Synthesis of Vanadium Oxo Alkylidene Complex and its Reactivity in Ring-Closing Olefin Metathesis Reactions

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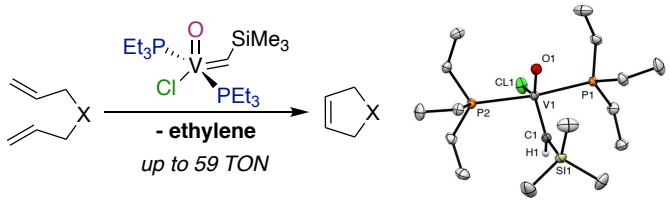
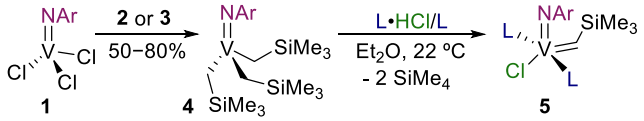


ABSTRACT: V imido alkylidenes have been applied for the ring-opening metathesis polymerization involving cyclic olefins. However, those complexes found limited application in reactions with acyclic terminal olefins due to instability toward ethylene. Experimental and theoretical studies show that the *β*-hydride elimination from unsubstituted metallacyclobutene is the primary decomposition pathway in those systems. Herein, we report the synthesis of the first catalytically active V oxo alkylidene, $VO(CHSiMe_3)(PEt_3)_2Cl$, that exhibits the highest reported productivity with various terminal olefins in ring-closing metathesis reactions among known V catalysts. Presented DFT studies indicate that *β*-hydride elimination is significantly disfavored for V oxo species.

Since its discovery, the olefin metathesis (OM) reaction has found numerous applications in total synthesis,[1] industrial processes,[2] pharmaceutical,[3] and material chemistry.[4] Ru, Mo, and W-based homogeneous catalysts are the most prominent due to their high activity and functional group stability.[5-7] However, the transition to more abundant first-row metals is desirable due to the low cost, decreased environmental footprint, and reduced toxicity. In addition, first-row metal alkylidenes can offer a unique reactivity, such as C-H bond activation,[8, 9] which has the potential to be coupled with OM. Although first-row metal alkylidenes can perform the critical steps of OM (cycloaddition and cycloreversion), catalytic systems based on those metals remain underdeveloped.[10, 11]

V alkylidenes are a promising class of compounds that have shown reactivity in OM,[12] especially in ring-opening metathesis polymerization (ROMP) of cyclic olefins.[13, 14] Recently, our group reported a method of promoting α-hydrogen abstraction from V trialkyl complexes **4** by using phosphonium hydrochlorides to obtain complexes **5a-e** in good yields (Scheme 1).[15] Complexes **5a-e** are active catalysts in OM and can tolerate various functional groups. Furthermore, it was the first report of V-based catalysts capable of performing ring-closing metathesis (RCM) reactions, besides proposed backbiting reaction during ROMP of cyclopentene,[16] which resembles some elements of RCM. However, the described complexes have limited stability toward ethylene that precluded a high turnover number (TON) in reactions with terminal olefins, where ethylene is a byproduct. Two major pathways are known for catalyst deactivation: *β*-hydride (*β*-H) elimination of metallacyclobutane (MCB) and bimolecular decomposition of metal methylidene.[17] It has been shown that the main decomposition pathway of V-based catalysts is *β*-H elimination.[15, 18, 19] Noteworthy, the structure of V catalysts resembles the structure of Mo and W Schrock complexes. Thus, they are d^0, high oxidation state complexes with the second multiply bound ligand (imido) in addition to the alkylidene.

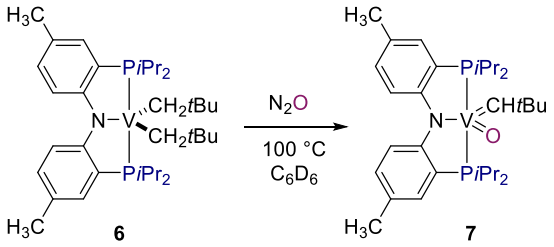


Scheme 1. Syntheses of V imido chloride alkylidenes.[14]

Mo and W oxo species are at the heart of many large-scale processes involving OM;[2] although the precise structure of the active species often remains elusive. In contrast, well-defined W oxo alkylidenes, known for four decades,[20] had limited application in homogenous catalysis due to the higher susceptibility toward bimolecular decomposition than imido complexes. One strategy to preclude bimolecular decomposition is to generate isolated active sites by grafting on a silica surface.[21] Using this approach, direct comparison between well-defined oxo and imido W complexes was achieved[22, 23] and the data suggest that the oxo complexes outperform imido counterparts when bimolecular decomposition is avoided. DFT calculations further supports

experimental results. Thus it has been shown that oxo Mo and W MCBs are significantly less prone to β-H elimination compared to imido complexes due to electronic reasons.[24] Those studies sparked a new interest in Mo[25] and W[26] oxo alkylidene chemistry and led to new highly efficient and selective homogenous well-defined catalysts.

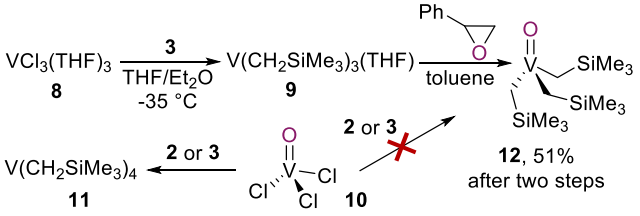
The synthesis and evaluation of V oxo alkylidenes is a logical next step in developing reliable V-based OM. However, there is only one example of a V oxo alkylidene (complex **7**, reported by the Mindiola group)[8, 27, 28] and it does not show OM activity. In **7**, the V oxo alkylidene moiety is stabilized by a pincer ligand (Scheme 2). During the catalytic cycle, active intermediates adopt different geometries. Rigid chelating ligands usually do not allow these conformational changes and are often associated with low catalytic activity.[29, 30]



Scheme 2. Reported V oxo alkylidene.

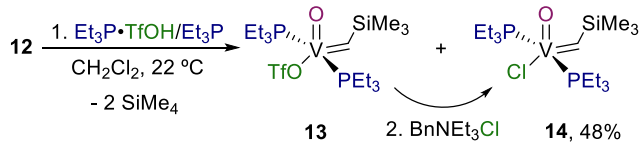
Here we report the first catalytically active V oxo alkylidene, its reactivity toward terminal dienes, and functional group tolerance. Furthermore, we provide DFT studies of the activation, productive metathesis, decomposition pathways, and comparison with the V imido counterparts.

The synthesis of V oxo alkylidene from the corresponding trialkyloxovanadium complex seems straightforward in analogy to V imido complexes. However, complex **12** (Scheme 3) is not readily available. Unlike the reaction of **1** with **2** or **3** (Scheme 1), direct alkylation of **10** leads to the reduction and formation of V(IV) complex **11**.[31, 32] The reported procedures for the synthesis of **12** did not reproduce well in our hands.[32-34] Eventually, we adapted a procedure reported for the preparation of (t-BuCH$_2$)$_3$VO.[35] Alkylation of **8** with **3** produced **9**, which was used for the next step immediately due to the limited stability.[36] The latter can be oxidized by several reagents, and styrene oxide was found to give the highest yield of **12**.



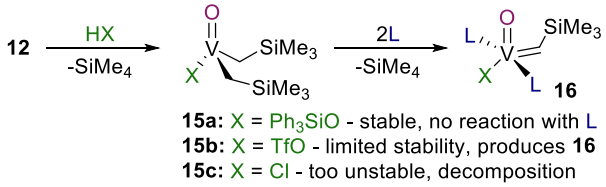
Scheme 3. Synthesis of V oxo trialkyl complex **12**.

With the complex **12** in hand, we tried our previously optimized conditions to prepare V alkylidenes.[15] Unfortunately, this mostly led to the decomposition of staring material into unidentified paramagnetic compounds. However, we observed a small amount of desired alkylidene complex by ^{1}H NMR (the presence of V=C<u>H</u> signal, 16.07 ppm, C_6D_6). After considerable optimization, which included searching for appropriate phosphine and anionic ligands, solvent, and a proton source, we found optimal reaction conditions. Treatment of **12** with PEt$_3$•TfOH in the presence of five equivalents of PEt$_3$ in CH_2Cl_2 resulted in two V alkylidenes **13** and **14** observed by ^{1}H NMR (Scheme 4). Initially, we proposed that a mixture of *syn* and *anti*-alkylidenes were formed. However, the ratio of two products varied from one experiment to another. Finally, we were able to crystallize one of them (**14**) and perform X-ray studies.[37] Surprisingly, the isolated complex contained chloride ligand instead of triflate (Figure 1). Complex **13** can be quickly converted to **14** by adding a Cl$^-$ source, such as BnNEt$_3$Cl. Formation of complex **14** can be explained by slow release of Cl$^-$ by the reaction of CH_2Cl_2 and PEt$_3$.[38] When the reaction was attempted in the presence of BnNEt$_3$Cl, it resulted in decomposition than the formation of alkylidene.



Scheme 4. Synthesis of oxo alkylidene complexes**.**

The proposed mechanism of the formation of V oxo alkylidenes includes protonation of one of three alkyl groups with acid (HX) to form **15** (Scheme 5). The second critical step of the alkylidene formation is the α-hydrogen abstraction induced by the coordination of the L-type ligand. The nature of the X group plays a crucial role in alkylidene formation. Some imido V complexes (Ar'O-V(NAr)(CH$_2$TMS)$_2$) are isolable and can be converted to alkylidenes upon the addition of PMe$_3$.[39] In contrast, isolable Ph$_3$SiO-VO(CH$_2$TMS)$_2$ (**15a**) complex[33] does not react with neutral ligands to form V oxo alkylidene.[40] **15b** has limited stability in solution. Still, it can react with neutral ligands to form alkylidenes **16**. In the case of **15c**, the rate of decomposition is higher than alkylidene formation.



Scheme 5. Proposed mechanism of alkylidene formation.

Complex **14** is a mixture of *syn* and *anti*-alkylidenes in the ratio 97:3 in the solution by ^{1}H NMR (C_6D_6). An X-ray structural study showed that *syn*-**14** (Figure 1) has a distorted trigonal bipyramidal geometry with phosphines in axial positions [V–P1 2.4884(8) Å, V–P2 2.4701(8) Å, P1–V–P2 164.89(2)°]. The V1–C1 distance is 1.8403(19) Å and V1–O1 bond is 1.6079(15) Å, that are similar to reported V oxo alkylidene.[27] The large V=C–Si angle (140.01(12)°) is indicative of α-hydrogen agostic interactions with V center.[15]

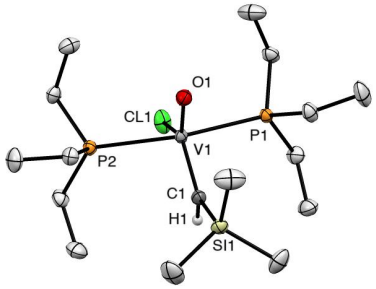


Figure 1. Molecular structure of *syn*-**14**. The thermal ellipsoids are shown at 50% probability level.

We explored the metathesis activity of **14** with diallyl *N*-tosylamide **17** and compared its reactivity with V imido complex **5b** (**entry 1 and 2,** Table 1). Catalyst **14** outperforms **5b** in reaction with **17.** Notably, conversion to **18** is higher in an open vial in both cases (see table S3), suggesting that the active species are sensitive to ethylene.[41, 42]

Table 1. RCM catalyzed by **14** and **5b**.

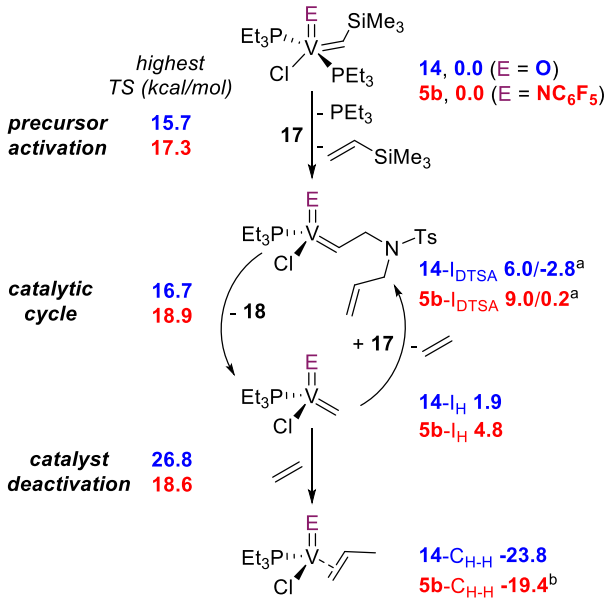
17, Ts = *p*-$CH_3C_6H_4SO_2$ **18** **ethylene**

#	cat.	solvent	cat, mol%	conv., %[a]	TON
1	**5b**	benzene	5	63 (42)[b]	12.6
2	**14**	benzene	5	87 (67)[b]	17.4
3	**14**	chloroform	1	59 (56)[b]	59.0
4	**14**	chloroform	2	83 (66)[b]	41.5
5	**14**	chloroform	3	91 (69)[b]	30.3
6	**14**	chloroform	4	94 (73)[b]	23.5
7	**14**	chloroform	5	96 (76)[b]	19.2
8	**14**	chloroform	6	97 (76)[b]	16.2

[a] by ^{1}H NMR. [b] closed vial. The catalytic experiments were carried out in a glovebox.

To investigate the mechanism of catalyst deactivation, we conducted a reaction of **14** with ethylene. Initially, we observed the formation of a small amount of new alkylidene signal (m, 13.8 ppm, C_6D_6, presumably V methylidene) and vinyl-TMS. After several hours at room temperature, we observed the complete decomposition of alkylidenes. The reaction of **14** with ethylene produces only traces of propylene by ^{1}H NMR, which is in contrast to the analogous reaction of **5b**, where propylene is the primary decomposition product.[15] To examine the contribution of bimolecular decomposition in the deactivation of the catalysts, we tested the reaction of **14** with **17** at different catalysts loadings (entries 3-8, Table 1). Important to mention, we performed reactions in chloroform since it gives the highest conversion among tested solvents (see table S1). The decrease of the catalyst loading led to an increase of TON, suggesting that bimolecular decomposition plays a role in the catalyst deactivation. Noteworthy, the TON of 59 is the highest reported TON for V-based OM involving terminal olefins.[15, 18, 19]

To explain the difference in stability of **14** and **5b** toward ethylene, we performed DFT calculations on the full catalytic cycle, which includes precursor activation, productive RCM cycle, and mononuclear catalyst deactivation (See SI for structures and detailed energetics). Scheme 6 summarizes the Gibbs energies of key intermediates relative to *syn*-**14** (blue) and *syn*-**5b (red) and** the highest transition states of each part of the global process (see SI for complete processes). Computed Gibbs energy barriers for the precursor activation and RCM catalytic cycle with *syn*-**5b** and *syn*-**14** are consistently low (below 19 kcal mol^{-1}). The difference between the energy span of *syn*-**14** and that of *syn*-**5b** is only 2.2 kcal mol^{-1} (16.7 vs. 18.9 kcal mol^{-1}). Therefore, calculations suggest that RCM occurs readily at reaction conditions, and the two precursors behave similarly in the absence of catalyst deactivation. Mononuclear catalyst deactivation occurs through β-H elimination from MCB. This step has the highest energy barrier similar to other d^0 complexes.[43] The β-H elimination transition state is 26.8 and 18.6 kcal mol^{-1} above initial reactants for **14** and **5b**, which agrees with the experimentally observed larger stability toward ethylene of the V oxo complex. The β-H elimination imposes the allyl fragment almost trans to the oxo or imido ligand (Figure 2), and this causes a strong trans influence between the two groups. Since the oxo acts as a stronger σ-donating ligand than the imido,[24] the destabilization of the β-H transition state is more significant for **14**, hindering its deactivation. The computed energy barriers are consistent with the deactivation taking place in a few hours for **5b** and a longer time for **14**, suggesting that other deactivation processes, such as bimolecular decomposition, are important for **14**.



Scheme 6. Gibbs energies (kcal mol^{-1}) of the key intermediates and the highest transition states relative to *syn*-**14** (blue) and *syn*-**5b** (red). [a] the difference between the two values is the RCM Gibbs reaction energy. [b] triplet ground state.

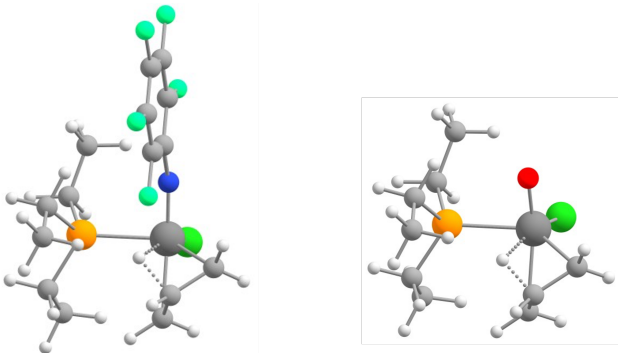
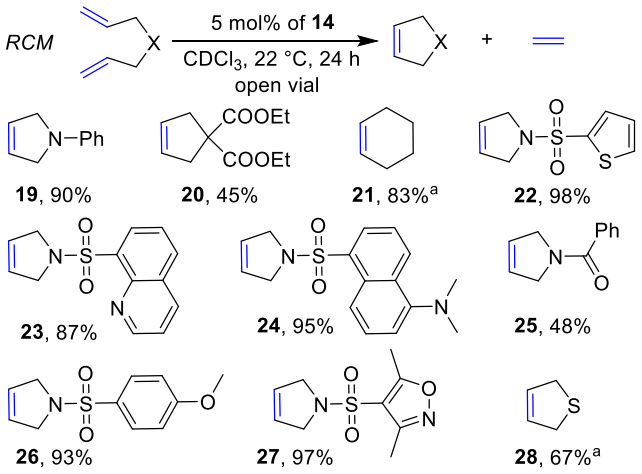


Figure 2. Optimized structures (left: V imido; right: V oxo) for the β-H elimination transition states.

Noteworthy, we found a difference in reactivity between **14** and **5b**. Thus, cycloaddition reaction between V imido alkylidenes and olefin occurs trans to the strongest σ-donating ancillary ligand (PEt_3) to form a trigonal bipyramidal (TBP) MCB intermediate similar to other d^0 OM catalysts.[24, 43-45] TBP isomer can undergo cycloreversion step (productive OM) or rearrange to square pyramidal (SP) MCB, which is off-cycle intermediate.[46] Mononuclear d^0 catalyst deactivation implies a β-H elimination trans to the weakest σ-donating ligand (Cl,

Figure 2) from the SP isomer.[47] The geometry optimizations for V oxo MCB evolved to a distorted TBP, where oxo is not strictly in axial position. Consequently, one single MCB cannot be involved in the cycloaddition/cycloreversion steps, and MCB rearrangement is necessary (see SI for details). However, the MCB interconversion implies low energy barriers that have a small impact on the process.

We explored the scope of RCM, and the results are summarized in Scheme 7.



Scheme 7. Scope of RCM catalyzed by **14**. [a] closed vial.

Products containing tertiary aniline (**19**, **24**), thiophene (**22**), quinoline (**23**), ether (**26**), and isoxazole (**27**) can be synthesized by using **14** with high conversions. Substrates bearing an ester (**20**), a tertiary amide (**25**), and a thioether (**28**) exhibit lower conversions, probably due to competing binding to the catalyst.

CONCLUSIONS

We have shown that V oxo alkylidene **14**, the active catalysts for olefin metathesis, can be prepared directly from $VO(CH_2SiMe_3)_3$ complex. Furthermore, experimental and computational studies strongly suggest that the β-H elimination from metallacyclobutane is significantly disfavored for V oxo species compared to V imido counterparts. As a result, catalyst **14** exhibits the highest reported productivity among known V alkylidenes in ring-closing metathesis of various terminal dienes due to the greater tolerance to ethylene. The bimolecular decomposition is the primary deactivation pathway for **14**, the challenge that is currently addressed in our group to develop reliable V-based olefin metathesis catalysts.

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 *syn*-**14**, computational details, and complete energy profiles (PDF).
X-ray crystallographic files of *syn*-**14** (CIF).
Cartesian Coordinates of the DFT structures (xyz).

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Notes

The authors declare no competing financial interests.

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