Inorganic Chemistry
Article
pubs.acs.org/IC

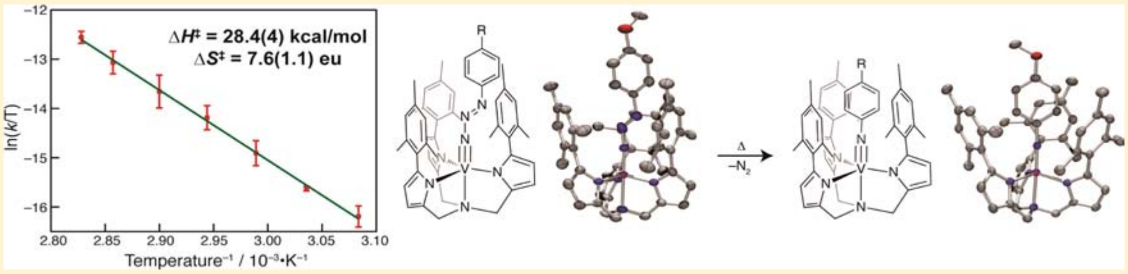
Well-Defined Vanadium Organoazide Complexes and Their Conversion to Terminal Vanadium Imides: Structural Snapshots and Evidence for a Nitrene Capture Mechanism

W. Hill Harman,[†,‡] Michael F. Lichterman,[†] Nicholas A. Piro,[†,‡] and Christopher J. Chang*[,†,‡,§]

[†]Department of Chemistry and [§]The Howard Hughes Medical Institute, University of California, Berkeley, California 94720, United States

[‡]Chemical Sciences Division, Lawrence Berkeley National Laboratory (LBNL), Berkeley, California 94720, United States

Supporting Information



ABSTRACT: We report the synthesis and structural characterization of a family of well-defined organoazide complexes supported by a three-fold-symmetric pyrrolide scaffold and their conversion to the corresponding terminal imido congeners. Kinetic measurements on a series of structurally homologous but electronically distinct vanadium organoazide complexes reveal that the azido-to-imido transformations proceed via a process that is first-order in the metal complex and has a positive entropy of activation. Further studies suggest that these reactions may involve metal-mediated generation and capture of nitrene fragments.

■ INTRODUCTION

The formation and study of metal imido complexes is of fundamental interest because of their intermediacy in a wide array of catalytic chemical and biological processes ranging from C−N bond-forming reactions to nitrogen fixation.[1] Such species are often formed through the oxidative installation of a neutral nitrene fragment ("NR") onto a reducing metal precursor. Organic azides are the most common nitrene source in this context, wherein reaction of the azide with a reduced metal center results in dinitrogen extrusion and concomitant formation of a metal−nitrogen multiple bond. Despite the fact that metal organoazide species have been proposed as intermediates in these reactions,[2] the isolation and characterization of such species remain rare.[3−11] Interestingly, kinetic studies have revealed surprising mechanistic diversity for this basic transformation. A seminal study by Proulx and Bergman on the conversion of mononuclear tantalum azide adducts into tantalum imido complexes identified a unimolecular mechanism involving a four-membered triazametallacyclic species that undergoes dinitrogen loss to give the imide product.[3] Parallel work by Cummins et al. on a related vanadium trianilide system provided evidence for an imide formation pathway that is second order in an azide adduct.[4] Alternately, reactions of manganese and chromium corrole complexes with organoazides to form imido species have been shown by Abu-Omar et al. to proceed via thermal decomposition of the free organoazide followed by trapping of the incipient nitrene fragment by the reduced metal complex.[12] Isolated nickel azide adducts studied by Waterman and Hillhouse[10] appear to form imides by the classical mechanism elucidated by Proulx and Bergman.[3] Finally, a ruthenium system recently reported by Peters et al. catalyzes the formation of azoarenes from organoazides via postulated nitrene release from a low-valent ruthenium organoazide adduct, with some production of the corresponding imide complexes depending on the organoazide substrate.[11b]

To contribute to this area, we now report a new family of well-defined, structurally characterized metal organoazide complexes featuring a three-fold-symmetric vanadium pyrrolide platform and their conversion to the corresponding terminal imido species. Although these molecules find their closest analogues in those reported by Proulx and Bergman[3] and Cummins et al.,[4] mechanistic studies reveal patent differences with both of these landmark systems. In particular, Eyring analysis shows that the organoazide-to-imido transformation on this vanadium pyrrolide platform proceeds with a positive entropy of activation, which is unique in comparison to other previously studied monometallic systems.[3,10] Moreover, the Hammett relationship established for this pyrrolide system is

Received: July 30, 2012
Published: August 24, 2012

dx.doi.org/10.1021/ic301673g | *Inorg. Chem.* 2012, 51, 10037−10042

opposite to that elucidated in Proulx and Bergman's system, although both systems are first-order in an azide adduct. Finally, further experiments provide evidence to suggest the participation of metal-mediated generation and capture of nitrene fragments in an azide-to-imido conversion process.

■ EXPERIMENTAL SECTION

General Procedures. Unless otherwise noted, all manipulations were carried out at room temperature under an atmosphere of dinitrogen in a VAC Atmospheres glovebox or using Schlenk techniques. Pentane and toluene were dried using a VAC Atmospheres solvent purification system prior to use. Benzene was distilled from purple sodium benzophenone ketyl. Benzene-d_6 was purchased from Cambridge Isotopes Laboratory, brought into the glovebox, degassed, and stored over sieves. Potassium hydride was purchased as a suspension in mineral oil, washed with pentane, and used as a dry solid inside the glovebox. Literature procedures were used for the preparation of (tpa^{Mes})V(THF) (**1**)[13] and the aryl azides, including $NN^{15}NPh$.[14] All other reagents and solvents were purchased from chemical suppliers and used as received. NMR spectra were recorded on Bruker spectrometers operating at 500 MHz unless otherwise noted. Chemical shifts are reported in ppm and referenced to a residual protiated solvent; coupling constants are reported in hertz. Mass spectra and elemental analyses were performed at the Mass Spectrometry and Microanalytical Facilities at the University of California, Berkeley.

(tpaMes)V[η^1-N_3(*p*-C_6H_4OMe)]·0.5Toluene (2a·0.5Toluene). In the glovebox, a 20 mL scintillation vial was charged with **1** (46.4 mg, 0.0637 mmol), which was dissolved in toluene (5 mL). To this solution was added a solution of N_3(*p*-C_6H_4OMe) (9.3 mg, 0.064 mmol) in toluene with constant stirring. A rapid color change to a red-black was observed. The reaction was stirred for 20 min before the solvent was concentrated to ~1 mL in vacuo. The resulting solution was layered with pentane and placed in a freezer at −35 °C overnight, providing a first crop of 42.7 mg (79%) of black crystals. Further recrystallizations from the mother liquor provide a combined yield of ~90%. Crystals suitable for X-ray diffraction were grown via this method. Because of the thermal instability of this compound, satisfactory elemental analysis could not be obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.84 (br s, 2H), 6.77 (s, 2H), 6.52 (s, 3H), 6.36 (s, 3H), 6.03 (s, 2H), 5.73 (d, J = 2.1 Hz, 3H), 4.57 (br s, 3H, methylene), 4.21 (br s, 3H, methylene), 3.92 (s, 3H, *p*-OCH_3), 2.08 (s, 9H, mesityl methyl), 1.92 (s, 9H, mesityl methyl), 1.38 (s, 9H, mesityl methyl). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.06, 139.22, 138.13, 135.96, 134.73, 128.13, 127.96, 125.16, 120.21, 115.35, 113.48, 108.62, 103.92, 55.87, 55.06, 21.15, 20.74, 20.12. IR (cm^{-1}): 2103 (wk), 1593, 1331, 1223.

(tpa^{Mes})V(η^1-N_3Ph)·0.5Toluene (2b·0.5Toluene). In the glovebox, a 20 mL scintillation vial was charged with **1** (88.5 mg, 0.122 mmol), which was dissolved in toluene (5 mL). To this solution was added a solution of N_3Ph (15.1 mg, 0.127 mmol) in toluene with constant stirring. A rapid color change to dark orange-black was observed. The reaction was stirred for 1 h before the solvent was concentrated to ~1 mL in vacuo. The resulting solution was layered with pentane and placed in a freezer at −35 °C overnight, providing 72 mg (72%) of black crystals. Because of the thermal instability of this compound, satisfactory elemental analysis could not be obtained. NMR characterization was carried out at low temperature because of the high degree of fluxionality at room temperature. ^{1}H NMR (235 K, 500 MHz, $CDCl_3$): δ 7.34 (s, 3H), 6.81 (s, 2H), 6.55 (s, 3H), 6.39 (s, 3H), 6.02 (s, 3H), 5.76 (s, 3H), 4.60 (d, J = 13.0 Hz, 3H), 4.32 (d, J = 13.3 Hz, 3H), 2.10 (s, 9H), 1.88 (s, 9H), 1.35 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.86, 141.38, 138.79, 137.88, 136.98, 136.15, 134.15, 132.30, 129.09, 128.29, 128.10, 127.98, 127.72, 122.53, 108.33, 103.78, 54.78, 20.98, 20.55, 19.93. IR (cm^{-1}): 2127 (wk), 1445, 1332, 1225. The isotopomer (tpa^{Mes})V(η^1-$NN^{15}NPh$) was prepared in an analogous manner utilizing $NN^{15}NPh$. IR (cm^{-1}): 2113 (wk), 1445, 1332, 1225.

(tpa^{Mes})V[η^1-N_3(*p*-Tol)]·0.5Toluene (2c·0.5Toluene). In the glovebox, a 20 mL scintillation vial was charged with **1** (95.1 mg, 0.131 mmol), which was dissolved in toluene (5 mL). To this solution was added a solution of N_3(*p*-Tol) (23.5 mg, 0.177 mmol) in toluene with constant stirring. A rapid color change to dark orange-black was observed. The reaction was stirred for 45 min before the solvent was concentrated to ~1 mL in vacuo. The resulting solution was layered with pentane and placed in a freezer at −35 °C overnight, providing 62 mg (57%) of black crystals. Crystals suitable for X-ray diffraction were grown in this fashion. Because if the thermal instability of this compound, satisfactory elemental analysis could not be obtained. NMR characterization was carried out at low temperature because of the high degree of fluxionality at room temperature. ^{1}H NMR (263 K, 500 MHz, $CDCl_3$): δ 7.12 (d, J = 7.8 Hz, 2H, aryl), 6.70 (d, J = 7.6 Hz, 2H, aryl), 6.53 (s, 3H, mesityl), 6.37 (s, 3H, mesityl), 6.00 (s, 3H, pyrrole), 5.75 (s, 3H, pyrrole), 4.58 (d, J = 13.6 Hz, 3H, methylene), 4.28 (d, J = 12.5 Hz, 3H, methylene), 2.44 (s, 3H, aryl *p*-CH_3), 2.08 (s, 9H, mesityl methyl), 1.89 (s, 9H, mesityl methyl), 1.31 (s, 9H, mesityl methyl). ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.57, 138.92, 138.14, 137.07, 136.18, 134.36, 128.98, 128.10, 127.84, 118.85, 108.45, 103.86, 54.91, 22.04, 21.13, 20.68, 20.03. IR (cm^{-1}): 2103 (wk), 1445, 1332, 1225.

(tpa^{Mes})V[N_3(η^1-*p*-$C_6H_4NMe_2$)·0.5Toluene (2d·0.5Toluene). In the glovebox, a 20 mL scintillation vial was charged with tpa^{Mes}V-(THF) (87.7 mg, 0.120 mmol), which was dissolved in toluene (5 mL). To this solution was added a solution of N_3PhNMe_2 (19.5 mg, 0.120 mmol) in toluene with constant stirring. A rapid color change to teal-black was observed. The reaction was stirred for 20 min before the solvent was concentrated to ~1 mL in vacuo. The resulting solution was layered with pentane and placed in a freezer at −35 °C overnight, providing a first crop of 80.0 mg (77%) of black crystals; further recrystallization of the mother liquor provideed yields of ca. 90%. Crystals suitable for X-ray diffraction were grown from a saturated solution of benzene placed in a pentane vapor chamber. Because of the thermal instability of this compound, satisfactory elemental analysis could not be obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.72 (d, J = 8.3 Hz, 2H, aryl), 6.56 (d, J = 9.0Hz, 2H, aryl), 6.53 (s, 3H, mesityl), 6.39 (s, 3H, mesityl), 6.00 (s, 3H, pyrrole), 5.76 (d, J = 2.8Hz, 3H, pyrrole), 4.52 (d, J = 13.9 Hz, 3H, methylene), 4.16 (d, J = 13.9 Hz, 3H, methylene), 3.18 (s, 6H, *p*-$N(CH_3)_2$), 2.10 (s, 9H, mesityl methyl), 1.95 (s, 9H mesityl methyl), 1.41 (s, 9H, mesityl methyl). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.58, 141.97, 139.09, 138.86, 137.00, 135.74, 135.04, 128.04, 127.81, 111.10, 108.59, 103.69, 54.81, 40.48, 21.24, 20.77, 19.99.

(tpa^{Mes})V[N(*p*-C_6H_4OMe) (3a). A Schlenk tube was charged with **2a** (35 mg, 0.041 mmol) and dissolved in benzene (10 mL). The solution was degassed and heated to reflux for 1 h, during which time a color change to orange-black was observed. The solvent was reduced to ~1 mL in vacuo and pentane added (9 mL). The resulting mixture was filtered and the solvent removed from the filtrate in vacuo. The solid residue was rinsed with pentane and dried under vacuum to yield 20 mg (63%) of a brown powder. Crystals suitable for X-ray diffraction were grown over the course of multiple days by the slow diffusion of pentane into a concentrated benzene solution. HRESIMS. Calcd for $C_{49}H_{53}N_5OV$ ([M + H]$^+$): *m/z* 778.3648. Found: *m/z* 778.3663. ^{1}H NMR (300 MHz, C_6D_6): δ 6.59 (s, 3H), 6.47 (s, 3H), 6.06 (d, J = 3.0 Hz, 3H), 6.01 (d, J = 3.0 Hz, 3H), 5.86 (d, J = 9.0 Hz, 2H, aryl), 5.20 (d, J = 9.0 Hz, 2H, aryl), 4.20 (d, J = 14.0 Hz, 3H, methylene), 4.03 (d, J = 14.0 Hz, 3H, methylene), 3.65 (s, 3H, *p*-OCH_3), 2.15 (s, 9H, mesityl methyl), 2.04 (s, 9H, mesityl methyl), 1.46 (s, 9H, mesityl methyl). ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.08, 141.96, 139.28, 137.96, 137.82, 136.46, 135.52, 132.13, 128.14, 110.07, 109.82, 103.93, 55.30, 53.83, 21.17, 21.12, 20.21.

(tpa^{Mes})V(NPh) (3b). A Schlenk tube was charged with **2b** (72 mg, 0.088 mmol) and benzene (10 mL). The solution was degassed and heated to reflux for 3 h, during which time a color change to orange-black was observed. The solvent was reduced to ~1 mL in vacuo and pentane added (9 mL). The resulting mixture was filtered through celite, and the volatiles were removed from the filtrate in vacuo. The solid residue was rinsed with pentane and dried in vacuo to yield 52

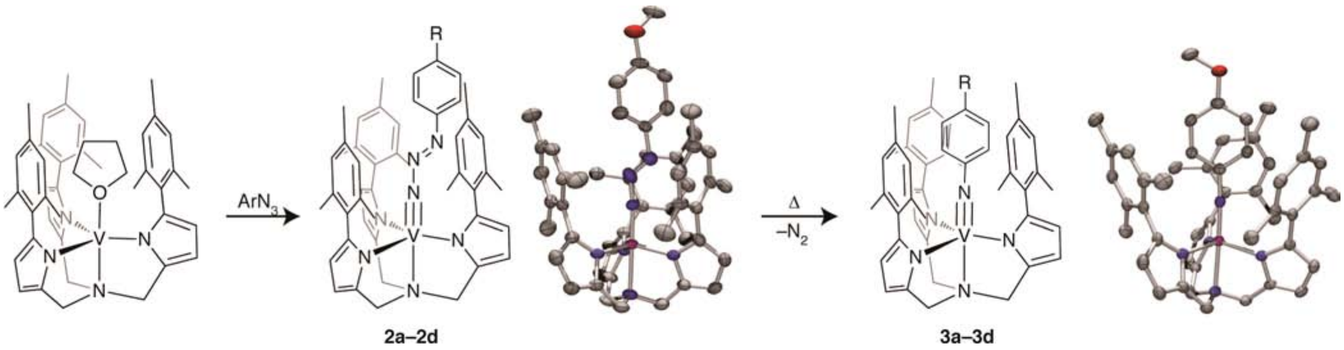


Figure 1. Synthetic scheme for the formation of vanadium(V) diazenylimido and vanadium(V) imido species supported by the tripyrrolide ligand tpa^{Mes}; R = OMe (**a**); H (**b**); OMe (**c**), NMe$_2$ (**d**). ORTEP crystal structures for **2a** and **3a** with thermal ellipsoids drawn at 50% probability, with solvent molecules and hydrogen atoms omitted for clarity, are also shown.

mg (79%) of a brown powder. Crystals suitable for X-ray diffraction were grown over the course of multiple days by the slow diffusion of pentane into a concentrated benzene solution. HRESIMS. Calcd for $C_{48}H_{50}N_5V$ ([M + H]$^+$): m/z747.3497. Found: m/z 747.3497. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.49 (m, 4H, mesityl and p-aryl), 6.39 (s, 3H, mesityl), 6.21 (t, J = 7.5 Hz, 2H, m-aryl), 6.00 (s, 3H, pyrrole), 5.79 (s, 3H, pyrrole), 4.94 (d, J = 7.8 Hz, 2H, o-aryl), 4.45 (d, J = 13.9 Hz, 3H, methylene), 4.08 (d, J = 14.0 Hz, 3H, methylene), 2.15 (s, 9H, mesityl methyl), 2.03 (s, 9H, mesityl methyl), 1.46 (s, 9H, mesityl methyl). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.04, 139.18, 137.99, 137.82, 136.59, 135.27, 129.71, 128.58, 128.54, 128.15, 125.08, 124.99, 109.75, 104.02, 53.85, 21.13, 21.08, 20.14.

(tpa^{Mes})V[N(p-Tol)] (3c). A Schlenk tube was charged with **2c** (70 mg, 0.084 mmol) and benzene (10 mL). The solution was degassed and then heated to reflux for 3 h. The solvent was reduced to ~1 mL in vacuo and pentane added (9 mL). After filtration through celite, the volatiles were removed in vacuo. The solid residue was rinsed with pentane and dried in vacuo to yield 60 mg (79%) of a green-black powder. Crystals suitable for X-ray diffraction were grown by the slow diffusion of pentane vapor into a concentrated benzene solution of the product. HREIMS. Calcd for $C_{49}H_{52}N_5V$ ([M]$^+$): m/z 761.3662. Found: m/z 761.3674. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.49 (s, 3H, mesityl), 6.39 (s, 3H, mesityl), 5.98 (m, 5H, pyrrole and aryl), 5.77 (d, J = 2.5 Hz, 3H, pyrrole), 4.82 (d, J = 8.1 Hz, 2H, aryl), 4.42 (d, J = 13.9 Hz, 3H, methylene), 4.04 (d, J = 14.0 Hz, 3H, methylene), 2.15 (s, 9H, mesityl methyl), 2.12 (s, 3H, aryl p-CH_3), 2.03 (s, 9H, mesityl methyl), 1.45 (s, 9H, mesityl methyl). ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.05, 139.13, 9 137.95, 137.80, 136.60, 135.51, 135.38, 129.80, 128.48, 128.06, 127.83, 125.60, 109.75, 103.94, 53.83, 21.46, 21.16, 21.09, 20.16.

(tpa^{Mes})V[N(p-$C_6H_4NMe_2$) (3d). A Schlenk tube was charged with **2d** (37 mg, 0.043 mmol) and benzene (10 mL). The solution was degassed and heated to reflux for 30 min, during which time a color change to green-black was observed. The solvent was reduced to ~1 mL in vacuo and pentane added (9 mL). After filtration through celite, the volatiles were removed from the filtrate in vacuo. The solid residue was rinsed with pentane and dried in vacuo to yield 30 mg (88%) of a green-black powder. Crystals suitable for X-ray diffraction were grown by the slow diffusion of pentane vapor into a concentrated benzene solution of the product. HRESIMS. Calcd for $C_{50}H_{56}N_6V$ ([M + H]$^+$): m/z 791.4001. Found: m/z 791.3985. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.50 (s, 3H, mesityl), 6.42 (s, 3H, mesityl), 5.98 (d, J = 1.9 Hz, 3H, pyrrole), 5.80 (d, J = 2.8 Hz, 3H, pyrrole), 5.38 (d, J = 9.0 Hz, 2H, aryl), 4.84 (d, J = 9.0 Hz, 2H, aryl), 4.36 (d, J = 13.9 Hz, 3H, methylene), 3.98 (d, J = 14.0 Hz, 3H, methylene), 2.89 (s, 6H, p-NC_2H_6), 2.17 (s, 9H, mesityl methyl), 2.04 (s, 9H, mesityl methyl), 1.49 (s, 9H, mesityl methyl). ^{13}C NMR (126 MHz, $CDCl_3$): δ 147.07, 141.86, 139.28, 137.86, 137.78, 136.04, 135.74, 132.40, 128.61, 128.05, 127.84, 109.73, 108.06, 103.69, 53.70, 40.13, 21.23, 21.16, 20.26.

Stability of N_3 (p-C_6H_4OMe) in C_6D_6 at 75 °C. A solution of N_3 (p-C_6H_4OMe) in C_6D_6 (ca. 30 mM) in an NMR tube was inserted into a NMR probe preheated to 75 °C, and a single-pulse ^{1}H NMR spectrum was collected every 1 min for 12 h. No diazene formation or azide decomposition was observed.

Stability of 3a in the Presence of Excess N_3 (p-C_6H_4OMe) at 75 °C. Both **3a** (5 mg) and N_3 (p-C_6H_4OMe, 25 mg) were dissolved in C_6D_6, and the resulting solution was transferred to an NMR tube fitted with a Teflon valve. The tube was heated to 75 °C and monitored by ^{1}H NMR for 12 h. No diazene formation, azide decomposition, or imido (**3a**) decomposition was observed.

Catalytic N_2 [(p-C_6H_4OMe)$_2$] Formation from N_3 (p-C_6H_4OMe) in the Presence of 2a. Both **2a** (5 mg) and N_3 (p-C_6H_4OMe, 25 mg) were dissolved in C_6D_6, and the resulting solution was transferred to an NMR tube fitted with a Teflon valve. The tube was inserted into an NMR probe preheated to 55 °C, and a single-pulse ^{1}H NMR spectrum was collected every 1 min for 12 h. The results are shown in Figure S2 in the Supporting Information and indicate azoarene formation corresponding to ~9 turnovers.

Representative Kinetic Experiment for the Conversion of 2a to 3a. Crystals of **2a** and ferrocene were dissolved in C_6D_6 to a concentration of ca. 5 mM in **2a** and ca. 1 mM in ferrocene, and the resulting dark solution was transferred to an NMR tube fitted with a Teflon valve. The tube was inserted into an NMR probe preheated to the temperature of interest, as determined by an ethylene glycol standard calibrated thermocouple. A single-pulse ^{1}H NMR spectrum was then recorded every 1 min until the reaction was complete. In higher temperature measurements where peak broadening resulted in overlap with the ferrocene standard, a residual solvent was used as an internal standard. Integration data from a well-isolated resonance corresponding to **2a** were plotted as a function of time fit to an exponential function of the form $f(t) = ae^{-kt} + c$, giving the rate constant k. Data from the first few minutes of the runs were excluded from the fits in order to remove errors due to temperature equilibration.

Error Analysis. Errors for the Hammett and Eyring analyses were determined by setting the confidence interval to be mean ± $ts/n^{1/2}$, where t is the Student's t (12.706 for 2 runs, 4.303 for 3 runs, etc.), s is the standard deviation of the values, and n is the number of runs for a given compound at a given temperature (2 or 3 runs). Error bars for Eyring analysis are set to the 95% confidence interval as the magnitude of the 95% confidence interval over the mean, whereas error bars for Hammett analysis are set to 0.434 times the magnitude of the 95% confidence interval over the mean.

■ RESULTS AND DISCUSSION

The recently reported vanadium(III) complex (tpa^{Mes})V(THF) (**1**; THF = tetrahydrofuran) provides a readily accessible source of the [(tpa^{Mes})V] fragment.[13] The treatment of **1** with p-methoxyphenyl azide (N_3Ar^{OMe}) in toluene at room temperature results in an immediate color change from bright orange to dark red/black. Layering of the reaction mixture under pentane and subsequent storage at −35 °C overnight affords dark, block-shaped crystals revealed by X-ray diffraction to be the η^1-azide adduct (tpa$^{\mathrm{Mes}}$)V(η^1-N_3Ar^{OMe}) (**2a**). The ^{1}H NMR spectrum of this complex features peaks exclusively in the diamagnetic region of the spectrum consistent with a formal two-electron transfer from the vanadium center to the bound ligand to give a complex best described as a diazenylimidovanadium(V) species.[4] Structurally, the bent geometry at the β-nitrogen of the aryl azide [N5−N6−N7 = 118.2(4)°] of **2a** supports this formulation. Furthermore, the observed short V−N$_{\mathrm{azide}}$ bond distance [V1−N5 = 1.693(4) Å] and the near-linear geometry at the imido nitrogen [V1−N5−N6 = 170.5(3)°] are consistent with a V−N pseudo triple bond.[1a] Isolable transition-metal organozide adducts of any type are rare, and **2a** represents one of only a few well-defined terminal diazenylimido complexes.[3−5]

Given that organic azide adducts of transition-metal fragments are frequently invoked as intermediates in the formation of imido complexes, we investigated the reactivity of **2a** in this context. Indeed, thermolysis of **2a** in benzene results in a smooth conversion to a new diamagnetic product with ^{1}H NMR spectroscopic features consistent with the formation of the corresponding vanadium(V) terminal imido complex. X-ray diffraction studies performed on a single crystal of this product confirmed its identity as (tpa$^{\mathrm{Mes}}$)V(NAr$^{\mathrm{OMe}}$) (**3a**; Figure 1). The short V−N distance [V1−N5 = 1.687(2) Å] and nearly linear arrangement of the imido ligand [V1−N5−C43 = 177.08(8)°] indicate a V−N triple bond.[1]

With a pair of well-defined, structurally characterized terminal organoazide and imide complexes of vanadium and data suggesting a clean organoazide-to-imide conversion in hand, we proceeded to examine the kinetics of this process. Although relatively few mechanistic investigations of the thermolysis of metal organoazide complexes to the corresponding metal imidos have been reported,[3,4,6,10] these studies have uncovered a surprisingly mechanistic diversity. For the present case, thermolysis of **2a** in C_6D_6 proceeds with a first-order decay with $k_{\mathrm{obs}} = 5.5(4) \times 10^{-5}$ s^{-1} at 55 °C as monitored by ^{1}H NMR. Eyring analysis (Figure 2) of the first-order rate constants determined for the decay of **2a** over a temperature range of 50−78.5 °C yields activation parameters of $\Delta H^‡$ = 28.4(4) kcal mol^{-1} and $\Delta S^‡$ = 7.6(1.1) eu. Interestingly, the positive entropy of activation obtained for this vanadium pyrrolide system is distinct compared to what was observed in other metal organoazide platforms studied by the groups of Bergman[3] and Hillhouse.[10] In these previously reported systems, thermolysis of the organoazide adduct is found to proceed with a negative entropy of activation, consistent with dinitrogen extrusion from a highly ordered four-membered cyclic species in which both the α- and γ-nitrogen atoms of the organic azide fragment are bound to the transition-metal center. The positive entropy of activation for thermolysis of **2a** is inconsistent with rate-limiting metallacycle formation. Although we cannot rule out potential rate-limiting isomerization pathways giving rise to the small, positive entropy of activation, we speculate that the sterically demanding nature of [tpa$^{\mathrm{Mes}}$] may impede the formation of such a species in the present system, a phenomenon noted in Floriani's tungsten calixarene systems.[5] Interestingly, small quantities of azoanisole were formed in these reactions (<3 mol %), suggesting that a different mechanism for decomposition of the organoazide and formation of the imido may be operative.

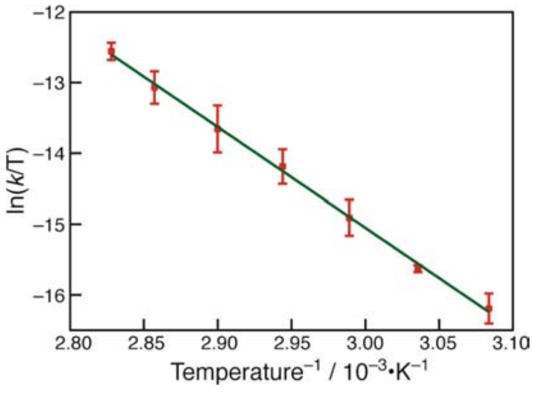


Figure 2. Eyring plot for thermolysis of **2a** between 50 and 78.5 °C with 95% confidence error bars; R^2 = 0.9984.

To further probe the mechanism of dinitrogen loss from **2a**, we synthesized a structurally homologous series of organoazide complexes of the type (tpa$^{\mathrm{Mes}}$)V(η^1-N_3Ar^{R}), where the electronic properties of these adducts were systematically tuned by varying the *para* substituents of the aryl ring [R = H (**2b**), Me (**2c**), NMe$_2$ (**2d**)]. As was observed for the complex **2a**, thermolysis reactions of all four vanadium organoazide complexes proceed with clean first-order kinetics (see the Supporting Information). We then moved on to determine the first-order rate constants for the thermolysis of each complex at the same temperature (55 °C) and subjected the resulting data to Hammett analysis (Figure 3). Surprisingly, in further contrast to Proulx and Bergman's $Cp_2TaMe(N_3Ar)$ system,[3] the only other terminal metal organoazide system for which a detailed Hammett analysis has been performed, the conversions of **2a−2d** to **3a−3d** are accelerated by electron-donating substituents with $\rho = -1.5$. As in the case of **2a**, small amounts

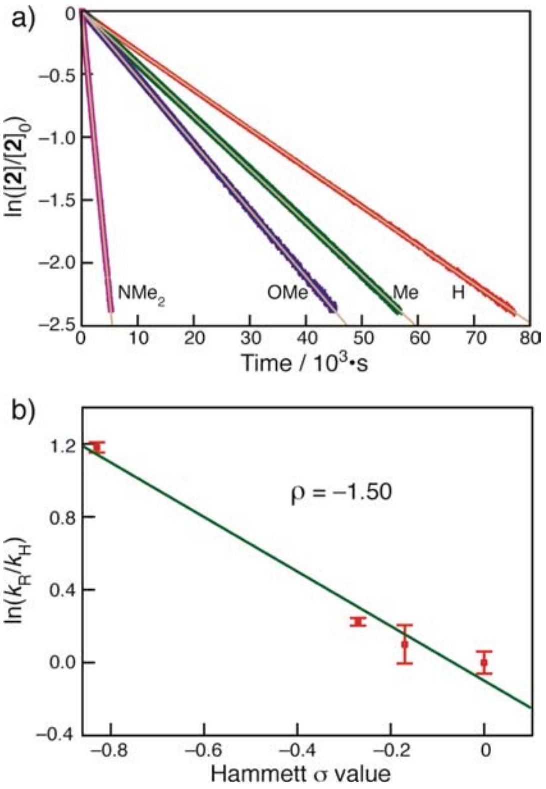


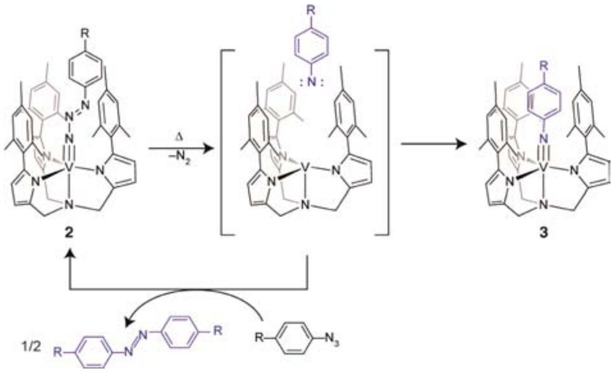
Figure 3. (a) Plots of ln [**2**]/[**2**$_0$] versus time for **2a−2d** at 55 °C. (b) Hammett correlation plot.

of the corresponding diazenes were formed in these thermolysis reactions. Furthermore, a double-label experiment in which equal amounts of (tpa^{Mes}-D_6)V(η^1-N_3Ph) and (tpa^{Mes})V(η^1-NN^{15}NPh) were thermolyzed together showed complete label crossover. However, thermolysis of (tpa^{Mes})V(η^1-NN^{15}NPh) alone provides only the labeled imido (tpa^{Mes})V(^{15}NPh).

In contrast to the stoichiometric thermolysis reactions with an isolated and structurally characterized vanadium organoazide complex alone, when a C_6D_6 solution of **2a** and 25 equiv of N_3Ar^{OMe} is heated to 75 °C for 8 h, azoanisole is generated catalytically (TON ≈ 9) and formation of the imido **3a** is markedly impeded. Control experiments in which either the azide alone or the azide and imido **3a** were subjected to analogous conditions did not yield detectable amounts of the diazene product by ^{1}H NMR. An experiment that directly demonstrates the trapping of free nitrene by an external substrate under these conditions would provide compelling evidence for this process; however, our efforts to date using singlet nitrene traps (e.g., cyclooctene) have been inconclusive. We note that triplet nitrene, the likely form of transient nitrene in this system, is difficult to trap in these conditions given that the most effective traps either are themselves organoazides or react with the complexes under study (e.g., nitroso compounds).[14]

Taken together, these experiments suggest the possibility of metal-mediated generation and trapping of nitrene fragments in the formation of imido products **3a**−**3d**, a proposal recently advanced by Peters et al. for a ruthenium phosphine system.[11b] Because solutions of N_3Ar^{OMe} do not appreciably decompose when subjected to the conditions employed for the formation of **3a**, simple trapping of the nitrene fragment NAr^{OMe} generated by free azide thermolysis is inconsistent with the observed kinetic data in our system. The kinetic experiments were carried out in a dark NMR probe, thereby ruling out photochemical pathways. These results complement related work in different systems showing that manganese and chromium imido complexes can be formed through thermal liberation of nitrene fragments from free azides without involvement of the metal.[12] Likewise, catalytic diazene formation from organoazides has been demonstrated for a trigonal-bipyramidal iron system in which N−N coupling takes place between two imidoiron(III) species,[11a] but the apparent stability of **3a** in solution rules out this mechanism in the present case. We favor a mechanism in which nitrene loss occurs directly from **2a**−**2d** (or an isomer thereof) to give an incipient low-valent vanadium complex that, in the absence of excess organoazide, traps the nitrene fragment to yield **3a**−**3d**. The more electron-rich organoazides decompose more quickly as they facilitate the two-electron reduction of the metal center required for nitrene release, consistent with the results from the Hammett analysis (vide supra). In the presence of excess organoazide, binding of a second equivalent of organoazide to reform **2a**−**2d** occurs competitively with nitrene capture. The nitrene fragments thus generated can either dimerize or react with a second equivalent of free azide,[15] leading to the observed catalytic diazene formation (Scheme 1).

Scheme 1. Proposed Mechanism for the Formation of 3 through Nitrene Capture and Nitrene Dimerization To Give Diazene



To close, we have described the synthesis, structure, and reactivity of a unique family of metal organoazide complexes supported by a vanadium pyrrolide platform and their thermal conversion to the corresponding metal imido species. Kinetic measurements on a series of structurally homologous but electronically distinct metal organoazide adducts indicate that the organoazide-to-imido transformation proceeds with a positive entropy of activation and is first-order in metal, and further studies suggest the involvement of metal-generated nitrene intermediates, which can lead to diazene formation. This latter insight is significant in that the present system demonstrates that reducing metal fragments capable of facile reaction with organoazides may, nonetheless, generate free nitrene species on their way to metal imido formation and adds to the rich mechanistic diversity of transition-metal-mediated nitrene chemistry. Further studies to utilize this information to develop reactive yet controlled nitrogen-based catalytic reactions are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, experimental details, supporting figures, and X-ray structure information. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: chrischang@berkeley.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by DOE/LBNL Grant 403801. C.J.C. is an investigator with the Howard Hughes Medical Institute. We thank Arkema (W.H.H.) and the Miller Institute for Basic Research (N.A.P.) for fellowship support and Prof. Bob Bergman and Dr. Ayumi Takaoka for helpful discussions.

■ REFERENCES

(1) (a) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Mulitple Bonds*; John Wiley & Sons: New York, 1988. (b) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*.

(2) (a) Hillhouse, G. L.; Haymore, B. L. *J. Am. Chem. Soc.* **1982**, *104*, 1537. (b) Hillhouse, G. L.; Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1982**, *21*, 2064. (c) Gambarotta, S.; Chiesi-Villa, A.; Guastini, C. *J. Organomet. Chem.* **1984**, *270*, C49. (d) Osborne, J. H.; Rheingold, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 7945. (e) Antonelli, D. M.; Schaefer, W. P.; Parkin, G.; Bercaw, J. E. *J. Organomet. Chem.* **1993**, *462*, 213. (f) Cenini, S.; Gallo, E.; Caselli, A.; Ragaini, F.; Fantauzzi, S.; Piangiolino, C. *Coord. Chem. Rev.* **2006**, *250*, 1234.

(3) (a) Proulx, G.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 6382. (b) Proulx, G.; Bergman, R. G. *Organometallics* **1996**, *15*, 684.

(4) Fickes, M. G.; Davis, W. M.; Cummins, C. C. *J. Am. Chem. Soc.* **1995**, *117*, 6384.

(5) Guillemot, G.; Solari, E.; Floriani, C.; Rizzoli, C. *Organometallics* **2001**, *20*, 607.

(6) Hanna, T. A.; Baranger, A. M.; Bergman, R. G. *Angew. Chem., Int. Ed.* **1996**, *35*, 653.

(7) Barz, M.; Herdtweck, E.; Thiel, W. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 2262.

(8) Dias, H. V. R.; Polach, S. A.; Goh, S. K.; Archibong, E. F.; Marynick, D. S. *Inorg. Chem.* **2000**, *39*, 3894.

(9) Albertin, G.; Antoniutti, S.; Baldan, D.; Castro, J.; Garcia-Fontan, S. *Inorg. Chem.* **2008**, *47*, 742.

(10) Waterman, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2008**, *130*, 12628.

(11) (a) Mankad, N. P.; Muller, P.; Peters, J. C. *J. Am. Chem. Soc.* **2010**, *132*, 4083. (b) Takaoka, A.; Moret, M.-E.; Peters, J. C. *J. Am. Chem. Soc.* **2012**, *134*, 6695−6706.

(12) (a) Edwards, N. Y.; Eikey, R. A.; Loring, M. I.; Abu-Omar, M. M. *Inorg. Chem.* **2005**, *44*, 3700. (b) Abu-Omar, M. M.; Shields, C. E.; Edwards, N. Y.; Eikey, R. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6203.

(13) Piro, N. A.; Lichterman, M. F.; Harman, W. H.; Chang, C. J. *J. Am. Chem. Soc.* **2011**, *133*, 2108.

(14) (a) Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1025. (b) Smith, P. A. S.; Brown, B. B. J. *J. Am. Chem. Soc.* **1951**, *73*, 2438−2441.

(15) Liang, T.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1987**, *109*, 7803.

(16) Reiser, A.; Willets, F. W.; Terry, G. C.; Williams, V.; Marley, R. *Trans. Faraday Soc.* **1968**, *64*, 3265.