar}$[b]	63.14	51.83

[a] From ref. [57].

[b] C$_{Ar}$-O$_{phenolate}$-O$_{phenolate}$-C$_{Ar}$: C1-O1-O2-C18 for **1** and C5-O1-O2-C19 for **5**.

appear in the range δ -528 ppm to -613 ppm, which are less and more shielded than the V(═O)(O*i*Pr)$_3$ (δ -641 ppm) and V(═O)Cl$_3$ (δ -5 ppm), respectively. A substantial increase of the half-line widths (with a $\Delta\nu_{1/2}$ ranging from 243 to 421 Hz) were observed compared to the narrow $\Delta\nu_{1/2}$ for both precursors owing to a decrease in symmetry ($C_{3v} \rightarrow C_s$) and enhanced interactions between the solvent and the bulky NHC oxo-vanadium complexes (Table 1) [66,67]. As previously reported for high-valent oxo-vanadium complexes, the trend in the vanadium shielding for complexes **1**–**3** is following the inverse of electronegativity dependence [67–69], where the δ ^{51}V shielding increases with increasing electronegativity of the mono-ligating elements (i.e. increasing δ ^{51}V shielding: Cl < N$_3$ < O*i*Pr). For **4** and **5**, similar trend is observed, even though an additional contribution to the shielding may arise from the bulky electron-withdrawing CF$_3$ group as indicated with the broad half-line width for **5** ($\Delta\nu_{1/2}$: 421 Hz for **5** vs. 243 Hz for **4**) [66–68].

After several attempts to isolate complexes **2**–**5** by recrystallization, only complex **5** could be isolated affording single crystals suitable for X-ray analysis (Table 2). A view of the molecular geometry of **5** is shown in Fig. 1, with selected distances and angles listed in Table 3 as well as the ones previously reported for complex **1** [57].

Complex **5** crystallizes as a monomeric five-coordinate complex, with a basally distorted square pyramidal geometry ($\tau_5 = 0.25$) and the vanadium ion sitting at 0.459 Å above the mean-plane of the three oxygen atoms (O1, O2 and O3) and carbon atom (C1) that form the basal plane of the pyramid. One striking structural feature of complex **5**, is that the trifluoro acetate ligand appears not bis-ligated as expected, but rather as mono-ligated ligand showing a V1⋯O5 intermolecular distance of 3.275 Å that falls within short range of the van der Waals gap [70]. In addition the presence of bulky trifluoro acetate in basal position displace the *mer*-tridentate bis(phenolate) NHC ligand away from the vanadium center, reducing the bite angle (β_n) ∠O1-V1-O2 = 144.35(2)° compared to the less sterically hindered five-coordinate complex ([κ^3-O, C,O]-^{Is}NHC)V(═O)Cl **1** (β_n = 150.96(10)°). Although the deviation from planarity of the *mer*-NHC unit in **5** is less pronounced with a difference in torsion angle of 11.27° compared to complex **1**, there is nearly no impact on the following V—C$_{carbene}$, V═O, V—O$_{Ar}$ bond distances, which are in similar range than the ones observed for **1**, except for the V—OAc^F bond distance which is shorter compared to V—Cl bond distance (Table 3). This latter observation is consistent with the increase of the δ ^{51}V shielding by enhancing co-ligand X electronegativity as mentioned above, that correlates well to an increase of co-ligand strength to V^{5+} ion (V—O > V—Cl). The high absorption frequency of V═O vibration (996 cm^{-1}) also correlates well with a shorter bond distance for **5** compared to **1** (980 cm^{-1}), and are consistent with the bond distances found in the solid-state structures (Table 1).

Other attempts to recrystallize complexes **2**, **3** and **4** were unfruitful, and solely the molecular structure of the decomposed product due to their extreme sensitivity to adventitious moisture could be established (Scheme 2). Both NMR and DRIFT data on isolated crystals, and X-ray structure determination (low quality crystals, Fig. 2, Tables 1 and 2 and Fig. S3) indicate that the compound is an oxo-bridged complex {([κ^3-O, C,O]-^{Is}NHC)V(═O)}$_2$(μ-O) **6** (Scheme 2). The molecular unit of the partially hydrolyzed compound is composed of two {([κ^3-O,C,O]-^{Is}NHC) V(═O)} moieties symmetrically linked together through the bridging O4 atom (not orthogonally, but with rotation angle ∠O3-V1-V2-O7 of 70.17° for both units) with V—O bond lengths of 1.7939(19) and 1.7921 (19) Å for V1-O4 and V2-O4, respectively. Interestingly, the solid-state structure of **6** reveals a basally distorted square pyramidal geometry around each V metal center with the V═O in the apical position along with an oxo-bridged atom and the *mer*-tridentate NHC in basal positions. Both vanadium ions are out of the mean-plane formed by the three oxygens and the carbon atoms by 0.505 Å for V1 and 0.508 Å for V2. The bond lengths reported in **6**, and those reported for **1** and **5** are very

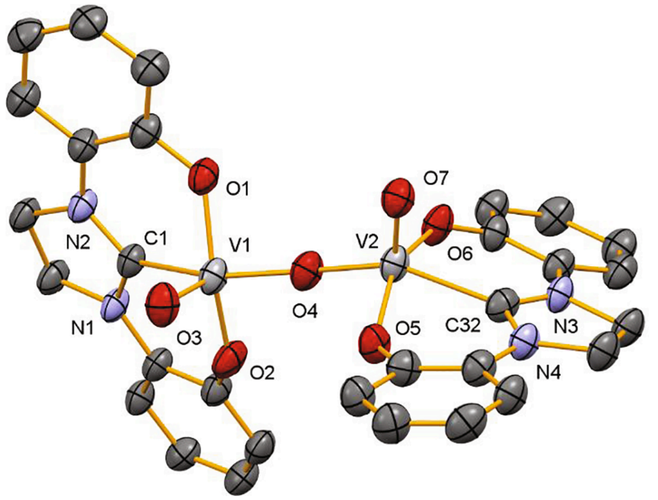


Fig. 2. Crystal structure of **6**. Hydrogen atoms and *t*Bu groups are omitted for clarity.

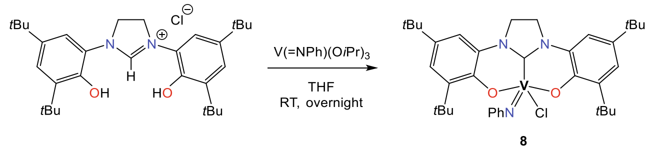
similar, except for the V—C$_{carbene}$ bond lengths. The latter are slightly more elongated in complex **6** (V1—C1 = 2.128(2) Å and V2—C32 = 2.132(3) Å) than the ones found in other complexes cause most likely by the *trans* influence from the nearly linear oxo-bridged atom ($\angle$V1-O4-V2 = 171.25(11)°), suggesting the greater participation of the π-interactions from oxygen atom in the vanadium oxo-bridged bonding.

Owing to the good activity and high selectivity previously reported in the copolymerization of epoxides with CO$_2$ for the *mer*-tridentate bis (phenolate) benzannulated NHC (^{Bz}NHC) complexes of titanium and hafnium, we were also interested to preparing an analogous oxo-vanadium(V) complex containing a benzimidazol-2-ylidene moiety. The complex (^{Bz}NHC)V(=O)Cl **7** was straightforwardly prepared in 94% isolated yield via the isopropanol elimination route involving the direct and slow addition of *N,N′*-di(2-hydroxy-3,5-di-*tert*-butylphenyl) benzoimidazolium chloride salt to a solution of V(=O)(O*i*Pr)$_3$. Although all attempts to obtain suitable crystals of **7** for single crystal X-ray analysis were unsuccessful, the elemental analysis, DRIFT and NMR spectroscopy provide a good insight on the molecular structure of **7**. Notably, the ^{1}H NMR spectrum exhibits the characteristic multiplet patterns for the benzylidene NHC backbone protons at δ 7.81 and 6.96 ppm [36,39]. As for previous ^{13}C NMR spectra of NHC oxo-vanadium complexes, the C$_{carbene}$ chemical resonance is not visible, but the ^{51}V NMR spectrum reveals only one chemical resonance at δ –513 ppm which is a slight shifted downfield compared to the structurally analogous complex **1** with a $\Delta\delta$ of 15 ppm (Table 1). The DRIFT spectrum shows the presence of two strong absorption bands at 1483 and 1435 cm^{-1} attributable to the delocalized C=N vibrations within the ^{Bz}NHC ligand, and one absorption band at 1003 cm^{-1} for the V=O vibration corresponding to a short bond length compared to **1** (Table 1 and Fig. S4). Together, both the short V=O bond length and the de-shielded ^{51}V chemical resonance indicate a weaker coordination of the benzannulated NHC moiety to the vanadium metal center compared to the one found for **1** bearing a saturated NHC moiety, suggesting that ^{Bz}NHC moiety is the least electron-donor carbene. This weak interaction between the d^0 metal and the carbene observed for the ^{Bz}NHC ligand is consistent with our previous computational results using DFT and NBO analyses for determining the electronic properties of the d^0 Ti-carbene bonds, where bis (phenolate) ^{Bz}NHC was also found to be a weaker electron-donating ligand related to the bis(phenolate) ^{Is}NHC moiety [39].

Coupling reaction experiments of cyclohexene oxide (CHO) with CO$_2$ were carried out with complexes ([κ^3-O,C,O]-^{Is}NHC)V(=O)X **1–5** in presence of one equiv. of bis(triphenylphosphine)iminium chloride ([PPN]Cl) as co-catalyst under these conditions: 2 bar of CO$_2$ at 80 °C for 24 h, CHO:V = 1250:1. The coupling reaction of neat CHO with CO$_2$ shows only selective formation of *cis*-cyclohexene carbonate (*cis*-CHC) (conv. = 12% (**1**), 6% (**2**), 10% (**3**), 8% (**4**), 5% (**5**), with TOFs = 3–6 h^{-1}) with no formation of poly(cyclohexene carbonate) (PCHC) or homopolymers (Table S1). The preliminary investigation with the addition of one equiv. of [PPN]Cl to **1**, shows that there is no sign of reactivity, and that the expected formation of anionic species [([κ^3-O,C,O]-^{Is}NHC)V(=O)Cl$_2$]$^-$ did not occur as previously shown with the anionic catalysts [([κ^3-O,C,O]-^{Is}NHC)HfCl$_3$]$^-$ [38] and [([κ^4-N,O,O,O]-ATP)TiCl(OiPr)]$^-$ (ATP = amino-tris(phenolate)) [71]. This indicates that the presumably vacant site *trans* to the V=O bond is probably not available for any nucleophile (here Cl$^-$) and/or neutral ligand/solvent (here CHO). Consistent with this result, none of the following complexes ([κ^3-O,C,O]—NHC)V(=O)X **2**, **3**, **4** and **5** seems to have the ability to form THF-adducts in *trans* to the V=O bond (at best forming a weak interaction with the acetate group, as exemplified with **5**), when those are synthesized in presence of THF, which is in clear contrast to most of the complexes ([κ^3-O,C,O]-^{Is}NHC)MX$_2$(THF) (with M = Ti, Zr and Hf) synthesized under similar conditions [34–39]. This lack of strong interactions of such oxo-vanadium complexes with weakly coordinating neutral ligands (including solvents) and nucleophiles seems to efficiently prevent activating the epoxides and/or forming a six-coordinate anionic species upon reaction with the co-catalyst [34–39], thus rendering them ineffective in the copolymerization. Contrary to catalyst systems **1**–**5**/[PPN]Cl, complex (^{Bz}NHC)V(=O)Cl **7** in presence of [PPN]Cl is slightly more active (TOF = 15 h^{-1}) leading mostly to the formation of *cis*-CHC, in addition to PCHC (Sel$_{PCHC}$ = 27%, Table S2) along with traces of *trans*-CHC (1%). This modest increase in activity and selectivity towards PCHC most probably derives its origin from the less electron-donating benzannulated NHC moiety, as identified by ^{51}V NMR spectroscopy, enhancing the coordination of CHO and/or the nucleophile to the electron-deficient oxo-vanadium complex **7**. The preliminary attempts to study the behavior of catalyst system **7** under various conditions, by varying the CHO:**7** ratio (1250:1 vs. 625:1), temperature (100 °C vs. 80 °C), CO$_2$ pressure (P_{CO2} = 6 vs. 2 bar) and using stronger nucleophile such as the [PPN]N$_3$ as co-catalyst did not show a significant effect on the activity and selectivity (Table S2). When employing substoichiometric amount of [PPN]Cl (0.5 vs. 1 equiv.) or running the reaction at low temperature (60 °C), a significant decrease in activity was observed (Table S2). Polymer analysis reveals atactic PCHCs with relatively low molecular weights and narrow polydispersities ($M_n \approx$ 1500–1100 g mol^{-1}, $Đ$ < 1.3, Table S2 and Figs. S5-6).

2.2. Bis(phenolate) NHC imido-vanadium complex and reactivity with CO$_2$

In view of diminishing the *trans* influence from the oxo ligand within these vanadium complexes, we were interested in replacing it with an imido ligand. Imido ligands are notoriously well-known for having elongated V=NR bond lengths versus V=O bonds [72] when sharing the same ligand surroundings [73], and thus in our case might potentially enhance the interaction with the nucleophiles and/or epoxides. Contrary to the first unsuccessful attempts to exchange the oxo-vanadium ligand in complex **1** via a direct [2 + 2] cycloaddition in the presence of phenyl isocyanate, the direct and slow addition of *N,N′*-di(2-hydroxy-3,5-di-*tert*-butylphenyl) imidazolidinium chloride salt to a

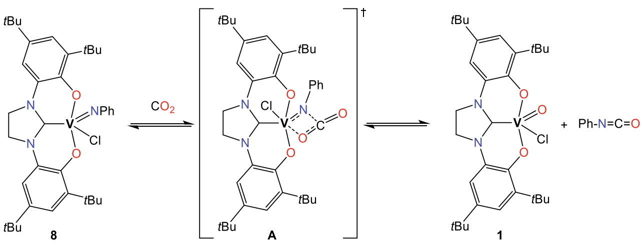


Scheme 3. Synthesis of *mer*-tridentate bis(phenolate) saturated NHC imido-vanadium complex **8**.

solution of V(=NPh)(O*i*Pr)$_3$ [74] in THF at room temperature afforded complex ([κ^3-O,C,O]-^{Is}NHC)V(=NPh)Cl **8** in quantitative yield (Scheme 3).

Although single crystals could not be obtained, the molecular structure of complex **8** was unambiguously determined through the ^{1}H, ^{13}C, ^{51}V NMR and DRIFT measurements. The ^{1}H NMR spectrum of imido-complex **8** shows similar chemical resonances pattern corresponding to the coordinated *mer*-tridentate ^{Is}NHC ligand in addition to the C*H*-Ar protons corresponding to the *N*-Ph chemical resonances. Akin to the previous complex **1**, the NC*H*$_2$ protons are not equivalent indicating a C_s-symmetry in solution and all protons are slightly shifted downfield ($\Delta\delta \approx 0.1$–0.8 ppm in benzene-d_6). Complex **8** was further characterized by ^{51}V NMR spectroscopy, and the NMR spectrum features a single resonance at δ -432 ppm (Table 1) corresponding to a downfield shift compared to **1**, and agrees with the inverse of electronegativity dependence of ^{51}V chemical shift as previously observed with other the oxo-vanadium complexes. This high chemical shift may be the result of both: *i*) from the coordination of the less-electronegative N atom (vs. the O atom), and *ii*) from a possible decreasing of imido-to-vanadium π-bonding interaction [66–68]. By comparing both complexes **1** and **8**, the only striking difference observed between the DRIFT spectra is the appearance of a weak absorption band at 1040 cm^{-1} which is in the expected range of imido-vanadium stretching vibrations (Table 1 and Fig. S4, $\nu_{(V=N)}$ stretching vibration is often difficult to observe, and when reported it is normally observed in the following range: 1300–940 cm^{-1} [73,75–77]).

Under identical copolymerization reaction conditions (2 bar of CO$_2$ at 80 °C for 24 h, CHO:**8**:[PPN]Cl = 1250:1:1) as used for the previous oxo-vanadium complexes, the catalyst system based on **8** shows activity and selectivity similar to **1**/[PPN]Cl towards *cis*-CHC with no formation of polycarbonates (conv. = 12%, TOF = 6 h^{-1}, Table S1). Intrigued by this result, we tried to isolate the expected anionic species [([κ^3-O,C,O]-^{Is}NHC)V(=NPh)Cl$_2$]$^-$ that would form upon addition of [PPN]Cl in CH$_2$Cl$_2$ at room temperature. Examination of the ^{51}V NMR spectrum in dichloromethane-d_2 reveals that the chemical shifts are nearly identical to **8** (only a slight downfield shift of $\Delta\delta \approx 2$ ppm), and even less significant for all chemical resonances in the ^{1}H NMR spectrum (Fig. 3). Addition of [PPN]N$_3$ to **8** results also for both ^{51}V and ^{1}H NMR spectra with identical chemical shifts (not shown), suggesting that the azide is not interacting with the imido-vanadium complex. Even though the formation of anionic species could not be confirmed, the addition of 2 bar of CO$_2$ to **8** at room temperature (or **8**/[PPN]Cl, not shown) leads unambiguously to the formation of oxo-vanadium complex **1** as shown in ^{51}V and ^{1}H NMR spectra (Fig. 3). After 12 h, the reaction mixture is mostly composed of complex **1** (87%) together with phenyl isocyanate, and 13% of complex **8**. This metathetic exchange seems to occur via a [2 + 2] cycloaddition of CO$_2$ to V=NPh bond forming a carbamate metallocycle intermediate **A**, which decomposes into **1** and phenyl isocyanate (Scheme 4). The observation of a [2 + 2] cycloaddition of CO$_2$ to M=NR moiety remains rare and limited to only few metals (Ti(IV) [69,78–83], Nb(V) [84], Mo(IV) [85] and U(IV) [86]), or remains as a stable four-membered carbamate metallocycle intermediate similar to **A** (Ti(IV) [80,82,87,88], W(VI) [89], Ce(IV) [90], (Ni(II) [91], Ir(III) [92], and Al(III) [93]), contrary to the reverse reaction, i.e. the [2 + 2] *retro*-cycloaddition step, which is a well-known method for the synthesis of imido-metal complexes from isocyanates and M=O species [73,94,95]. Therefore, the conversion of **8** into **1** upon addition of CO$_2$ accounts for their similar activity and selectivity.



Scheme 4. Proposed mechanism for the formation of **1** from **8** by a [2 + 2] cycloaddition reaction of CO$_2$ via a carbamate metallocycle intermediate **A**.

3. Conclusions

In summary, we report the synthesis and structural characterization of several oxo-vanadium(V) complexes, as well as the first example of an imido-vanadium(V) complex bearing a tridentate *O*-functionalized NHC ligand. Although known for decades, we also illustrate that the ^{51}V NMR spectroscopy due to its high sensitivity can be a reliable probe for evaluating the electronic properties within the NHC ligands in addition to other co-ligands with comparable molecular structures allowing for the determination of their electron-donating ability. Upon the addition of [PPN]Cl as co-catalyst, all the oxo- and imido-vanadium complexes were found to be selective though weakly active towards the formation of cyclic carbonates under low CO$_2$ pressure. While the variation of co-ligands in oxo-vanadium complexes were found to have no effect on the activity, the oxo-vanadium complex bearing a less electron-donating NHC ligand is found to slightly improve the activity and selectivity towards formation of polycarbonates. In contrast, when imido-vanadium complex is employed, it decomposes into oxo-vanadium complex upon contact with CO$_2$, thus exhibiting activity and selectivity similar to the saturated NHC oxo-vanadium catalytic systems. Further modifications to the benzannulated NHC oxo-vanadium systems for improving the activity and selectivity towards the copolymerization of epoxide with CO$_2$ are currently underway.

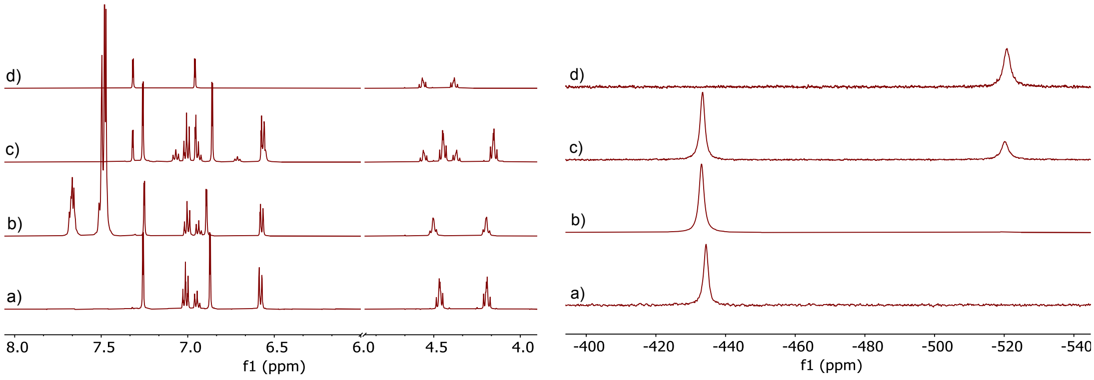


Fig. 3. ^{1}H NMR (left) and ^{51}V NMR (right) spectroscopy in dichloromethane-d_2 of a) complex **8**, b) complex **8** and [PPN]Cl at RT for 3 h, c) complex **8** and CO$_2$ at RT for 3 h, and d) complex **1**.

4. Experimental

4.1. General procedures

All operations were performed with rigorous exclusion of moisture and air, using standard Schlenk-line system and glovebox techniques under argon atmosphere (MB Braun MB200B-G, <1 ppm O_2 and <1 ppm H_2O). Hexane, toluene, THF and dichloromethane were purified, by using Grubbs columns (MBraun solvent purification system). Pentane, benzene-d_6, chloroform-*d*, dichloromethane-d_2, and CHO were degassed and dried overnight over sodium or CaH_2, back transferred and then employing the freeze–pumpthaw procedure. All chemicals were obtained from Sigma-Aldrich/Merck, except V(═O)(O*i*Pr)$_3$ and V(═O)Cl$_3$ which were obtained from Strem Chemicals, and all were used as received. Proligands *N,N*′-di(2-hydroxy-3,5-di-*tert*-butylphenyl) imidazolidinium chloride [57,96] and *N,N*′-di(2-hydroxy-3,5-di-*tert*-butylphenyl) benzoimidazolium chloride [96–99] and V(═NAr)(O*i*Pr)$_3$ [74] were prepared according to the literature procedures. [PPN]Cl was recrystallized prior to use [100]. Carbon dioxide purity grade (99.999%) was further dried through molecular sieves (3 Å). The NMR spectra of air and moisture sensitive compounds were recorded by using J. Young valve NMR tubes at 25 °C on a Bruker BioSpsin AV500 ultrashield 500 plus (5 mm BBO with z-gradient BTO, ^{1}H: 500.13 MHz; ^{13}C: 125.75 MHz; ^{51}V NMR: 131.55 MHz), and a Bruker BioSpin 500 widebore ascend spectrometers (5 mm BBO with z-gradient BBI, ^{19}F NMR: 470.70 MHz). Residual ^{1}H resonances from deuterated solvent were used to reference the ^{1}H spectrum with the methyl resonance of TMS at 0.0 ppm and *t*he ^{13}C spectrum is referenced through the solvent ^{13}C resonance. ^{51}V signals were referenced to V(═O)Cl$_3$ in benzene-d_6, and ^{19}F signal was referenced to lock frequency and are given relative to the CCl_3F in benzene-d_6. Coupling constants and half-width values, $\Delta\nu_{1/2}$, are given in Hz. DRIFT spectra were recorded by using a Nicolet protégé 460 ESP FTIR spectrometer and a DRIFT cell (KBr window) under argon atmosphere. The spectra were averaged over 64 scans; the resolution was ±4 cm^{-1}. Elemental analysis of C, H and N elements was performed on an Elementar Vario EL III at the University of Bergen. The M_n and M_w of the PCHC were determined using a GPC-*SEC* from Viscotek. Narrow polystyrene PS-99K ($M_w = 99.284$ kg mol^{-1}, $M_n = 97.381$ kg mol^{-1} and IV = 0.477 dL g^{-1}) and all calibration standards were obtained from Malvern PolyCAL. The sample solutions (≈2.0–4.0 mg mL^{-1} in THF) were filtered through syringe filter Whatmann (0.45 µm pore size) prior to injection. Chromatographic separation was performed at a column temperature of 30 °C with a flow rate of 1 mL min^{-1}. Signals were calibrated against polystyrene standards ($Đ < 1.2$, from 0.12 to 400 kg mol^{-1}).

4.2. X-ray crystallographic details

Suitable crystals for diffraction experiments were selected in a glovebox and mounted in a minimum of Parabar 10312 oil (Hampton Research) in a nylon loop and then mounted under a nitrogen cold stream from an Oxford Cryosystems 700 series open-flow cryostat. Data collection on compound **5** was done on a Bruker AXS TXS rotating anode system with an APEXII Pt^{135} CCD detector using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data collection and data processing were done using [101], SAINT [102], and SADABS [103] version 2012/1. Data collection on compound **6** was done on beamline BM01 at the Swiss-Norwegian Beamlines at the ESRF synchrotron in Grenoble, France, using Si double-mirror monochromated radiation (λ = 0.82495 Å) and a Pilatus2M detector utilizing the experimental software CrysAlisPro [104]. Structure solution and final model refinement were done using SHELXS [105] version 2013/1 or SHELXT [106] version 2014/4 and SHELXL [107] version 2014/7. Details of the single crystals data, intensity collection and refinement for refinement **5** and **6** (Tables 2 and 3) and in CIF files, CCDC reference codes 2047609 (**5**) and 2047610 (**6**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

4.3. Synthesis of bis(phenolate) NHC oxo- and imido-vanadium

4.3.1. Synthesis of ([k^3-O,C,O]-^{Is}NHC)V(═O)Cl (1)

Complex **1** was prepared following a slightly modified procedure [57]. In a glove box, to a stirring solution of the *N,N*′-di(2-hydroxy-3,5-di-*tert*-butylphenyl) imidazolidinium chloride salt (210.9 mg, 0.409 mmol) in THF (8 mL) was added at room temperature a THF solution (4 mL) of V(═O)(O*i*Pr)$_3$ (100 mg, 0.409 mmol). The colourless solution instantly turned reddish black upon addition of the vanadium precursor. The reaction mixture was stirred overnight at room temperature to yield a dark red solution, which was evaporated, *extensively* washed with hexane for removing the unreacted V(═O)(O*i*Pr)$_3$, and dried under vacuum for obtaining **1** as pure dark red solid in high yield (yield: 93%). Anal. Calcd for $C_{31}H_{44}ClN_2O_3V$: C, 64.30; H, 7.66; N, 4.84%. Found: C, 64.10; H, 7.25; N, 4.58%. ^{1}H NMR (500.13 MHz, benzene-d_6, 298 K): δ 7.47 (d, $J_{HH} = 2.2$ Hz, 2H, Ar-*H*), 6.42 (d, $J_{HH} = 2.2$ Hz, 2H, Ar-*H*), 2.78 (m, 4H, NC*H*$_2$), 1.85 (s, 18H, *t*Bu), 1.38 (s, 18H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, benzene-d_6, 298 K): δ 153.0 (C_q, Ar), 143.08 (C_q, Ar), 138.1 (C_q, Ar), 126.9 (C_q, Ar), 120.3 (*C*H-Ar), 110.9 (*C*H-Ar), 46.9 (N*C*H$_2$), 36.0 (C_q, *t*Bu), 34.8 (C_q, *t*Bu), 31.8 (*C*H, *t*Bu), 30.2 (*C*H, *t*Bu) ppm (V-C$_{carbene}$ ^{13}C NMR resonance was not observed). ^{51}V NMR (131.55 MHz, benzene-d_6, 298 K): δ −528 ppm (s, $\Delta\nu_{1/2} = 380$ Hz). DRIFT (KBr, ν/cm^{-1}, [4000–400]): 2955s, 2909m, 2863m, 1492vs, 1454s, 1391w, 1359w, 1348w, 1327m, 1288w, 1265w, 1248w, 1212vw, 1187vw, 1072vw, 1114m, 980m, 938w, 914w, 864m, 765w, 750w, 666w, 649vw, 584w, 508vw, 508vw, 494vw, 450vw, 430vw.

4.3.2. Synthesis of ([k^3-O,C,O]-^{Is}NHC)V(═O)OiPr (2)

To a solution of **1** (80 mg, 0.138 mmol) in 3 mL THF was added dropwise LiO*i*Pr (10 mg, 0.138 mmol) dissolved in 3 mL THF. The solution was stirred at room temperature for 24 h, then dried under vacuum and extracted with hexane. The dark green solution mixture was centrifuged, filtered, washed with hexane, and then dried under vacuum affording a dark green powder **2** (yield: 55%). Anal. Calcd for $C_{34}H_{51}N_2O_4V$: C, 67.75; H, 8.53; N, 4.65%. Found: C, 67.46; H, 8.30; N, 4.68%. ^{1}H NMR (500.13 MHz, benzene-d_6, 298 K): δ 7.47 (d, $J_{HH} = 1.7$ Hz, 2H, Ar-*H*), 6.49 (d, $J_{HH} = 1.7$ Hz, 2H, Ar-*H*), 5.91 (sept, $J_{H\text{-}H} = 6.1$ Hz, 1H, O—C*H*(CH$_3$)$_2$), 2.83 (m, 4H, NC*H*$_2$), 1.82 (s, 18H, *t*Bu), 1.76 (d, $J_{H\text{-}H} = 6.1$ Hz, 6H, O—CH(C*H*$_3$)$_2$), 1.43 (s, 18H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, benzene-d_6, 298 K): δ 152.8 (C_q, Ar), 140.7 (C_q, Ar), 137.8 (C_q, Ar), 128.8 (C_q, Ar), 119.7 (*C*H—Ar), 111.2 (*C*H—Ar), 80.2 (O—*C*H(CH$_3$)$_2$), 46.9 (N*C*H$_2$), 36.0 (C_q, *t*Bu), 34.7 (C_q, *t*Bu), 32.1 (*C*H, *t*Bu), 30.4 (*C*H, *t*Bu), 26.3 (O—CH(*C*H$_3$)$_2$) ppm (V-C$_{carbene}$ ^{13}C NMR resonance was not observed). ^{51}V NMR (131.55 MHz, benzene-d_6, 298 K): δ −613 (s, $\Delta\nu_{1/2} = 304$ Hz) ppm. DRIFT (KBr, ν/cm^{-1}, [4000–400]): 2958s, 2930m, 2906m, 2867m, 1492vs, 1455s, 1391w, 1361w, 1327m, 1290w, 1264w, 1251w, 1208vw, 1114m, 985m, 845m, 754w, 666vw, 617vw, 564w.

4.3.3. Synthesis of ([k^3-O,C,O]-^{Is}NHC)V(═O)N$_3$ (3)

To a solution of **2** (20 mg, 0.03 mmol) in 4 mL toluene was added an excess of Me_3SiN_3. The solution was stirred at 80 °C for 4 h, and then all volatiles were removed under vacuum. Then, to the dark brown solid was added 2 mL of hexane, the mixture was centrifuged, and the remaining dark brown solid was dried under vacuum affording a brown powder **3** (yield: 56%). Anal. Calcd for $C_{31}H_{44}N_5O_3V$: C, 63.58; H, 7.57; N, 11.96%. Found: C, 61.99; H, 7.27; N, 12.35%. After several attempts, no correct elemental analysis data was obtained. ^{1}H NMR (500.13 MHz, benzene-d_6, 298 K): δ 7.45 (d, $J_{HH} = 2.1$ Hz, 2H, Ar-*H*), 6.42 (d, $J_{HH} = 2.1$ Hz, 2H, Ar-*H*), 2.78 (m, 4H, NC*H*$_2$), 1.80 (s, 18H, *t*Bu), 1.38 (s, 18H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, benzene-d_6, 298 K): δ 152.9 (C_q, Ar), 142.8 (C_q, Ar), 138.3 (C_q, Ar), 134.8 (C_q, Ar), 120.3 (*C*H—Ar), 111.0 (*C*H—Ar), 46.9 (NCH$_2$), 36.0 (C_q, *t*Bu), 34.8 (C_q, *t*Bu), 31.8 (*C*H, *t*Bu), 30.2 (*C*H, *t*Bu) ppm (V-*C*$_{\text{carbene}}$ ^{13}C NMR resonance was not observed). ^{51}V NMR (131.55 MHz, benzene-*d*$_6$, 298 K): *δ* −540 (s, $\Delta\nu_{1/2} = 247$ Hz) ppm. DRIFT (KBr, *ν*/cm^{-1}, [4000–400]): 2958s, 2907m, 2867m, 2080vs, 1480s, 1453s, 1393w, 1362w, 1348w, 1331m, 1291w, 1268w, 1251w, 1214vw, 1189vw, 1067vw, 1114m, 982m, 939w, 916w, 867m, 846vw, 763w, 750w, 669w, 649vw, 584w, 513vw, 500w, 452w, 434w

4.3.4. *Synthesis of ([k^3-O,C,O]-^{Is}NHC)V(═O)OAc (4)*

To a solution of **1** (100 mg, 0.153 mmol) in 3 mL THF was added dropwise 1.1 equiv. of NaOAc (15.6 mg, 0.189 mmol) dissolved in 3 mL THF. The solution was stirred at room temperature overnight, then dried under vacuum and extracted with dichloromethane. The dark red solution mixture was centrifuged, filtered, and then dried under vacuum affording a dark red powder **4** (yield: 90%). Anal. Calcd for $C_{33}H_{47}N_2O_5V$: C, 65.77; H, 7.86; N, 4.65%. Found: C, 65.69; H, 7.49; N, 4.67%. ^{1}H NMR (500.13 MHz, benzene-*d*$_6$, 298 K): *δ* 7.50 (d, $J_{\text{HH}} = 2.0$ Hz, 2H, Ar-*H*), 6.52 (d, $J_{\text{HH}} = 2.0$ Hz, 2H, Ar-*H*), 2.71 (m, 4H, NC*H*$_2$), 2.00 (s, 3H, OAc) 1.78 (s, 18H, *t*Bu), 1.41 (s, 18H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, benzene-*d*$_6$, 298 K): *δ* 170.6 (O(*C*O)Me), 154.1 (*C*$_{\text{q}}$, Ar), 142.1 (*C*$_{\text{q}}$, Ar), 136.5 (*C*$_{\text{q}}$, Ar), 128.5 (*C*$_{\text{q}}$, Ar), 119.7 (*C*H—Ar), 111.4 (*C*H—Ar), 47.5 (N*C*H$_2$), 35.9 (*C*$_{\text{q}}$, *t*Bu), 34.8 (*C*$_{\text{q}}$, *t*Bu), 31.9 (*C*H, *t*Bu), 30.2 (*C*H, *t*Bu), 23.0 (*C*H, O(CO)*Me*) ppm (V-*C*$_{\text{carbene}}$ ^{13}C NMR resonance was not observed.^{51}V NMR (131.55 MHz, benzene-*d*$_6$, 298 K *δ* −533 (s, $\Delta\nu_{1/2} = 243$ Hz) ppm. DRIFT (KBr, *ν*/cm^{-1}, [4000–400]): 2951s, 2905 m, 2864 m, 1621 m, 1599m, 1489vs, 1454s, 1391w, 1361w, 1324m, 1285m, 1265m, 1250m, 1241w, 1215w, 1186vw, 1062vw, 987m, 986m, 942vw, 914vw, 857m, 758w, 698w, 667w, 651vw, 576w, 479vw, 456vw, 440vw.

4.3.5. *Synthesis of ([k^3-O,C,O]-^{Is}NHC)V(═O)OAc^F (5)*

To a solution of **1** (80 mg, 0.138 mmol) in 3 mL THF was added dropwise 1.1 equiv. of NaOAc^F (20.6 mg, 0.152 mmol) dissolved in 3 mL THF. The solution was stirred at room temperature overnight, then dried under vacuum and extracted with dichloromethane. The dark red solution mixture was centrifuged, filtered, and then dried under vacuum affording a dark red powder **5** (yield: 90%). Anal. Calcd for $C_{33}H_{44}F_3N_2O_5V.CH_2Cl_2$: C, 55.07; H, 6.25; N, 3.78%. Found: C, 55.37; H, 6.38; N, 3.67%. ^{1}H NMR (500.13 MHz, benzene-*d*$_6$, 298 K): *δ* 7.44 (d, $J_{\text{HH}} = 1.7$ Hz, 2H, Ar-*H*), 6.41 (d, $J_{\text{HH}} = 1.7$ Hz, 2H, Ar-*H*), 2.66 (m, 4H, NC*H*$_2$), 1.70 (s, 18H, *t*Bu), 1.37 (s, 18H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, benzene-*d*$_6$, 298 K): *δ* 163.9 (O(*C*O)CF$_3$), 153.3 (*C*$_{\text{q}}$, Ar), 143.6 (*C*$_{\text{q}}$, Ar), 137.5 (*C*$_{\text{q}}$, Ar), 127.9 (*C*$_{\text{q}}$, Ar), 120.5 (*C*H—Ar), 115.6 (O(CO)*C*F$_3$), 111.3 (*C*H—Ar), 47.1 (N*C*H$_2$), 35.8 (*C*$_{\text{q}}$, *t*Bu), 34.8 (*C*$_{\text{q}}$, *t*Bu), 32.7 (*C*H, *t*Bu), 30.0 (*C*H, *t*Bu) ppm (V-*C*$_{\text{carbene}}$ ^{13}C NMR resonances was not observed). ^{51}V NMR (131.55 MHz, benzene-*d*$_6$, 298 K): *δ* −585 (s, $\Delta\nu_{1/2} = 421$ Hz) ppm. ^{19}F NMR (470.70 MHz, benzene-*d*$_6$, 298 K): *δ* −74.75 (s, $\Delta\nu_{1/2} = 1.7$ Hz) ppm. DRIFT (KBr, *ν*/cm^{-1}, [4000–400]): 2960s, 2909m, 2871m, 1718s, 1598m, 1493vs, 1458s, 1392m, 1363m, 1349w, 1323s, 1292vw, 1266 , 1252 m, 1238m, 1205m, 1181vs, 1154m, 1065w, 996m, 946w, 913vw, 869m, 792vw, 765w, 751vw, 721w, 668m, 650vw, 620m, 524w, 484vw, 451vw.

4.3.6. *Purification of {([k^3-O,C,O]-^{Is}NHC)V(═O)}$_2$(μ-O) (6)*

Attempts to recrystallize compounds from either **2**, **3** or **4** in a solution of CH_2Cl_2 or toluene (2–3 mL) in presence of adventitious moisture at room temperature after 2–3 weeks afforded crystals of **6**. The crystals were further washed with pentane and dried under vacuum affording a dark brown powder **6**. Anal. Calcd for $C_{33}H_{44}F_3N_2O_5V.CH_2Cl_2$: C, 67.50; H, 8.04; N, 5.08%. Found: C, 67.46; H, 7.70; N, 4.68%. ^{1}H NMR (500.13 MHz, benzene-*d*$_6$, 298 K): *δ* 7.57 (d, $J_{\text{HH}} = 2.1$ Hz, 2H, Ar-*H*), 7.29 (d, $J_{\text{HH}} = 2.3$ Hz, 2H, Ar-*H*), 6.61 (d, $J_{\text{HH}} = 2.1$ Hz, 2H, Ar-*H*), 6.54 (d, $J_{\text{HH}} = 2.3$ Hz, 2H, Ar-*H*), 3.00 (m, 8H, NC*H*$_2$), 2.13 (s, 18H, *t*Bu), 1.50 (s, 18H, *t*Bu), 1.48 (s, 18H, *t*Bu), 1.36 (s, 18H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, benzene-*d*$_6$, 298 K): *δ* 154.4 (*C*$_{\text{q}}$, Ar), 154.4 (*C*$_{\text{q}}$, Ar), 153.5 (*C*$_{\text{q}}$, Ar), 140.9 (*C*$_{\text{q}}$, Ar), 140.4 (*C*$_{\text{q}}$, Ar), 138.9 (*C*$_{\text{q}}$, Ar), 137.3 (*C*$_{\text{q}}$, Ar), 119.9 (*C*H—Ar), 119.4 (*C*H—Ar), 110.9 (*C*H—Ar), 47.2 (N*C*H$_2$), 47.1 (N*C*H$_2$), 36.4 (*C*$_{\text{q}}$, *t*Bu), 35.6 (*C*$_{\text{q}}$, *t*Bu), 35.8 (*C*$_{\text{q}}$, *t*Bu), 34.6 (*C*$_{\text{q}}$, *t*Bu), 32.0 (*C*H, *t*Bu), 31.9 (*C*H, *t*Bu), 30.8 (*C*H, *t*Bu), 30.2 (*C*H, *t*Bu) ppm (V-*C*$_{\text{carbene}}$ and two *C*$_{\text{q}}$-Ar ^{13}C NMR resonances were not observed). ^{51}V NMR (131.55 MHz, benzene-*d*$_6$, 298 K): *δ* −635 (s, $\Delta\nu_{1/2} = 698$ Hz) ppm. DRIFT (KBr, *ν*/cm^{-1}, [4000–400]): 2956s, 2922 m, 2906 m, 2867 m, 1601vw, 1489vs, 1459s, 1392 m, 1360 m, 1360 m, 1348 m, 1329s, 1289 m, 1269 m, 1269 m, 1238 m, 1214w, 1188w, 1070vw, 984 m, 940w, 916vw, 853 m, 772s, 754s, 720s, 669 m, 651 m, 568 m, 541 m, 481vw, 545vw, 442w, 416 m.

4.3.7. *Synthesis of ([k^3-O,C,O]-^{bz}NHC)V(═O)Cl (7)*

In a glove box, a THF solution (4 mL) of **1** (43.4 mg, 0.177 mmol) was added at room temperature via a pipette to a stirring THF solution (8 mL) of the benzimidazolium chloride salt (100 mg, 0.177 mmol). The initial yellowish solution slowly turned greenish black upon addition of the vanadium reagent. The reaction mixture was stirred overnight at room temperature to yield a dark green solution which was evaporated to dryness to compound **8** after washing several times with hexane and CH_2Cl_2 as a dark green solid in high yield (yield: 94%). Anal. Calcd for $C_{35}H_{44}ClN_2O_3V.1/2CH_2Cl_2$: C, 63.68; H, 6.67; N, 4.18%. Found: C, 63.77; H, 6.88; N, 4.44%. ^{1}H NMR (500.13 MHz, benzene-*d*$_6$, 298 K): *δ*, 7.81 (m, 2H, Ar$_{\text{bz}}$-*H*), 7.67 (d, *J* = 1.9 Hz, 2H, Ar-*H*), 7.65 (d, *J* = 1.9 Hz, 2H, Ar-*H*), 6.96 (m, 2H, Ar$_{\text{bz}}$-*H*), 1.87 (s, 18H, *t*Bu), 1.36 (s, 18H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, benzene-*d*$_6$, 298 K): *δ*, 155.4 (*C*$_{\text{q}}$, Ar), 143.2 (*C*$_{\text{q}}$, Ar), 139.9 (*C*$_{\text{q}}$, Ar), 133.2 (*C*$_{\text{q}}$, Ar), 125.4 (*C*$_{\text{q}}$, Ar), 123.5 (*C*H—Ar), 123.4 (*C*H—Ar), 115.4 (*C*H—Ar), 114.4 (*C*H—Ar), 36.2 (*C*$_{\text{q}}$, *t*Bu), 34.9 (*C*$_{\text{q}}$, *t*Bu), 31.7 (*C*H$_3$, *t*Bu), 30.2 (*C*H$_3$, *t*Bu) ppm (V-*C*$_{\text{carbene}}$ ^{13}C NMR resonance was not observed). ^{51}V NMR (131.55 MHz, benzene-*d*$_6$, 298 K): *δ* −513 (s, $\Delta\nu_{1/2} = 324$ Hz) ppm. DRIFT (KBr, *ν*/cm^{-1}, [4000–400]): 2960vs, 2906m, 2869m, 1593w, 1572w, 1550w, 1483s, 1469m, 1435vs, 1392m, 1366m, 1331vw, 1289m, 1267s, 1254vs, 1198w, 1163w, 1117m, 1109m, 1068w, 1003s, 971m, 924m, 861s, 811m, 797m, 760m, 748s, 701m, 645w, 608vw, 586m, 493m, 472w, 426m.

4.3.8. *Synthesis of ([k^3-O,C,O]- ^{Is}NHC)V(═NPh)Cl (8)*

In a glove box, a THF solution of the *N,N′*-di(2-hydroxy-3,5-di-*tert*-butylphenyl) imidazolidinium chloride salt (120 mg, 0.233 mmol) was added at room temperature via a pipette to a stirring solution of V(═NPh)(O*i*Pr)$_3$ (74.5 mg, 0.23 mmol) in THF (8 mL). The reaction mixture was stirred overnight at room temperature. The dark brown solution was centrifuged, washed with pentane, and evaporated to dryness under vacuum to yield a pure brown powder of **9** (yield: 88%). Anal. Calcd for $C_{41}H_{57}ClN_3O_3V$: C, 67.93; H, 7.55; N, 6.42%. Found: C, 67.20; H, 7.52; N, 5.68%. After several attempts, no correct elemental analysis data was obtained. ^{1}H NMR (500.13 MHz, benzene-*d*$_6$, 298 K): *δ* **7**.48 (d, $J_{\text{HH}} = 2.0$ Hz, 2H, Ar-*H*), 6.69 (m, 2H, *o*-Ph-*H*), 6.48 (d, $J_{\text{HH}} = 2.0$ Hz, 2H, Ar-*H*), 6.44 (m, 2H, *m*-Ph-*H*), 6.33 (m, 1H, *p*-Ph-*H*), 2.82 (m, 4H, NC*H*$_2$), 1.93 (s, 18H, *t*Bu), 1.38 (s, 18H, *t*Bu) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, benzene-*d*$_6$, 298 K): *δ*, 154.9 (*C*$_{\text{q}}$, Ar), 142.0 (*C*$_{\text{q}}$, Ar), 138.4 (*C*$_{\text{q}}$, Ar), 129.2 (*C*$_{\text{q}}$, Ar), 129.2 (*C*$_{\text{q}}$, Ar)¸ 128.3 (*C*H—Ar)¸127.3 (*C*H—Ar), 125.7 (*C*H—Ar), 120.2 (*C*H—Ar), 110.0 (*C*H—Ar), 47.0 (N*C*H$_2$), 36.1 (*C*$_{\text{q}}$, *t*Bu), 34.8 (*C*$_{\text{q}}$, *t*Bu), 31.9 (*C*H, *t*Bu), 30.2 (*C*H, *t*Bu) ppm (V-*C*$_{\text{carbene}}$, ^{13}C NMR resonances were not observed). ^{51}V NMR (131.55 MHz, benzene-*d*$_6$, 298 K): *δ* −432 (s, $\Delta\nu_{1/2} = 187$ Hz) ppm. DRIFT (KBr, *ν*/cm^{-1}, [4000–400]): 2960vs, 2905 m, 2869 m, 1641w, 1598vw, 1572vw, 1489vs, 1469s, 1454s, 1444 m, 1361 m, 1319 m, 1288 m, 1268 m, 1252 m, 1243 m, 1211w, 1201w, 1187w, 1061w, 1040w, 1022vw, 976vw, 941w, 911w, 883w, 846 m, 755s, 680 m, 668 m, 646vw, 565 m, 559 m, 484w, 459vw, 441w, 421w, 419w.

4.3.9. *Reaction of ([k^3-O,C,O]- ^{Is}NHC)V(═NPh)Cl (8) with CO$_2$*

In a glovebox, complex **8** (5 mg, 7.64 μmol) was dissolved in dichloromethane (1 mL) and to this solution was added 2 bar of CO_2. The solution was stirred at room temperature for 3 h, and then the dark brownish mixture was evaporated to dryness resulting in a mixture of compounds **1**, **8** and phenyl isocyanate (Fig. 3). For **8**: ^{1}H NMR (500.13 MHz, *d*ichloromethane-d_2, 298 K): δ **7.26** (d, $J_{HH} = 2.1$ Hz, 2H, Ar-*H*), 7.03 (m, 2H, *o*-Ph-*H*), 6.95 (m, 1H, *p*-Ph-*H*), 6.87 (d, $J_{HH} = 2.1$ Hz, 2H, Ar-*H*), 6.58 (m, 2H, *m*-Ph-*H*), 4.33 (m, 4H, NC*H*$_2$), 1.55 (s, 18H, *t*Bu), 1.36 (s, 18H, *t*Bu) ppm. ^{51}V NMR (131.55 MHz, *d*ichloromethane-d_2, 298 K): δ −434 (s, $\Delta\nu_{1/2} = 191$ Hz) ppm. For **1**: ^{1}H NMR (500.13 MHz, *d*ichloromethane-d_2, 298 K): δ 7.31 (d, $J_{HH} = 2.2$ Hz, 2H, Ar-*H*), 6.96 (d, $J_{HH} = 2.2$ Hz, 2H, Ar-*H*), 4.47 (m, 4H, NC*H*$_2$), 1.54 (s, 18H, *t*Bu), 1.37 (s, 18H, *t*Bu) ppm. ^{51}V NMR (131.55 MHz, *d*ichloromethane-d_2, 298 K): δ −520 ppm (s, $\Delta\nu_{1/2} = 324$ Hz). For PhNCO: ^{1}H NMR (500.13 MHz, *d*ichloromethane-d_2, 298 K): δ 7.09–7.05 (m, 2H, *o*-Ph-*H*), 6.70 (m, 1H, *p*-Ph-*H*), 6.59 (m, 2H, *m*-Ph-*H*, signal overlapping with the one at 6.58 ppm of **8**).

4.4. General procedure for the copolymerization of CHO with CO_2

In a glovebox, an oven-dried vial equipped with a magnetic stirring bar, a solution of the cocatalyst (8 μmol) in dichloromethane (1 mL) was added under vigorous stirring to a solution of vanadium complex (8 μmol) in dichloromethane (1 mL). After 15 min, the solvent was removed and dried for 30 min under vacuum. The resulting solid was then dissolved in a precooled (−30 °C) solution of CHO and transferred to a reaction tube for low-pressure reactions. The mixture was stirred at the desired pressure and temperature. After 24 h, the reaction was cooled down to room temperature and the pressure was released. An aliquot of the solution was taken for determining the conversion and selectivity by ^{1}H NMR spectroscopy in chloroform-*d*.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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