

Vanadium Imido NHC Complexes for the Ring-Closing Olefin Metathesis Reactions

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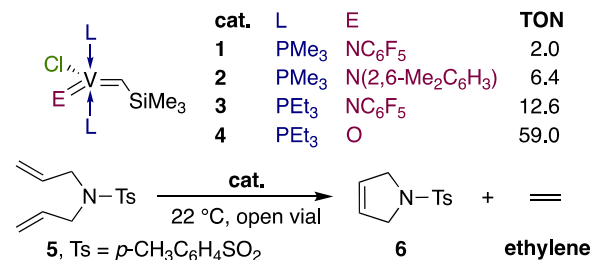
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ABSTRACT: Vanadium bis-phosphine imido and oxo chloride alkylidenes have been extensively applied in the ring-closing metathesis of various acyclic olefins. However, their reactions involving ethylene showed limited productivity due to rapid decomposition. The primary degradation pathway involving V bis-phosphine imido complexes is β -H elimination at unsubstituted metallacyclobutane. In contrast, β -H elimination is disfavored for V oxo species, but bimolecular decomposition precludes its high productivity. Herein, we present the synthesis of V imido NHC complexes that are the most productive V catalysts toward various terminal olefins in ring-closing metathesis reactions. Experimental and computational studies suggest that β -H elimination and bimolecular decomposition are disfavored for V imido NHC complexes.

Ru, Mo, and W-catalyzed olefin metathesis (OM)¹⁻³ have been applied to produce commodity chemicals,⁴ pharmaceuticals,⁵ and advanced materials.⁶ The shift to more easily accessible and abundant first-row transition metals is desirable to lower the cost of the obtained materials and decrease the environmental footprint. However, only a few first-row transition metal complexes demonstrate the capacity to complete the OM catalytic cycle.⁷⁻⁸ Among 3d transition metals, OM catalysts based on V are the most developed,⁹ presumably due to the diagonal relationship between V and Mo.¹⁰ V alkylidenes containing imido, alkoxide, and phosphine ligands have been applied for ring-opening metathesis polymerization (ROMP) of cyclic olefins showing high activity and selectivity.¹¹⁻¹³ However, those complexes exhibit low productivity toward acyclic terminal olefins.¹⁴⁻¹⁵

Recently, we reported the facile access to V imido chloride alkylidenes **1-3** (Scheme 1) and showed the first example of productive ring-closing metathesis (RCM) utilizing those complexes.¹⁶ The reported equilibrium between polymerization-depolymerization of cyclopentene is an example of unproductive RCM.¹⁷ Complexes **1-3** can tolerate various common functional groups. However, those catalysts quickly decompose under ethylene due to β -hydride (β -H) elimination at unsubstituted metallacyclobutane (MCB). In the following report, we described the first catalytically active V oxo alkylidene **4**, which outperformed **1-3** in reactions involving ethylene (Scheme 1).¹⁸ We found that V oxo alkylidenes significantly disfavor β -H elimination, but the relatively small oxo ligand can bridge two metal centers and encourage bimolecular decomposition.¹⁹ In contrast, V imido counterparts are significantly more stable toward bimolecular decomposition and their further development to prevent β -H elimination is highly desirable.

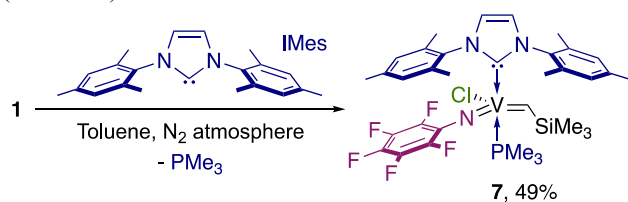


Scheme 1. Previously synthesized V alkylidenes, model RCM reaction, and maximum turnover number (TON) for each catalyst in the model RCM reaction.^{16, 18}

Increased imido group size and electron-donating properties improve RCM productivity (**1** and **2**, Scheme 1). The change of PMe₃ to PEt₃ leads to an even more pronounced effect (**1** and **3**, Scheme 1). N-heterocyclic carbene (NHC) as a neutral ligand is desirable due to high σ -donating abilities and controllable steric properties,²⁰⁻²¹ which can prevent β -H elimination and bimolecular decomposition. Previously, NHC complexes were utilized to prepare air-stable, highly active, selective, and functional group tolerant Mo and W alkylidenes.²² V alkylidene complexes of type V(NR)(CHSiMe₃)(CH₂SiMe₃)(NHC), where R is adamantyl²³ or 2,6-Y₂C₆H₂ (Y = Me²³⁻²⁴ or Cl²⁴) have been reported, but have limited activity in ROMP of norbornene at ambient temperature unless C₆X₅OH (X = F or Cl) is added. Two resulting complexes V[N(2,6-Cl₂C₆H₂)](CHSiMe₃)(OC₆X₅)(IMes) have been isolated in 24% (**A**, X = F) and 21% (**B**, X = Cl) yields. Complex **A** showed a TOF of 208 s⁻¹ in ROMP of norbornene, the highest reported activity among V alkylidenes. Unfortunately, complexes **A** and **B** have not been structurally characterized by X-ray crystallography.²⁴ Studies of catalytic activity of V imido alkylidenes bearing neutral ligands other than phosphines

toward acyclic olefins have not been reported. Here we present the synthesis of V imido NHC chloride alkylidenes, their X-ray structures,²⁵ DFT studies, and activity in RCM of various terminal olefins.

Complex **7** was synthesized from **1** utilizing ligand exchange reaction in the presence of IMes in 49% yield (Scheme 2).



Scheme 2. Synthesis of complex **7**.

The X-ray structural study showed that complex **7** is *syn*-isomer (Figure 1) and has a distorted trigonal bipyramidal geometry with IMes and PMe₃ in axial positions [V1–C11 2.1828(11) Å, V1–P1 2.4545(3) Å, C11–V1–P1 154.52(3)°]. The V1–C1 distance is 1.8300(11) Å and the large V=C–Si angle 145.94(7) is indicative of α -hydrogen agostic interaction with V center.¹⁶

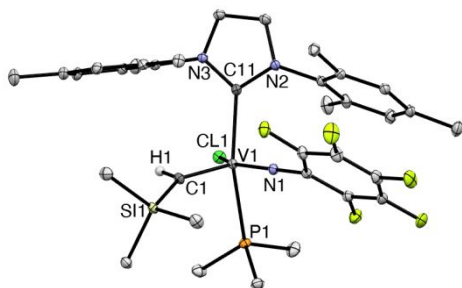
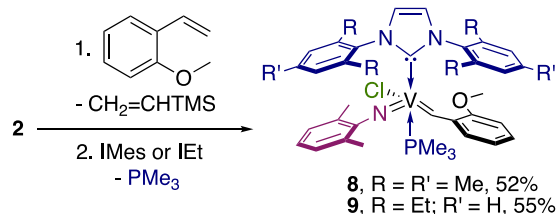


Figure 1. Perspective view of the crystal structure of complex **7** with thermal ellipsoids shown at 30% probability.

The direct exchange of one PMe₃ to IMes is a suitable method to synthesize **7** bearing a small imido group (NC₆F₅). However, in the case of larger imido group (N(2,6-Me₂C₆H₃)), the resulting complex V(N(2,6-Me₂C₆H₃)(CHSiMe₃)(IMes)Cl (**C**) does not contain PMe₃ confirmed by NMR spectroscopy. Unfortunately, the isolation of **C** was challenging due to the high solubility in common crystallization solvents and slow decomposition of **C** in solution. To overcome this challenge, we exchanged TMS-alkylidene for the less sterically demanding *o*-MeO-benzylidene. The following replacement of one phosphine by NHCs led to complexes **8** and **9** in 52% and 55% yield, respectively, after two steps. (Scheme 3). In both cases, only one isomer was observed by ¹H NMR spectroscopy.



Scheme 3. Synthesis of complexes **8** and **9**.

Although it is assumed that V-based OM involves the Chauvin mechanism, the isolation and characterization of key intermediates of the catalytic cycle, such as MCB or new alkylidene, have not been reported previously. Therefore, the presented alkylidene exchange is important from a fundamental standpoint and further supports the Chauvin mechanism in V-based OM. In addition, complexes **8** and **9** are the first examples of well-defined catalytically active V alkylidenes that do not contain TMS-alkylidene moiety. From a historical perspective, a transient V benzylidene is thought to be the active catalyst in early work on V-based ROMP.²⁶

Complexes **8** and **9** were successfully crystallized and studied by X-ray crystallography (Figure 2).

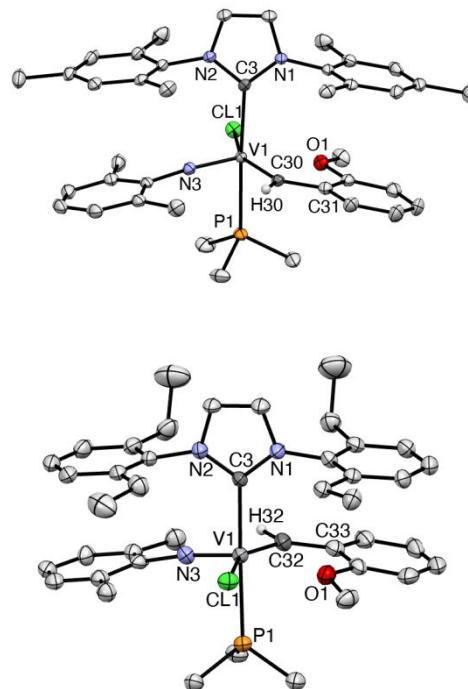


Figure 2. Perspective view of the crystal structures of complexes **8** (top) and **9** (bottom) with thermal ellipsoids shown at 30% probability.

o-MeO-benzylidene moiety was chosen to form 6-coordinated complexes. However, the long distance between the V and methoxy group (2.524 Å in **8** and 2.517 Å in **9**) does not confidently define V1–O1 as a bond. Therefore, we describe the geometry of **8** and **9** as a distorted square pyramid ($\tau^{27} = 0.38$ in **8** and $\tau = 0.36$ in **9**) with the imido group in the apical position with a weak interaction between V and methoxy group trans to the imido group. Both **8** and **9** are *anti*-isomers with neutral ligands trans to each other and have similar bond distances and angles. Complex **8**: V1–C3 2.231(2) Å, V1–P1 2.4939(7) Å, C3–V1–P1 172.80(6)°, V1–C30 1.952(2), V1–C30–C31 124.64 (17)°. Complex **9**: V1–C3 2.240(5) Å, V1–P1 2.4994(17) Å, C3–V1–P1 172.40(15)°, V1–C32 1.944(7), V1–C32–C33 125.6(5)°. As expected, the V=C distances in **8** and **9** are longer and V=C–C angles are smaller than analogous bond and angle in **7** due to the absence of α -hydrogen agostic interactions.^{16, 28}

We tested complexes **7–9** toward our model substrate **5**. Noteworthy, the reactions in open and closed vials showed

similar conversions for **7-9** suggesting that studied complexes are stable toward ethylene. The results and comparison with **1-4** at the same conditions are summarized in Table 1.

Table 1. Model RCM of diallyl-*N*-tosylamide **5**.^a

$5 \xrightarrow[22\text{ }^{\circ}\text{C, C}_6\text{D}_6, \text{ closed vial}]{\text{V catalyst}} 6 + \text{ethylene}$					
#	cat.	cat., mol%	time, h	conv., % ^b	TON
1	1	5	5	8	1.6
2	2	5	5	29	5.8
3	3	5	5	42	8.4
4	4	5	5	67	13.4
5	7	5	5	54	10.8
6	8	5	5	96	19.2
7	9	5	5	87	17.4
8	8	1	0.5	76	76.0
9	8	0.5	0.5	70	141
10	8	0.1	0.5	14	140
11	8	0.1^c	0.5	17	170
12	9	0.1 ^c	0.5	14	140
13	8	3^{c,d}	1.3	>99	33.3
14	8	3 ^c	0.5	91	30.3
15	8	3 ^{c,e}	0.5	2	0.7

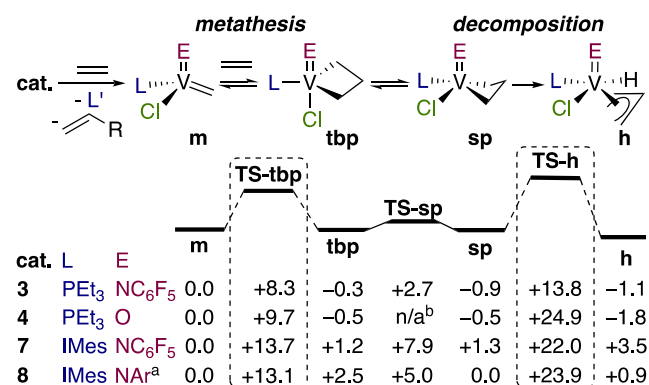
^a0.12 M **5**. ^bby ¹H NMR. ^c0.24 M **5**. ^d1% increments followed by 1% B(C₆F₅)₃. ^e4 equiv. of PMe₃

Complexes **7-9** outperform their bis-phosphine counterparts **1-3** in the model RCM reaction. Complex **8** is the most effective catalyst among the studied, showing productivity higher than V oxo complex **4** (entries 1-7, Table 1). **8** is not observed by ¹H NMR spectroscopy after 30 minutes of the reaction in all cases. The decrease of the catalyst's loading leads to the increase of TON (entries 8-10, Table 1) with the maximum TON of 170 at 0.1 mol% of **8** at a higher concentration of **5** (entry 11, Table 1), which is the highest reported TON of V-based OM involving acyclic terminal olefins.

Following the catalysis with **8** by ¹H NMR spectroscopy showed the formation of triplet at 14.1 ppm (³J_{HP} = 8.9 Hz), which corresponds to alkylidene signal of bis-phosphine complex V(N(2,6-Me₂C₆H₃)(CHAr')(PMe₃)₂)Cl (**D**, Ar' = *o*-(OMe)C₆H₄), observed previously during the PMe₃→NHC exchange reaction. We explain the formation of **D** by the reverse NHC→PMe₃ exchange reaction in the presence of PMe₃, formed during the initiation step. Complex **D** quickly decomposes in the presence of ethylene in analogy to **1** via β-H elimination.¹⁶ Thus, the reaction between **8** and ethylene showed the formation of **D** and propene (see Supporting Information). Based on our observation, the larger IET ligand dissociates more readily than IMes to form **D**, explaining the lower productivity of **9** compared to **8**. The rates of two competitive reactions, **8**→**D** and OM, depend on the concentrations of PMe₃ and **5** correspondingly. Therefore, low catalyst loading and increased substrate concentration led to higher productivity. The reaction in the presence of 4 equiv. of PMe₃ showed low conversion supporting our hypothesis (entry 15, Table 1). In contrast, the reaction in the presence of phosphine scavenger (B(C₆F₅)₃) allowed completing the

reaction. The optimal conditions included the addition of **8** in 1% increments followed by 1% increments of B(C₆F₅)₃ to remove free PMe₃ before adding a new portion of **8** to suppress the formation of **D**. This strategy resulted in the full conversion of **5** to **6** and required 3 mol% of **8** (entry 13, Table 1).

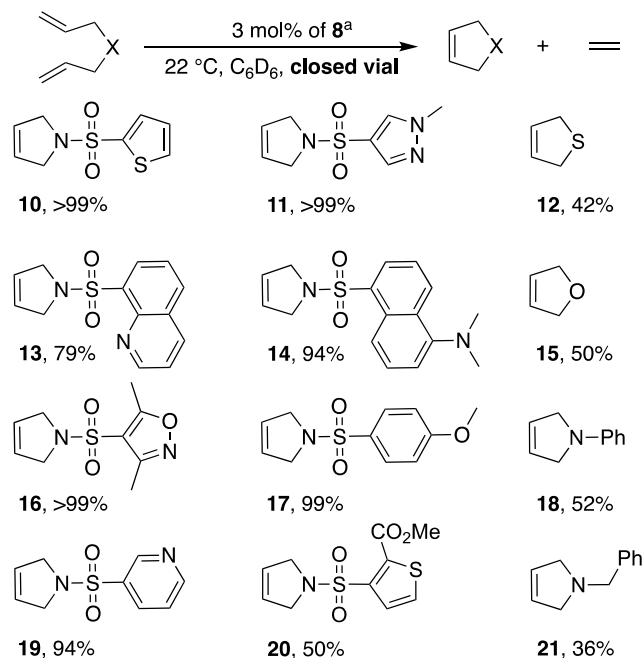
To further understand the role of the NHC ligand on catalyst stability, we performed DFT (B3LYP-D3)²⁹⁻³¹ calculations on the unimolecular catalyst deactivation. It is nowadays well accepted that OM with d⁰ alkylidene complexes implies the coordination of the olefin trans to the strongest ancillary σ-donor ligand to form the trigonal bipyramidal MCB (**tbp**, Scheme 4).³²⁻³³ Unimolecular deactivation starts from the resting-state square pyramidal MCB (**sp**) and occurs through a β-H elimination trans to the weakest σ-donor ligand.³⁴⁻³⁵ We recently showed that V alkylidenes proceed through the same reaction mechanism.¹⁸ Therefore, we explored OM between the methylidene derivatives of **7** and **8** and ethylene and the subsequent β-H elimination (Scheme 4). For comparison, we include the Gibbs energies for methylidene derivatives of **3** and **4** reported previously.¹⁸



Scheme 4. Gibbs energies (kcal mol⁻¹) of OM and unimolecular decomposition of methylidene derivatives of **3**, **4**, **7**, and **8**. ^aAr = 2,6-Me₂C₆H₃. ^bsee ref.¹⁸

According to calculations, the energy barrier for the cycloaddition step with **7-m** is 5.4 kcal mol⁻¹ higher than that of **3-m**. Moreover, the **tbp** and **sp** MCBs of **7** are less stable with respect to separated reactants than those of **3**. Both factors suggest that **7** is slightly less prone to undertake OM. The lower activity of **7** arises from a weaker alkylidene – olefin interaction at the transition state for cycloaddition due to the stronger σ-donating ability of IMes when compared to PEt₃. The substitution of the NC₆F₅ imido ligand by the more donating N(2,6-Me₂C₆H₃) has a small effect on the energy barrier and MCB stability. More importantly, the β-H elimination from the **sp** for both **7** and **8** requires overcoming high energy barriers, the transition state lying 22.0 and 23.9 kcal mol⁻¹ above separated reactants, respectively. These values are significantly higher than those computed for **3** (13.8 kcal mol⁻¹) and comparable to those obtained for the most stable V oxo alkylidene (24.9 kcal mol⁻¹). This agrees with the experimental results and suggests that the enhanced stability of **7-9** compared to **4** arises mainly by preventing the bimolecular decomposition.

We expanded the scope to 12 substrates using catalyst **8** and the best conditions obtained for **5** (Scheme 5).



Scheme 5. Scope of RCM catalyzed by **8**. ^a1% increments followed by 1% $B(C_6F_5)_3$.

Organic compounds containing thiophene (**10**), pyrazole (**11**), quinoline (**13**), tertiary aniline (**14**), isoxazole (**16**), methoxy group (**17**), and pyridine (**19**) are easily accessible by using **8** with high conversions. Substrates containing a thioether (**12**), an ether (**15**), *N,N*-diallylaniline (**18**), an ester (**20**), and tertiary amine (**21**) exhibit moderate conversions, presumably due to competing binding to the catalyst.

CONCLUSION

We have shown that V imido NHC chloride complexes can be prepared utilizing ligand exchange reaction from bis-phosphine precursors in the presence of free NHC. In the case of a larger imido group, the alkylidene exchange before the reaction with NHC is necessary to decrease the steric bulk around the metal center. The resulting NHC complexes exhibit high stability toward ethylene. As a result, catalyst **8** shows the highest reported OM productivity in reactions with terminal olefins in the presence of various common functional groups. Experimental and computational studies suggest that β -H elimination from metallacyclobutane is significantly disfavored compared to bis-phosphine counterparts. In addition, synthesized complexes are less prone to bimolecular decomposition than reported V oxo alkylidene. The dissociation of phosphine during the initiation step leads to the poisoning of the catalysts by forming the V bis-phosphine complex, a less active and stable catalyst. A phosphine scavenger was used to address this issue temporarily. The shift to phosphine-free systems is a logical strategy to develop a reliable V-based catalyst for olefin metathesis, the direction that is currently addressed in our group.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Synthesis details, NMR spectra, and details of X-ray studies of **7**–**9**, and computational details (PDF).

X-ray crystallographic files of **7**–**9** (CIF).

Cartesian Coordinates of the DFT structures (xyz).

Accession Codes

CCDC 2132696 (**7**), CCDC 2132697 (**8**), and CCDC 2132695 (**9**) contains the supplementary crystallographic data. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or by e-mail: deposit@ccdc.cam.ac.uk.

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Notes

The authors declare no competing financial interests.

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