

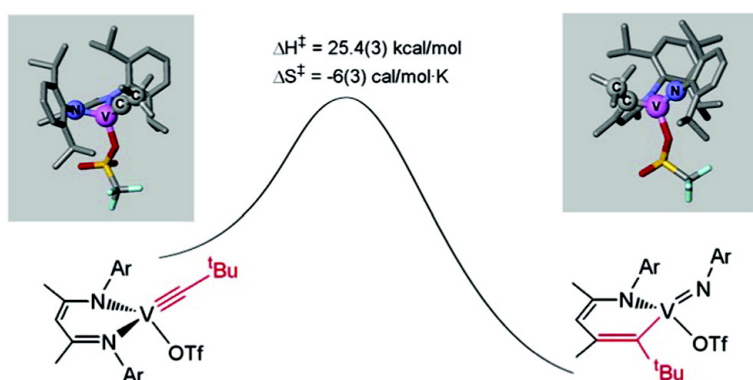
Communication

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Terminal Vanadium–Neopentylidyne Complexes and Intramolecular Cross-Metathesis Reactions to Generate Azametalacyclohexatrienes

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High-oxidation state complexes containing alkyldiyne functionalities continue to attract much attention due to their involvement in important reactions such as alkyne metathesis and CR group-transfer.¹ Prototypical among the immense family of group 5 and 6 early-transition metal alkyldynes is Schrock's (^tBuO)₃W≡C-^tBu,² an active alkyne metathesis catalyst that is prepared by two routes. One of these routes involves two consecutive α -hydrogen abstraction reactions,^{1b,2a} while the other is the direct rupture of nitriles/alkynes with Chisholm's (^tBuO)₃W≡W(O^tBu)₃.^{1a,2b,c,3} Although d⁰ early-transition metal complexes with the terminal alkyldiyne functionality are well-known, the vast majority of these systems contain second and third row transition metals,¹ and only a handful of Fischer-type carbynes have been reported for V⁴ and Cr.¹

Our interest in d⁰-metal complexes with metal–carbon multiple bonds⁵ triggered the pursuit for the thus far unknown vanadium–alkyldiyne functionality. Herein, we report a new class of vanadium(V) complexes having a terminal neopentylidyne that were prepared systematically by two consecutive α -hydrogen abstractions, each induced by one-electron oxidations. These complexes can engage in intramolecular cross-metathesis reactions to afford unusual azametalacyclohexatriene products. The energy profile of this reaction has been examined in detail using DFT calculations.

Previously, we showed that one-electron oxidation of (Nacnac)V-(CH₂^tBu)₂ (Nacnac⁻ = [Ar]NC(CH₃)CHC(CH₃)N[Ar], Ar = 2,6-(CHMe₂)₂C₆H₃) with AgBPh₄ followed by nucleophilic addition of MgI₂ promoted α -hydrogen abstraction to form the four-coordinate neopentylidene complex (Nacnac)V=CH^tBu(I) (Figure 1).^{5b} Inspired by this observation and realizing that vanadium–alkyldiyne complexes are unknown, we alkylated (Nacnac)V=CH^tBu(I) with LiCH₂SiMe₃ to form the neopentylidene–alkyl species (Nacnac)V=CH^tBu(CH₂SiMe₃) (**1**) in 72% yield after recrystallization from pentane at –35 °C (Figure 1).⁶ At room temperature, complex **1** exhibits a solution magnetic moment of 1.90 μ_B , and EPR spectra are in accordance with a V(IV) center.⁶ Single-crystal X-ray diffraction studies confirmed the proposed connectivity and reveal a short V=C bond length (1.791(6) Å), and an obtuse V=C–C_{tbu} angle of 163.1(4)° signifying α -agostic interaction of the V=C _{α} –H _{α} with the vanadium center (Figure 1).⁶

One-electron oxidation of **1** with AgOTf or AgBPh₄ yields the neutral (Nacnac)V≡C^tBu(OTf) (**2-OTf**) or cationic [(Nacnac)V≡C-^tBu(THF)][BPh₄] [**2-THF**][BPh₄] four-coordinate alkyldiyne complexes in 59 and 65% yield, respectively (Figure 1). ¹H NMR spectra are consistent with (**2-OTf**) and [**2-THF**]⁺ retaining C_s symmetry in solution, while the combination of ¹³C (δ :**2-OTf**, 375; [**2-THF**][BPh₄], 374)⁷ and ⁵¹V (δ : **2-OTf**, –882; [**2-THF**][BPh₄], –956) NMR spectra suggests that both systems contain the terminal vanadium(V)–neopentylidyne functionality.⁶

To confirm the proposed connectivity for each vanadium–alkyldiyne we collected single-crystal X-ray diffraction data from

both reactions.⁶ The molecular structure for **2-OTf** and [**2-THF**][BPh₄] reveals a highly distorted tetrahedral vanadium center with a terminal alkyldiyne ligand (Figure 1). In the crystal structures for each compound the short V–C bond length is consistent with a metal–ligand triple bond (**2-OTf**, 1.674(2) Å; [**2-THF**][BPh₄], 1.696(3) Å). These values are clearly shorter than the average for neutral and cationic four-coordinate vanadium–neopentylidene complexes (V=C \approx 1.79 Å, vide supra),^{5b} or for the Fischer-carbyne complex (CO)(dmpc)₂V≡COSiPh₃ (V≡C, 1.754(8) Å).⁴ In addition, the sp-hybridization of the alkyldiyne carbon is evident from the linear V–C _{α} –C _{β} angles (**2-OTf**, 177.6(9)°; [**2-THF**][BPh₄], 175.8(3)°). DFT calculations of **2-OTf** indicate a Mayer-bond order of 2.4, which lends additional support for the assignment of the triple bond.⁶

Although stable as solids, complexes **2-OTf** and [**2-THF**][BPh₄] transform slowly in solution to the vanadium–imido complex supported by the chelating amido-vinyl ligand, (^tBuC=C(Me)CHC(Me)N[Ar])V=NAr(OTf) (**3-OTf**) and [(^tBuC=C(Me)CHC(Me)N[Ar])V=NAr(THF)][BPh₄] [**3-THF**][BPh₄], as evidenced by ¹H and ¹³C NMR spectroscopy (85 and 81% isolated yield, respectively, Figure 1).⁶ Complexes **3-OTf** and [**3-THF**][BPh₄] have been fully characterized⁶ and are best described as an azametalacyclohexatriene system resulting from a cross-metathesis transformation. The VNC₄ metalacycle in the structure of **3-OTf** is far from being planar (V deviation from the NC₄ plane is 1.21 Å).⁸ This feature also places the metal center in contact with the β -carbons (C(3), 2.486(6) (Å); C(5), 2.387(7) Å). Thus, the term azametalabenzene seems inappropriate for the vanadium systems reported here.

The reaction of **2-OTf**→**3-OTf** in C₇D₈ was determined to be first order in vanadium with $k = 3.30(5) \times 10^{-5} \text{ s}^{-1}$ @ 74 °C. Temperature dependence studies from 56 to 91 °C for the **2-OTf**→**3-OTf** transformation allowed for extraction of the activation parameters $\Delta S^\ddagger = -6(3) \text{ cal/mol}\cdot\text{K}^{-1}$, $\Delta H^\ddagger = 25.4(3) \text{ kcal/mol}$ from the Eyring plot.⁶ In addition, the rate of formation of **3-OTf** from **2-OTf** was found to be independent of solvent (C₇D₈ vs THF-*d*₈), suggesting no involvement of dissociative or associative mechanisms.⁶

High-level DFT calculations of the **2-OTf**→**3-OTf** reaction also support an intramolecular rearrangement invoking an azametalacyclobutene ring in the transition state **2-TS** (Figure 2). The computed activation parameters match the experimental results ($\Delta S_{\text{calc}}^\ddagger = -10.3 \text{ cal/mol}\cdot\text{K}^{-1}$, $\Delta H_{\text{calc}}^\ddagger = 28.8 \text{ kcal/mol}$) quite well. In the reaction coordinate of **2-OTf**→**3-OTf** the cross-metathesis reaction is thermodynamically downhill by 21.3 kcal/mol (ΔG , 298 K). Calculations indicate no stable intermediate along the reaction coordinate, suggesting a fast and smooth reaction to yield product **3-OTf** once **2-TS** is traversed (Figure 2).⁶ As illustrated in Figure 2, the triflate ligand adopts a bidentate coordination geometry in

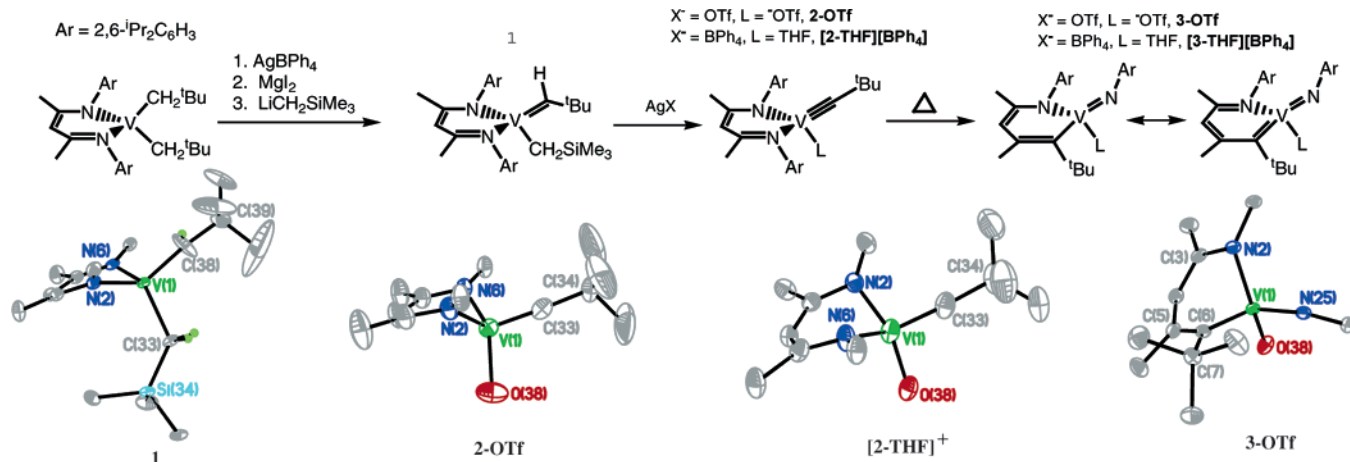


Figure 1. Synthesis of neutral and cationic four-coordinate vanadium(IV) alkylidyne complexes as well as the thermolysis product of each. Only the core structures of **1**, **2-OTf**, **[2-THF]⁺**, and **3-OTf**, are depicted with 50% thermal ellipsoid plots. Hydrogen atoms with the exception of α -H, aryl groups with the exception of ipso carbons, and SO_2CF_3 and carbon atoms on O(38) have been excluded for clarity.

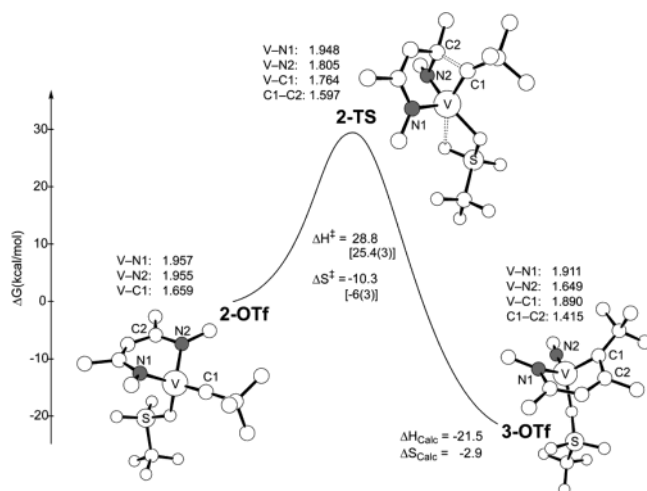


Figure 2. Calculated reaction energy profile for the conversion of **2-OTf** to **3-OTf**. Only the core structure is illustrated for clarity, all energies are in kcal/mol, entropies in cal/mol·K⁻¹, distances in Å. Experimental activation parameters are given in brackets.

2-TS, which is a minor, but notable feature promoting the transformation.

In summary, we have demonstrated that the (Nacnac)V framework is capable of stabilizing reactive vanadium–carbon double and triple bonds. Interestingly, our strategy to prepare d⁰ metal alkylidynes from vanadium–alkylidenes contrasts Schrock’s two-electron reduction reactions of high-valent alkylidenes to prepare Ta=C linkages (referred to as α -H elimination or 1,2-H migration).⁹ In the presence of 1 equiv of LiCH₂^tBu complex **2-OTf** readily polymerizes HC≡CPh to afford *M_n* in excess of ~7000. More detailed studies of the polymerization reaction are currently in progress in our laboratory.

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continue to inspire organometallic chemists. We thank Indiana University-Bloomington, the Camille and Henry Dreyfus Foundation, and the National Science Foundation (0116050 to Indiana University and CHE-0348941 to D.J.M.) for financial support. D.J.M. thanks Dr. Allen Siedle for insightful discussions.

Supporting Information Available: Complete experimental preparation, computational, and crystallographic data for compounds **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- See Supporting Information for complete experimental, crystallographic, and DFT calculation details.
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