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# Synthesis and Activity of Vanadium Oxo NHC Alkylidenes. Remarkable Preference for Degenerate Metathesis and Application for Carbon Isotope Exchange

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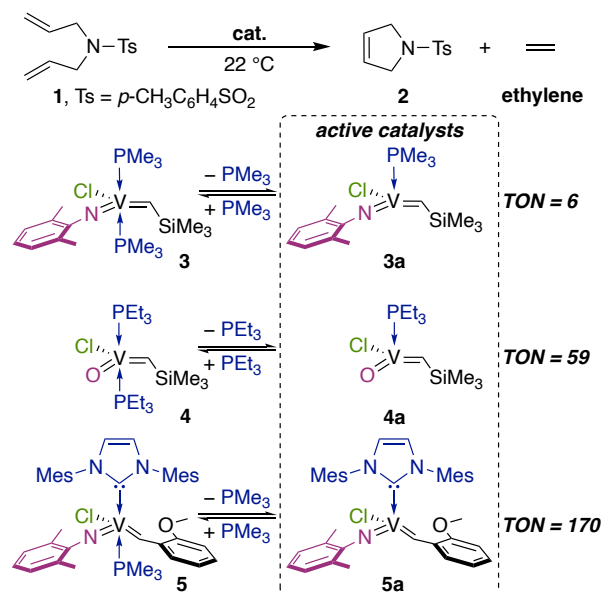
**ABSTRACT:** V imido NHC phosphine alkylidenes are the most efficient V catalysts for ring-closing olefin metathesis of various terminal dienes. The presence of imido and phosphine ligands is responsible for catalyst decomposition. Therefore, the development of phosphine-free V oxo NHC alkylidenes is a logical next step to further improve V-based olefin metathesis. Herein we report V oxo NHC chloride and alkoxide alkylidenes and their reactivity in olefin metathesis. V oxo NHC chloride is readily involved in cycloaddition/cycloreversion steps with olefins. However, a remarkable preference for the formation of 1,3-metallacyclobutane (MCB) leads to exclusive methylene groups exchange (degenerate metathesis) utilized for carbon isotope exchange. DFT studies further support the preference for the 1,3-MCB formation.

Olefin metathesis (OM) is a crucial reaction to construct C–C double bonds utilized to produce commodity and fine chemicals.<sup>1–3</sup> The first reported well-defined complex that can promote catalytic OM is Tebbe's reagent ( $\text{Cp}_2\text{TiCH}_2\text{ClAlMe}_2$ ), which can slowly catalyze the exchange of methylene groups (degenerate metathesis)<sup>4</sup> between two terminal olefins, as shown by Tebbe in 1979.<sup>5</sup> The subsequent research led to the development of highly efficient OM catalysts based on second- and third-row transition metals.<sup>6–8</sup> The recent progress, driven by green chemistry and economic factors, shows that the development of OM catalysts based on first-row metals, primarily vanadium, is achievable.<sup>9–13</sup> Thus, Nomura reported a series of highly active and selective V-based catalysts for ring-opening metathesis polymerization of cyclic olefins.<sup>14–16</sup> Some of those complexes have been utilized by Farrell in cross-metathesis (CM) but showed limited activity.<sup>17–18</sup>

Recently, our group has developed V-catalysts for ring-closing metathesis (RCM) of internal and terminal olefins and reported the highest V-based OM productivity involving terminal dienes.<sup>19–21</sup> Representative V alkylidene complexes **3–5** and their productivities (turnover number, TON) in RCM involving the model substrate **1** are shown in Scheme 1. The dissociation of one neutral ligand is required to access four-coordinate 14 electron active catalysts during the reaction. Catalyst **3** exhibits low RCM productivity with **1** due to limited stability toward ethylene. The main decomposition pathway involves the  $\beta$ -hydride ( $\beta$ -H) elimination at unsubstituted metallacyclobutane (MCB) formed during the catalysis.<sup>19</sup> Substitution of an imido group to oxo significantly disfavors  $\beta$ -H elimination leading to a higher RCM productivity with catalyst **4**. However, the bimolecular decomposition of V oxo phosphine alkylidenes becomes the primary reason for catalyst degradation.<sup>20</sup> Exchange of phosphine in imido complex **3** to N-heterocyclic carbene (NHC) ligand increases TON from 6 to 170 in reaction

with **1** by suppressing both  $\beta$ -H elimination from MCB and bimolecular decomposition. The main degradation pathway for catalysts **5** is the exchange of NHC to phosphine that forms during the initiation step leading to bis phosphine complex analogous to **3**, which is unstable toward ethylene.<sup>21</sup>

**Scheme 1. Maximum Turnover Numbers (TONs) for Previously Synthesized V Catalysts in the Model RCM Reaction.**

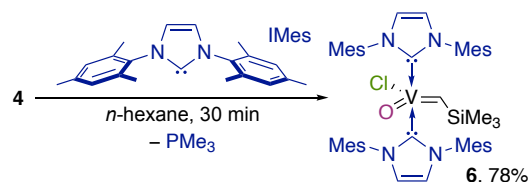


The next logical step for the catalyst optimization is the synthesis of V oxo NHC alkylidenes to preserve remarkable stability toward  $\beta$ -H elimination of V oxo complexes and disfavor bimolecular decomposition by introducing a large NHC ligand. In addition, we hypothesized that the shift to phosphine-free V oxo alkylidenes would improve catalysts' performance since

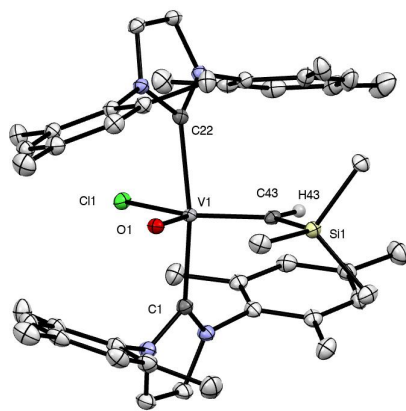
phosphines can participate in side reactions and deactivation pathways, such as reduction of high-oxidation state V complexes<sup>22</sup> and reaction with alkylidenes.<sup>23–24</sup> Here, we present the synthesis of phosphine-free V oxo NHC complexes and their reactivity in OM. We also report the unusual preference of the degenerate metathesis employed for carbon isotope exchange.

Complex **6** has been synthesized from **4** and 2 equiv. of IMes utilizing ligand exchange reaction in 78% yield (Scheme 2).

#### Scheme 2. Synthesis of complex **6**.



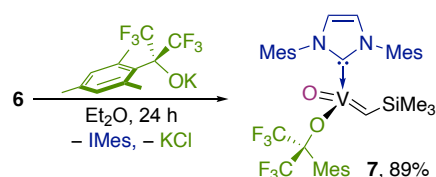
A <sup>1</sup>H NMR spectrum of **6** in C<sub>6</sub>D<sub>6</sub> showed that the alkylidene proton resonance is a singlet at 14.45 ppm (*J*<sub>CH</sub> = 114 Hz). The X-ray structural study revealed that **6** is a *syn*-isomer (Figure 1) and has a distorted trigonal bipyramidal geometry with NHCs in axial positions [V1–C1 2.173(2) Å, V1–C22 2.191(2) Å, C11–V1–C22 156.52(10)°], which is similar to imido NHC complex **5** [V–C(NHC) is 2.1828(11) Å and P–V1–C(NHC) 154.52(3)°]. The V1–C43 distance is 1.889(3) Å, and the V1–O1 bond is 1.586(2) Å, which are similar to **4**.<sup>20</sup> Noteworthy, the V=C–Si angle [133.01(15)°] is lower than the V=C–Si angle in **4** [140.03(9)°]. It can be explained by less extent of α-hydrogen agostic interaction with the metal center<sup>20</sup> due to the lower electrophilicity of V in **6** resulting from the high σ-donating abilities of two NHC ligands.<sup>25</sup>



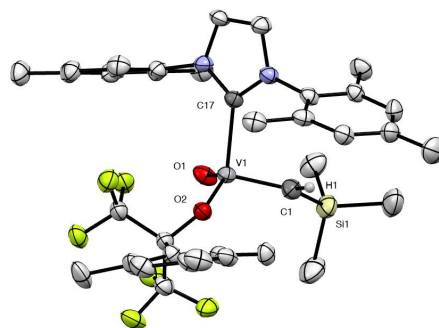
**Figure 1.** Perspective view of the crystal structure of complex **6** with thermal ellipsoids shown at 30% probability.

Surprisingly, complex **6** does not exhibit RCM activity with **1**. We initially hypothesized that one NHC-ligand does not dissociate readily to form a four-coordinate 14 electron active catalyst. To overcome this challenge, we decided to synthesize V oxo NHC complexes bearing bulky alkoxy ligands to facilitate the dissociation of one NHC. Screening various alkoxides (see the complete list in SI) led to the synthesis and isolation of complex **7** in 89% yield (Scheme 3).

#### Scheme 3. Synthesis of complex **7**.



Proton NMR spectrum of complex **7** in C<sub>6</sub>D<sub>6</sub> revealed a singlet resonance for alkylidene proton at 17.66 ppm (*J*<sub>CH</sub> = 112 Hz). X-ray studies showed that **7** is a four-coordinate complex (*syn*-isomer) with distorted tetrahedral geometry (Figure 2). Four-coordinate V alkylidenes are rare.<sup>26–29</sup> To our knowledge, complex **7** is the first crystallographically characterized four-coordinate V alkylidene that contains oxo or alkoxy ligands. The relevant bond distances are V1–C1 = 1.853(10) Å, V1–C17 = 2.140(7) Å, V1–O1 = 1.588(5) Å, and V1–O2 = 1.845(5) Å. The V=C–Si angle is 130.5(5)°, and V1–O2–C is 145.9(5)°.



**Figure 2.** Perspective view of the crystal structure of complex **7** with thermal ellipsoids shown at 30% probability.

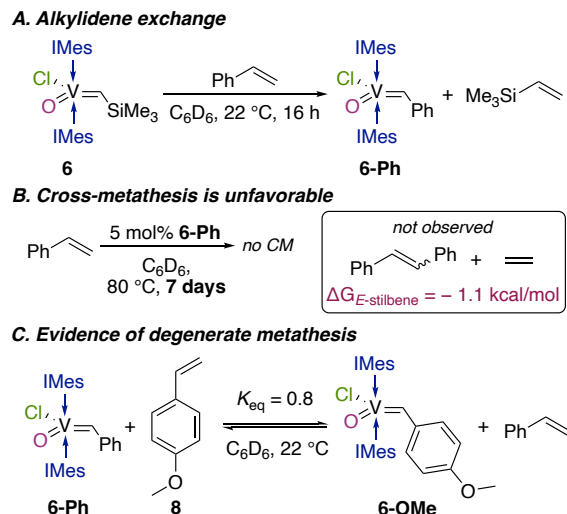
An important feature of an oxo ligand is the ability to coordinate Lewis acids. It has been shown that the coordination of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to W oxo alkylidene can improve the activity and selectivity of the OM catalysts.<sup>30</sup> However, adding B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to **6** in C<sub>6</sub>D<sub>6</sub> led to the rapid decomposition of **6**. The reaction between B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and **7** resulted in the formation of new alkylidene by <sup>1</sup>H NMR (singlet, 14.63 ppm, C<sub>6</sub>D<sub>6</sub>), presumably due to coordination of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to oxo ligand followed by slow degradation of 7•B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adduct.

Complex **7** does not react with **1**, 1,7-cyclooctadiene, 1-hexene, styrene, or ethylene at 22 °C. However, **7** slowly catalyze RCM reactions of **1** and 1,7-cyclooctadiene; and CM reaction of 1-hexene at 100 °C (1–4 TON after 3–4 days). Heating of **7** in the presence of ethylene led to slow decomposition of **7**. Corresponding methylidene and MCBs have not been observed by NMR. We believe bulky Mes(CF<sub>3</sub>)<sub>2</sub>CO alkoxy prevents the coordination of olefin to the metal center, suppressing the catalytic activity.

Complex **6** does not catalyze RCM of **1** or 1,7-cyclooctadiene and CM of 1-hexene or allylbenzene. However, **6** reacts with styrene to form V benzylidene complex **6-Ph** (Scheme 4A). The previously reported V imido alkylidene reacts with styrene to produce metallacyclopentane.<sup>31</sup> **6-Ph** does not catalyze RCM of **1** and CM of 1-hexene or styrene. Thus, heating of **6-Ph** in the presence of 20 equiv. of styrene at 80 °C for seven days does not lead to thermodynamically favorable *E*-stilbene (Scheme 4B). Noteworthy, **6-Ph** is relatively thermally stable in the solution. Thus, we observed ~50% decomposition of **6-Ph** at 80 °C after seven days.

The addition of 4-MeO-styrene to **6-Ph** results in an equilibrium between **6-Ph** and **6-OMe** (Scheme 4C),  $K_{eq}$  is 0.8 in  $C_6D_6$  at 22 °C. Noteworthy, benzylidene **6-OMe** can be formed directly from **6** and 4-MeO-styrene **8**. The addition of styrene to **6-OMe** leads to the same equilibrium between **6-Ph** and **6-OMe**. The presence of electron-donating groups in the phenyl ring destabilizes the negative charge on the  $\alpha$ -C atom, explaining the preference for **6-Ph**.

#### Scheme 4. Reactivity of complex **6**.



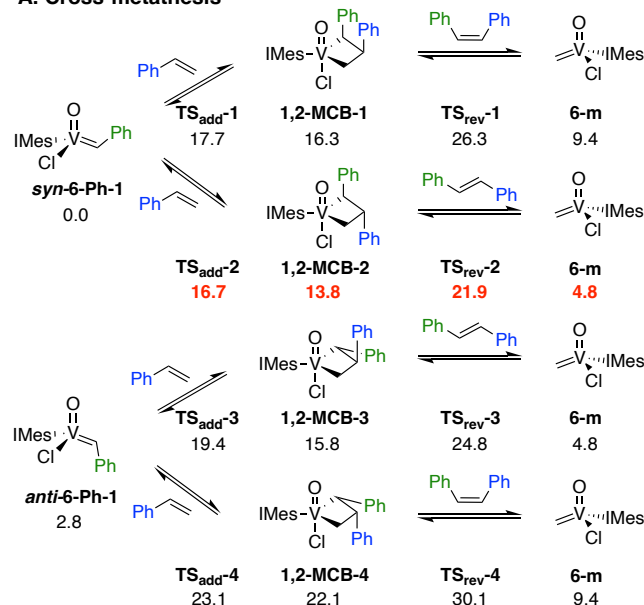
V oxo NHC complexes **6**, **6-Ph**, and **6-OMe** are readily involved in cycloaddition/cycloreversion steps with styrenes. However, the absence of CM products indicates that degenerate metathesis is remarkably favorable for V oxo NHC species.

We hypothesize that the formation of 1,3-MCB is significantly more favorable than 1,2-MCB for studied systems. To support our hypothesis, we performed DFT (B3LYP-D3)<sup>32-34</sup> studies on the cross (via 1,2-MCB) and degenerate (via 1,3-MCB) metathesis of styrene and propene. Dissociation of one neutral ligand in **6-Ph** is required to form an active four-coordinate complex **6-Ph-1** (Figure 3). Cycloaddition between **6-Ph-1** and styrene can lead to 8 possible pathways depending on the relative position of the substituents. Similarly, the reactivity of the four coordinated ethylidene **6-Me-1** with propene follows equivalent pathways (see SI). We computationally explored the 8 different pathways assuming the accepted OM reaction mechanism with  $d^0$  alkylidenes.<sup>35-36</sup> The productive MCB has a trigonal bipyramidal structure with apical oxo and chlorine ligands. We analyzed the accuracy of our computational methodology by reproducing the equilibrium constant between **6-Ph** and **6-OMe**. Calculations predict the thermodynamically favorable formation of **6-Ph** and **6-OMe** from **6** (see SI). Moreover, the reaction of **6-Ph** with **8** to form **6-OMe** is computed to be endergonic by 0.3 kcal mol<sup>-1</sup>. The computed equilibrium constant is thus 0.6, in excellent agreement with the experimentally determined value.

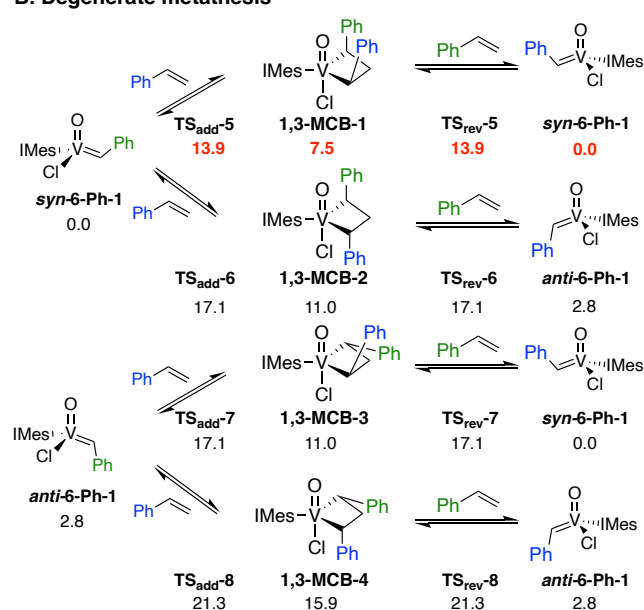
Figure 3 reports the Gibbs energies of the 8 pathways involved in the reaction of **6-Ph-1** with styrene (Figure S6 for **6-Me-1** with propene reaction). **Syn-6-Ph-1** + styrene is used as origin of energies. For the reaction of **6-Ph-1** with styrene, calculations show that the preferred CM pathway is 1,2-MCB-2 which implies **syn-6-Ph-1** and *trans*-stilbene as final product (Figure 3A). The preferred degenerate pathway implies the phenyls pointing toward the oxo ligand (1,3-MCB-1, Figure 3B). The transition state for cycloreversion determines in both

cases the feasibility of the two processes. This transition state is lower for the degenerate metathesis by 8.0 kcal mol<sup>-1</sup> and this corresponds to a 10<sup>-6</sup> ratio between the corresponding kinetic constants ( $k_{1,2}/k_{1,3}$ ). The reaction of **6-Me-1** with propene presents lower energy barriers in general. The most favorable CM pathways involve 1,2-MCB-1 and 1,2-MCB-2, but they are still 4.1 and 4.3 kcal mol<sup>-1</sup> higher in energy than the degenerate metathesis (10<sup>-3</sup>  $k_{1,2}/k_{1,3}$  ratio). For comparison, reported data on Ru NHC alkylidenes shows that 1,3-MCB is ~2 kcal/mol more favorable than 1,2-MCB.<sup>37</sup> We believe  $\alpha$ -C atoms in V MCBs have a higher negative charge than those in Ru MCBs due to the lower V electronegativity.<sup>38</sup> The higher polarization of the V=C bond favors that the substituted moiety of the reacting olefin interacts with the positively charged metal and, thus, overall 1,3-MCB.

#### A. Cross-metathesis



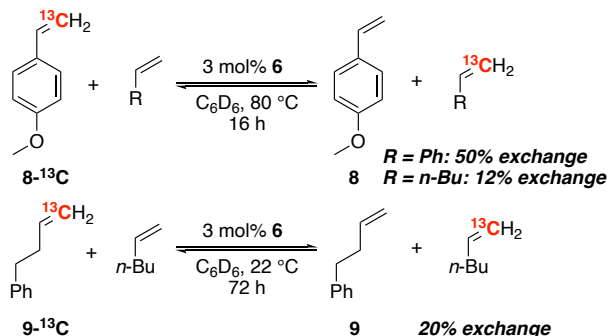
#### B. Degenerate metathesis



**Figure 3.** Calculated relative Gibbs free energies under benzene solvation (B3LYP-D3) in kcal/mol with respect to **syn-6-Ph-1**. Red values show the most favorable paths via 1,2- and 1,3- MCBs.

To further support the high preference for degenerate metathesis, we utilized  $^{13}\text{C}$ -labeled 4-MeO-styrene **8- $^{13}\text{C}$**  for carbon isotope exchange (CIE)<sup>39</sup> with styrene in the presence of 3 mol% of **6** (Scheme 5). CIE is slow at room temperature. Heating the reaction mixture at 80 °C for 16 hours led to 50% isotope exchange as expected at equilibrium conditions (assuming no isotope effect).

#### Scheme 5. Carbon isotope exchange (CIE) catalyzed by **6**.



CIE involving alkyl olefins is less efficient. Thus, the reaction between **8- $^{13}\text{C}$**  and 1-hexene led to 12% exchange after 16 hours at 80 °C. Noteworthy, we observed only the formation of benzylidene from 4-MeO-styrene during the reaction by  $^1\text{H}$  NMR. It can be explained by the higher stabilization of a negative charge at  $\alpha$ -C atom by the aryl group in benzylidene than by the alkyl group in butylidene (alkylidene derived from 1-hexene). To overcome the bias in forming alkylidenes we performed CIE between  $^{13}\text{C}$ -labeled 4-phenyl-1-butene **9- $^{13}\text{C}$**  and 1-hexene. However, the corresponding alkylidenes are not thermally stable. As a result, the reaction at elevated temperatures led to the catalyst's decomposition. CIE at room temperature resulted in 20% exchange after 72 hours. CM products were not observed in all cases, confirming the preference for 1,3-MCBs for substrates containing alkyl groups.

We have shown that V oxo NHC chloride complex **6** can be prepared from the corresponding phosphine complex by ligand exchange reaction. The following salt metathesis leads to the V oxo NHC alkoxide **7**. However, the bulky alkoxide ligand precludes the activity in olefin metathesis. Complex **6** is readily involved in cycloaddition/cycloreversion steps with terminal olefins. Unlike previously studied V oxo phosphine complex and V imido NHC and phosphine complexes, the V oxo NHC chloride complex strongly prefers the formation of 1,3-MCB for a reason not yet understood. This unusual reactivity can be applied to carbon isotope exchange reactions via degenerate metathesis.

## 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 **6** and **7**, and computational details (PDF).

X-ray crystallographic files of **6** and **7** (CIF).

Cartesian Coordinates of the DFT structures (xyz).

### Accession Codes

CCDC 2203752 (**6**) and CCDC 2203751 (**7**) 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](mailto:deposit@ccdc.cam.ac.uk).

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### Notes

The authors declare no competing financial interests.

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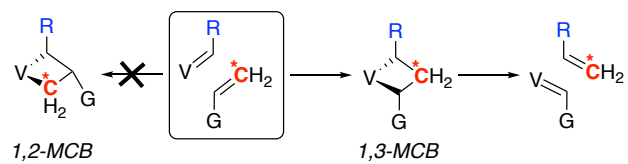
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