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Homogeneous Catalysis

Ring-Closing Olefin Metathesis Catalyzed by Well-Defined Vanadium Alkylidene Complexes

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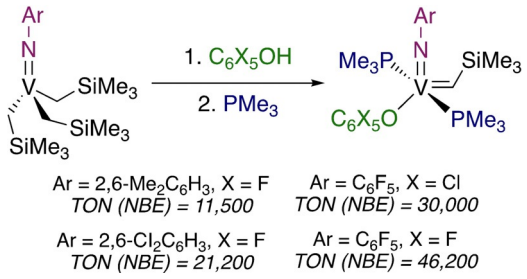
Abstract: Vanadium-based catalysts have shown activity and selectivity in ring-opening metathesis polymerization of strained cyclic olefins comparable to those of Ru, Mo, and W catalysts. However, the application of V alkylidenes in routine organic synthesis is limited. Here, we present the first example of ring-closing olefin metathesis catalyzed by well-defined V chloride alkylidene phosphine complexes. The developed catalysts exhibit tolerance to various functional groups, such as an ether, an ester, a tertiary amide, a tertiary amine, and a sulfonamide. The size and electron-donating properties of the imido group and the phosphine play a crucial role in the stability of active intermediates. Reactions with ethylene and olefins suggest that both β-hydride elimination of the metallacyclobutene and bimolecular decomposition are responsible for catalyst degradation.

Ring-closing metathesis (RCM) of dienes[1] is a widely applied method for the synthesis of natural products and biologically active compounds.[2] Nowadays, commonly used homogeneous catalysts for RCM are based on well-defined Ru,[3] Mo and W[4] alkylidenes; some of them exhibit remarkably high activity[5] and enantioselectivity.[6] Examples of RCM catalyzed by other well-defined transition metal complexes are rather limited. Thus, to the best of our knowledge, only two Os complexes capable of performing RCM were reported.[7] However, Os is among the rarest elements in the Earth's crust,[8] which narrows its use in catalysis. Although ill-defined complexes of Nb,[9] and Re[10] have been shown to promote RCM, the nature of the active species remains unknown. Tebbe's reagent, $Cp_2TiCH_2AlClMe_2$ can promote RCM,[11] but reaction requires stoichiometric amounts of the Ti complex.

In the last decade, high-oxidation-state vanadium alkylidene complexes of the type V(NR)($CHSiMe_3$)(X)(L), where R is an aryl[12–18] or 1-adamantyl group;[13,15,16,19] X is an amide,[12,15] alkyl,[13] or alkoxide;[14,16–19] and L is an NHC[13] or PMe_3[14–19] have been extensively explored by the Nomura group for the ring-opening metathesis polymerization (ROMP) of various cyclic alkenes.[20] The critical step of the alkylidene formation, the α-hydrogen abstraction in the presence of PMe_3, is shown in Scheme 1 along with examples of highly active V complexes for ROMP of norbornene (NBE).[16,17] Although those complexes contain two PMe_3 ligands, the dissociation of one of the phosphine ligands is required to access the 14-electron catalytically active species,[16] as is the case for Ru-[21] and Mo-based[22] catalysts. Important to mention, other phosphines have not been applied for V alkylidene synthesis.[20]



Scheme 1. Synthesis of V alkylidenes developed by Nomura. Bottom: turnover numbers (TON) for reaction with NBE are indicated.

Despite the successful application of V complexes for ROMP, examples of V-catalyzed olefin metathesis of acyclic olefins are surprisingly limited. Although a few examples of cross-metathesis (CM) have been reported recently utilizing Nomura's catalysts,[23,24] rapid V alkylidene decomposition precluded complete conversion.

The use of abundant first-row metals, such as vanadium, to make well-defined catalysts for RCM of olefins is highly desirable to provide less expensive and greener alternatives for existing methods. V is the 20th most abundant element in the Earth's crust. The abundance of V is $\approx 10^2$ times higher compared to Mo and W and $\approx 10^5$ times higher than for Ru.[25] As a result, it is substantially less expensive than the rare metals that are currently used. Additionally, purification, isolation, and recycling of precious metals consume energy and generate a significant amount of waste. Therefore, the use of V-based catalysts will make valuable olefins more accessible to consumers and decrease the human environmental footprint.

Recently, the Schrock group reported a method of promoting α-hydrogen abstraction from Mo dialkyl complexes by

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using phosphonium chlorides to obtain Mo chloride alkylidene phosphine complexes in good yields.[22,26] The resulting complexes are versatile starting material for the synthesis of highly active and *E/Z* selective catalysts.[27] Inspired by this work, we have now prepared several V chloride alkylidene phosphine complexes, a new class of compounds, and examined them in RCM reactions. To our knowledge, we report the first examples of RCM catalyzed by well-defined V alkylidene complexes.

Compounds **1 a**–**e** (Scheme 2) were each synthesized in one pot, starting from imido trialkyl V complexes in the presence of HCl and phosphines in Et_2O.

1a, 78%, *Ar = C_6F_5*; PR_3 = PMe_3; *syn:anti 9:1*
1b, 90%, *Ar = C_6F_5*; PR_3 = PEt_3; *syn:anti 5:1*
1c, 51%, *Ar = 2,6-$(Me)_2C_6H_3$*; PR_3 = PMe_3; *syn:anti 1:3*
1d, 49%, *Ar = 2,6-$(i\text{-}Pr)_2C_6H_3$*; PR_3 = PMe_3; *syn:anti 1:2*
1e, 44%, *Ar = 2,6-$(i\text{-}Pr)_2C_6H_3$*; PR_3 = $PPhMe_2$; *syn:anti 2:3*

Scheme 2. Prepared V chloride alkylidenes with isolated yields. *Syn:anti* ratio determined in solution by ^{1}H NMR at 22 °C (C_6D_6).

An X-ray diffraction study of **1 e** (Figure 1) revealed a mixture of two isomers: *anti*-**1 e** (≈91 %) and *syn*-**1 e** (≈9 %).[28] *anti*-**1 e** has a distorted trigonal bipyramidal geometry with phosphines in axial positions [V–P1 2.4708(4) Å, V–P2 2.4935(4) Å, P1-V-P2 170.12(2)°], similar to the structure reported for *anti*-V(*N*-2,6-(*i*Pr)$_2$C$_6$H$_3$)(CHSiMe$_3$)(OC$_6$F$_5$)(PMe$_3$)$_2$ (*anti*-**A**) [V–P1 2.472 Å, V–P2 2.480 Å, P1-V-P2 168.92°].[24] The V–N and V–C bond lengths and Si-C-V angles in *anti*-**1 e** (1.6873(14) Å, 1.9153(14) Å, 131.64(7)°) and *anti*-**A** (1.691 Å, 1.917 Å, 132.5°) are also similar. Notably, the differences in V–C bond distances and Si-C-V angles between *anti*-**1 e** (1.9153(14) Å, 131.64(7)°) and the reported *syn*-V(*N*-2,6-Me$_2$C$_6$H$_3$)(CHSiMe$_3$)(OC$_6$Cl$_5$)(PMe$_3$)$_2$[18] (1.845(3) Å, 167.53°) are more pronounced due to the agostic interaction (electron donation from C–H to V) in the *syn*-isomer, which gives the *V*=C bond partial triple-bond character; this has also been observed for Mo alkylidenes.[29]

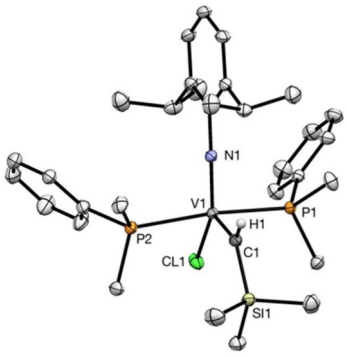


Figure 1. X-ray crystal structure of *anti*-**1 e**. Thermal ellipsoids shown at 50 % probability. Hydrogen atoms, except alkylidene hydrogen H1, have been omitted for clarity.

X-ray crystal structures of *anti*-**1 c** and *anti*-**1 d** were also obtained (see Supporting Information), though poor diffraction and complex disorder in the structures preclude detailed discussion of the respective bond lengths and angles.

The NMR studies of **1 d** further support the presence of an agostic interaction in the *syn*-isomer. The resonance of the alkylidene hydrogen H$_\alpha$ of the *anti*-isomer appears downfield of the *syn* H$_\alpha$ resonance (Figure 2), as it does in analogous Mo complexes.[30] The *anti* H$_\alpha$ signal gives a sharp triplet at 16.01 ppm ($^3J_{HP}$ = 8.0 Hz, $^1J_{CH}$ = 124 Hz, 22 °C), suggesting strong binding of the two PMe$_3$ ligands. Although the observed $^1J_{CH}$ is relatively small compared to the CH-coupling of a typical *anti*-alkylidene (for Mo and W),[31] the NOESY spectrum revealed the cross peaks between the alkylidene and imido methine protons, with no correlation between the methine and TMS-group protons. In contrast, the *syn*-alkylidene (H$_\alpha$ at 13.48 ppm, $^3J_{HP}$ = 4.0 Hz at −40 °C) shows no correlation between the alkylidene and methine protons but does exhibit cross peaks between the methine and TMS-group protons. The agostic interaction makes the *syn*-isomer less Lewis acidic than the *anti*-isomer, which leads to broadening of the *syn* H$_\alpha$ signal since the PMe$_3$ ligand is exchanging relatively rapidly with free PMe$_3$ at room temperature.[29] The *syn*-isomer is 5-coordinate; thus, the addition of five equivalents of free phosphine does not change the *syn:anti* ratio, which one might expect if there

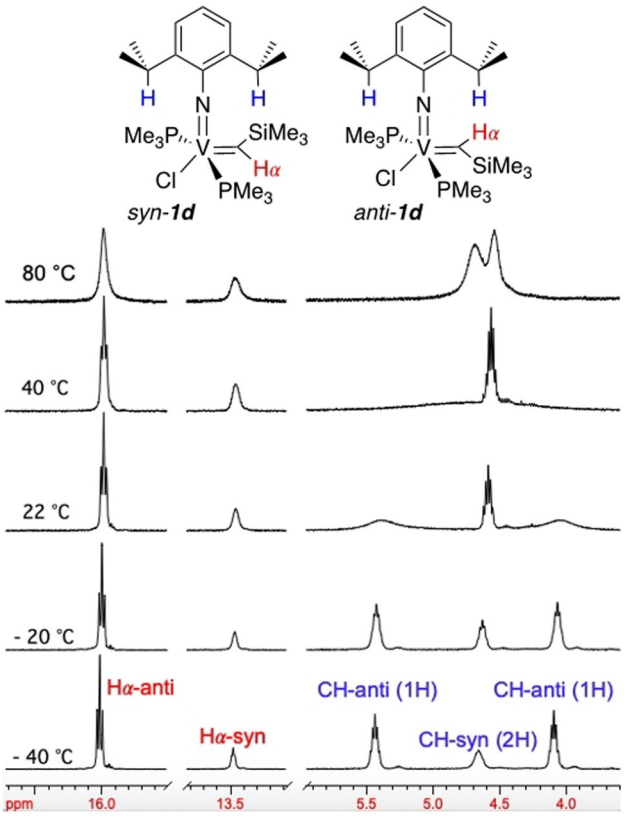


Figure 2. ^{1}H NMR spectra of the alkylidene (H$_\alpha$) and imido methine (H) regions of **1 d** at variable temperature (in [D$_8$]toluene).

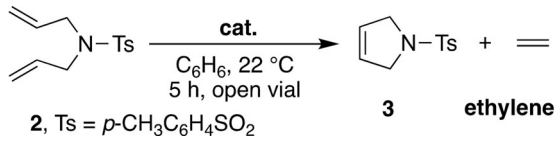
was an equilibrium between a 5-coordinate *anti*-isomer and a 4-coordinate *syn*-isomer.

The imido methine resonances of the *anti*-isomer appear as two broad signals at 22 °C and two sharp septets at −40 °C (Figure 2), suggesting that rotation of the arylimido group is restricted at reduced temperatures. The inequivalent methine resonances coalesce when coordinated PMe_3 begins to exchange rapidly with free PMe_3 at 80 °C, which results in broadening of the *anti*-alkylidene proton. In contrast, both methine protons in the *syn*-isomer appear as one sharp septet at 22 °C, which broadens at −40 °C. We conclude that rotation of the arylimido group occurs in a four-coordinate complex,[32] which is more accessible for the less Lewis acidic *syn*-isomer due to the agostic interaction mentioned above.

The catalyst **1 d** is relatively stable in the solution. Thus, we observed only 35% decomposition of **1 d** (0.023 M, C_6D_6) at 55 °C after 11 days, showing that **1 d** is more thermally stable compared to $Ru(CHPh)(PCy_3)_2(Cl)_2$ (50% decomposition after 8 days under the same conditions).[33]

The metathesis activity of complexes **1 a**–**e** in the RCM reaction with diallyl *N*-tosylamide **2** is summarized in Table 1.

Table 1. RCM of **2** catalyzed by **1 a**–**e**.



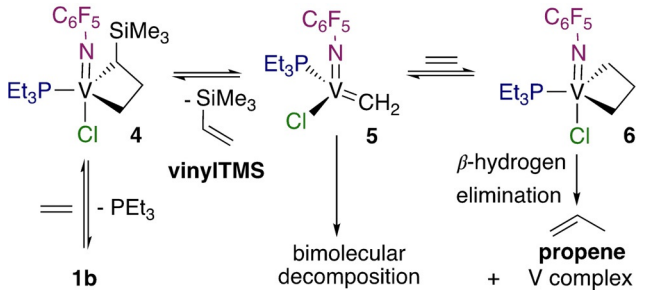
Entry	Cat.	Cat., mol%	Conv., %[a]	TON
1	**1 a**	5	10 (8)[b]	2.0
2	**1 b**	5	63 (42)[b]	12.6
3	**1 c**	5	32 (29)[b]	6.4
4	**1 d**	5	40 (22)[b]	8.0
5	**1 e**	5	59 (54)[b]	11.8
6	**1 e**	**5**	**95**[c]	**19**
7	**1 d**	1	9	9.0
8	**1 d**	10	72	7.2
9	**1 d**	15	80	5.3

[a] by ^{1}H NMR. [b] closed vial. [c] slow addition of **1 e**, 1.7 h.

Vanadium chloride alkylidene phosphine complexes are active catalysts in the RCM reaction of **2**. Variations in the imido group have a significant effect on catalytic activity. Thus, an increase in imido group size and electron-donating properties in the order **1 a**-**1 c**-**1 d** leads to a corresponding increase in the turnover number (TON, entries 1, 3, and 4, Table 1). An increase in phosphine size has an even more pronounced effect on the catalytic activity, as **1 b** and **1 e** are the most active of the five synthesized catalysts (entries 2 and 5, Table 1).

Following the catalytic reactions by ^{1}H NMR (entry 9, Table 1), we observed the formation of a new alkylidene species (see Supporting Information). Both *syn*- and *anti*-alkylidene signals of **1 d** and the new alkylidene slowly disappeared over a few hours, suggesting decomposition of the active species. Catalytic reactions were conducted in open vials to allow escape of ethylene gas from the reaction mixture.[34] Reactions in closed vials exhibited a lower conversion of **2** to **3** in all cases (entries 1–5, Table 1), confirming the catalyst's limited stability in the presence of ethylene. The slow addition of a stock solution of **1 e** to **2** over a period of 1.7 hours in an open vial allowed ethylene to escape from the reaction mixture. As a result, a 95% conversion to **3** was achieved (entry 6, Table 1).

The reaction of **2 b** with ethylene gas revealed slow decomposition of the alkylidene with formation of free phosphine, vinylTMS, propene, and a new paramagnetic complex (Scheme 3). The formation of propene can be explained by β-hydride elimination of the metallacyclobutane **6**.[35]

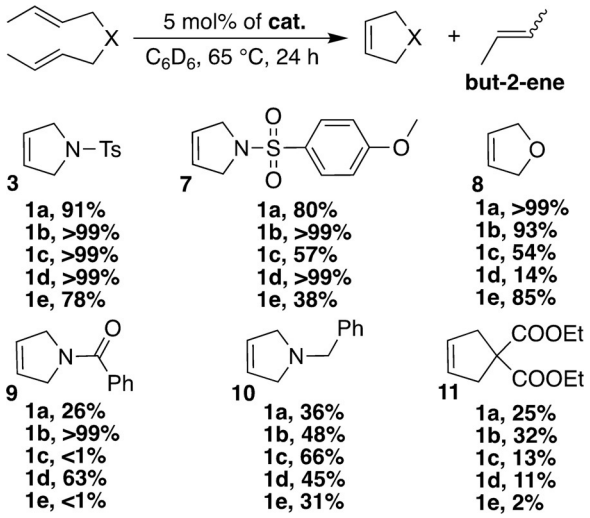


Scheme 3. The reaction of **1 b** with ethylene.

Notably, the stability of the active species depends on the catalyst concentration; thus, TON for **1 d** increases with lower catalyst loading (entries 4, 7–9, Table 1), suggesting that a bimolecular decomposition should be considered as a catalyst degradation pathway. The methylidene **5** (Scheme 2) is arguably the least sterically hindered complex and thus the most prone to bimolecular decomposition.[36] However, a 15-fold increase of the catalyst concentration did not lead to a significant decrease of TON (9.0 vs. 5.3, entries 7 and 9, Table 1). We conclude that β-hydride elimination of metallacyclobutane **6**, and not bimolecular decomposition, is the primary degradation pathway for our system, as is observed for V alkoxide complexes.[23,24]

We have also explored the RCM activity of **1 a**–**e** toward substrates containing crotyl groups (Scheme 4). The second product of the reactions is but-2-ene (usually, with *E*:*Z* ratio ≈7:3), which does not lead to catalyst decomposition. Thus, compound **3** was obtained with high conversion in all cases. The reaction proceeds slowly at room temperature (42% conversion to **3** in 24 h with catalyst **1 d**).

Products containing a tosylate (**3**, **7**), an ether (**7**, **8**), a tertiary amide (**9**), a tertiary amine (**10**), or an ester (**11**) were also accessed. However, an alkene capable of chelating to the V center (**11**) reacted with low yield in all cases. The metathesis activity depends on both catalyst and substrate. In particular, **1 a** gives the highest conversion for **8** while **1 c** exceeds other catalysts in the reaction to produce **10**. Although **1 b** and **1 e** have a similar activity toward **2**; **1 b** outperforms **1 e** in the reactions containing disubstituted olefins, presumably due to the steric hindrance resulting from two isopropyl groups and a large phosphine in **1 e**. Thus, less sterically demanding **1 d** ex-



Scheme 4. Scope of RCM catalyzed by **1a**–**e**.

hibits higher conversion than **1e** in all cases shown in Scheme 3, except **8**. Generally, catalyst **1b** displays the highest (**3**, **7**, **9**, **11**) or similar activity (**8**, **10**) toward tested substrates. We conclude that increasing the electrophilicity of the imido group and the σ-donating properties and size of the neutral ligand is the strategy to develop reliable V-based catalysts for olefin metathesis.

We have shown that V arylimido chloride alkylidene complexes can be prepared in the reaction of arylimido V trialkyls and HCl in the presence of phosphines. Our approach allows for the synthesis of V chloride alkylidenes bearing NC_5F_6, *N*-2,6-$Me_2C_6H_3$, and *N*-2,6-(*i*Pr)$_2C_6H_3$; and PMe_3, PEt_3, and $PPhMe_2$. All prepared complexes are a mixture of *syn*- and *anti*-isomers in solution. NMR studies show that *syn*-isomers do not strongly bind phosphines, presumably due to an agostic interaction between H-alkylidene and V; this may result in the difference of initiation, selectivity, and catalytic activity of two isomers.[32,37] The catalytic activity in RCM reactions strongly depends on the size and electron-donating properties of the imido group, as well as the size and σ-donating properties of the phosphine. The active intermediates have limited stability toward ethylene. Although bimolecular decomposition contributes to catalyst degradation, the primary decomposition pathway involves β-hydride elimination of the metallacyclobutane. We are now confident that V-based olefin metathesis catalysts for routine organic synthesis can be prepared. We are looking forward to exploring V chloride alkylidenes as versatile starting materials to alternate anionic and neutral ligands around a metal center to develop catalysts that are stable to ethylene and tolerant of various functional groups and to examining their reactions with olefins in detail.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: homogeneous catalysis · metathesis · ring-closing · vanadium · α-hydrogen abstraction

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