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

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High-oxidation state complexes containing alkylidyne 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 alkylidynes is Schrock's (^{t}BuO)$_3$W≡C-^{t}Bu,[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 (^{t}BuO)$_3$W≡W(O^{t}Bu)$_3$.[1a,2b,c,3] Although d^0 early-transition metal complexes with the terminal alkylidyne 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 V[4] and Cr.[1]

Our interest in d^0-metal complexes with metal−carbon multiple bonds[5] triggered the pursuit for the thus far unknown vanadium−alkylidyne 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-(CH$_2$^{t}Bu)$_2$ (Nacnac$^-$ = [Ar]NC(CH$_3$)CHC(CH$_3$)N[Ar], Ar = 2,6-(CHMe$_2$)$_2$C$_6$H$_3$) with AgBPh$_4$ followed by nucleophilic addition of MgI$_2$ promoted α-hydrogen abstraction to form the four-coordinate neopentylidene complex (Nacnac)V=CH^{t}Bu(I) (Figure 1).[5b] Inspired by this observation and realizing that vanadium−alkylidyne complexes are unknown, we alkylated (Nacnac)V=CH^{t}Bu(I) with LiCH$_2$SiMe$_3$ to form the neopentylidene−alkyl species (Nacnac)V=CH^{t}Bu(CH$_2$SiMe$_3$) (**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$_\alpha$−H$_\alpha$ with the vanadium center (Figure 1).[6]

One-electron oxidation of **1** with AgOTf or AgBPh$_4$ yields the neutral (Nacnac)V≡C^{t}Bu(OTf) (**2**)-OTf or cationic [(Nacnac)V≡C-^{t}Bu(THF)][BPh$_4$] **[2-THF][BPh$_4$]** four-coordinate alkylidyne complexes in 59 and 65% yield, respectively (Figure 1). ^{1}H NMR spectra are consistent with (**2**)-OTf and **[2-THF]**$^+$ retaining C_s symmetry in solution, while the combination of ^{13}C (δ: **2-OTf**, 375; **[2-THF][BPh$_4$]**, 374)[7] and ^{51}V (δ: **2-OTf**, −882; **[2-THF][BPh$_4$]**, −956) NMR spectra suggests that both systems contain the terminal vanadium(V)−neopentylidyne functionality.[6]

To confirm the proposed connectivity for each vanadium−alkylidyne we collected single-crystal X-ray diffraction data from both reactions.[6] The molecular structure for **2-OTf** and **[2-THF]-[BPh$_4$]** reveals a highly distorted tetrahedral vanadium center with a terminal alkylidyne 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][BPh$_4$]**, 1.696(3) Å). These values are clearly shorter than the average for neutral and cationic four-coordinate vanadium−neopentylidene complexes (V=C ≈ 1.79 Å, vide supra),[5b] or for the Fischer-carbyne complex (CO)(dmpe)$_2$V≡COSiPh$_3$ (V≡C, 1.754(8) Å).[4] In addition, the sp-hybridization of the alkylidyne carbon is evident from the linear V−C$_\alpha$−C$_\beta$ angles (**2-OTf**, 177.6(9)°; **[2-THF]-[BPh$_4$]**, 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][BPh$_4$]** transform slowly in solution to the vanadium−imido complex supported by the chelating amido-vinyl ligand, (^{t}BuC=C(Me)CHC-(Me)N[Ar])V=NAr(OTf) (**3**)-OTf and [(^{t}BuC=C(Me)CHC(Me)N-[Ar])V=NAr(THF)][BPh$_4$] **[3-THF][BPh$_4$]**, as evidenced by ^{1}H and ^{13}C NMR spectroscopy (85 and 81% isolated yield, respectively, Figure 1).[6] Complexes **3-OTf** and **[3-THF][BPh$_4$]** have been fully characterized[6] and are best described as an azametalacyclohexatriene system resulting from a cross-metathesis transformation. The VNC$_4$ metalacycle in the structure of **3-OTf** is far from being planar (V deviation from the NC$_4$ 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 C$_7$D$_8$ was determined to be first order in vanadium with $k = 3.30(5) \times 10^{-5}$ 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 $\Delta S^\ddagger = -6(3)$ cal/mol·K^{-1}, $\Delta H^\ddagger = 25.4(3)$ 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 (C$_7$D$_8$ 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 ($\Delta S_{calc}^\ddagger = -10.3$ cal/mol·K^{-1}, $\Delta H_{calc}^\ddagger = 28.8$ 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
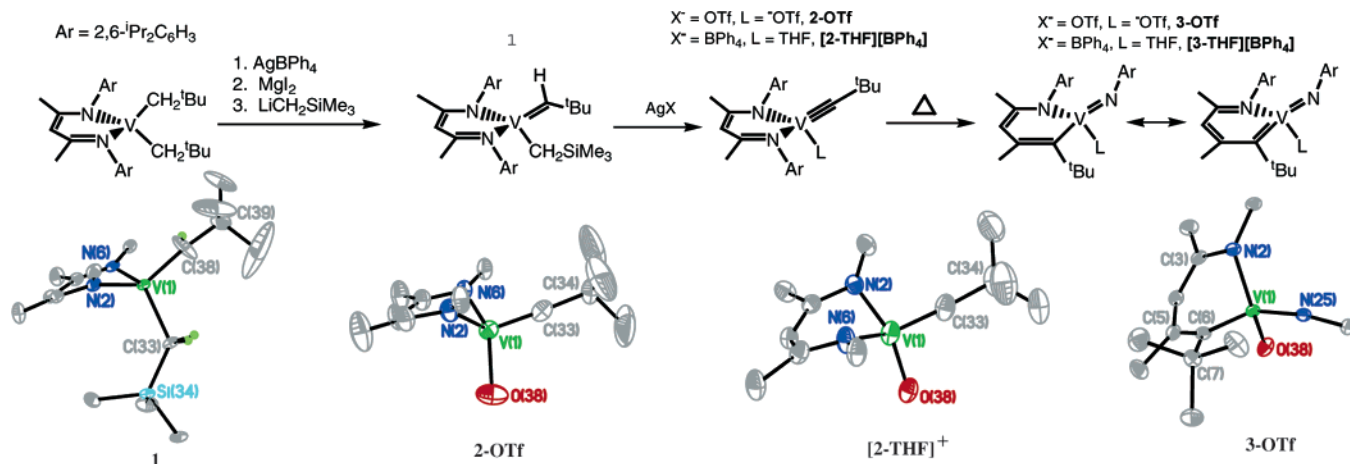
Figure 1. Synthesis of neutral and cationic four-coordinate vanadium(IV) alkylidyne complexes as well as the thermolysis product of each. Only the core structures of **1**, **2-OTf**, **[2-THF]**⁺, and **3-OTf**, are depicted with 50% thermal ellipsoid plots. Hydrogen atoms with the exception of α-H, aryl groups with the exception of ipso carbons, and SO₂CF₃ and carbon atoms on O(38) have been excluded for clarity.
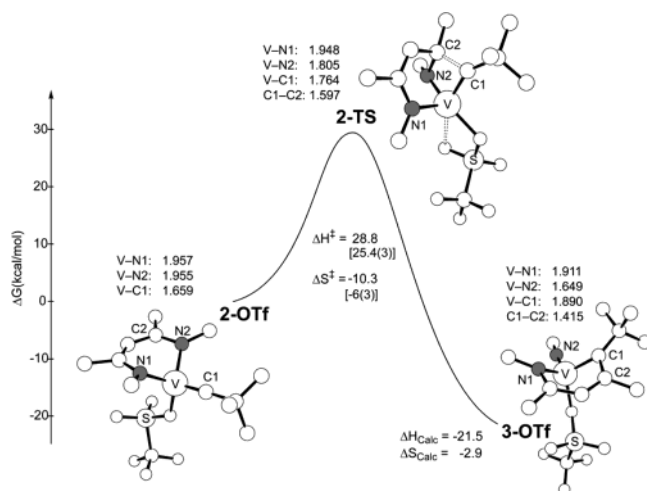
Figure 2. Calculated reaction energy profile for the conversion of **2-OTf** to **3-OTf**. Only the core structure is illustrated for clarity, all energies are in kcal/mol, entropies in cal/mol·K⁻¹, distances in Å. Experimental activation parameters are given in brackets.

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 LiCH₂ᵗBu 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.

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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(6) See Supporting Information for complete experimental, crystallographic, and DFT calculation details.

(7) Lowering the temperature of an NMR solution containing complexes **2**,**3** (−50 °C) increases the quadrupolar relaxation rate of the vanadium nucleus (⁵¹V, $I = ^7/_2$, 99.6% abundant) and results in the effective decoupling of the ⁵¹V scalar coupling from the ¹³C nucleus: Claridge, T. D. W. *High-Resolution NMR techniques in Organic Chemistry*; Pergamon: Amsterdam, 1999; pp 40−44.

(8) For an example of a planar metalapyridine system of group 5, see: Weller, K. J.; Filippov, I.; Briggs, P. M.; Wigley, D. E. *Organometallics* **1998**, *17*, 322−329 and references therein.

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