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Vanadium(V) Alkylidenes

A Transient V^{III}–Alkylidene Complex: Oxidation Chemistry Including the Activation of N_2 to Afford a Highly Porous Honeycomb-Like Framework**

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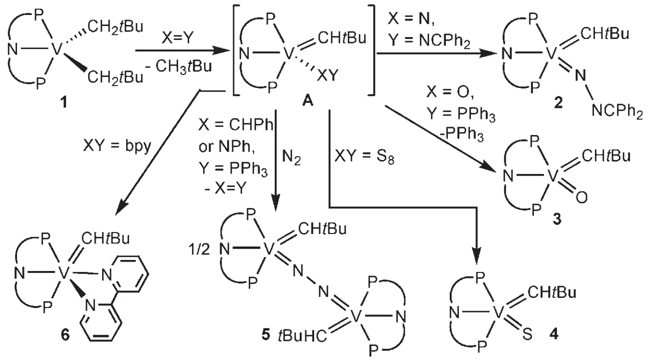
In memory of Rupert A. D. Wentworth and Harry G. Day

Terminal vanadium alkylidenes[1–4] still constitute a rare class of complexes, and this type of functional group, when combined with this metal, has been far less explored than its heavier congeners niobium[5,6] and tantalum.[6] Part of this limitation revolves around the ability of vanadium to populate low-valent oxidation states, especially the +3 state. As a result, alkylation reactions stemming from the high-valent metal complex often lead to reduction as opposed to the more prototypical transmetalation/α-hydrogen abstraction processes encountered in Nb^V and Ta^V alkylidenes.[6] Out of the few terminal vanadium alkylidene complexes known (e.g. V^{III},[1] V^{IV},[3] and V^V[4]), only the high-valent system appears to be highly reactive for ring-opening metathesis polymerization (ROMP).[4] Therefore, an entry to the V^V alkylidene group directly from a V^{III} precursor would represent an attractive synthetic strategy for this metal given the vast quantity of low-valent vanadium halide precursors available. In general, heat, photolysis, Lewis bases, or Brønsted bases can incite α-hydrogen abstraction to form Schrock-like M–C multiple bonds.[6,7] More recently, a one-electron oxidation step has been also shown to promote α-hydrogen abstraction.[7] When the metal is in a high-oxidation state, powerful Lewis acids such as $Al(CH_3)_3$ can also instigate α-hydrogen abstraction as well as trap the M–C multiple bond.[8–10] Although a handful of vanadium alkylidenes have been generated by treatment of a bis-alkyl precursor with PR_3,[1] the concept of using two-electron oxidants to promote α-hydrogen abstraction, to the extent of providing a facile entry to the V^V alkylidene unit, has not been realized.

Herein we demonstrate that π acids or two-electron oxidants can ultimately lead to α-hydrogen abstraction when the metal in question is a low-valent V^{III} bis-neopentyl species. As a result, a transient, four-coordinate V^{III} neopentylidene can be generated and trapped with a series of two-electron oxidants to afford a family of V^V alkylidenes. In the case where the π acid promoting the α-hydrogen abstraction is sterically crowded, N_2 becomes the substrate of choice to afford the first vanadium bridging end-on dinitrogen–alkylidene species. The solid state packing diagram for this complex displays a highly "porous" honeycomb-like framework along the activated N_2 unit. During the course of our investigation, we also discovered that the elusive V^{III} alkylidene generated in these set of reactions can be trapped with a chelate π acid such as 2,2′-bipyridine (bpy).

When the bis-alkyl precursor $[(PNP)V(CH_2tBu)_2]$ (**1**) ($PNP = N[4\text{-Me-}2\text{-}(PiPr_2)C_6H_3]_2^-$), readily prepared from a one-pot reaction of Li(PNP) and $[VCl_3(thf)_3]$ followed by alkylation with the appropriate stoichiometry of $LiCH_2tBu$,[11] was treated with N_2CPh_2 in diethyl ether, a gradual reaction ensued over a period of 12 h to afford the V^V alkylidene–diphenylmethylene hydrazido[12] complex $[(PNP)V(=CHtBu)(N_2CPh_2)]$ (**2**) in 62% yield after workup of the reaction mixture (Scheme 1). Likewise, treatment of **1** with $O=PPh_3$ in toluene over 24 h produces a color change from green to brown concurrent with formation of the alkylidene–oxo complex $[(PNP)V(=CHtBu)(O)]$ (**3**) and free PPh_3 (Scheme 1).[11] Complex **3** can be prepared, quantitatively and free of phosphine, by the reaction of **1** with N_2O in



Scheme 1. Synthesis of complexes **2**–**6** via intermediate **A** and from the bis-neopentyl–V^{III} precursor **1**. The $N[2\text{-}P(CHMe_2)_2\text{-}4\text{-methylphenyl}]_2$ framework has been simplified to the PNP cartoon.

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benzene at 90 °C. Treating **1** with other chalcogenide sources such as S_8 also results in α-hydrogen abstraction and two-electron oxidation at vanadium, to ultimately produce the terminal alkylidene–sulfide complex [(PNP)V(=CH*t*Bu)(S)] (**4**) in 32 % yield (Scheme 1). Further, this complex can be generated analogously to **3** by treatment of **1** with S=PR_3 in 48 % yield. As a result, two-electron redox chemistry in **1** appears to be a general process to produce the [(PNP)V^V(=CH*t*Bu)] scaffold. Characterization of **2**–**4** involves a combination of MS-CI, multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{31}P, and ^{51}V), and single crystal X-ray diffraction. Each system reveals diagnostic alkylidene α-hydrogen and α-carbon resonances in the ^{1}H ($\delta = 13.7$–4.78 ppm) and ^{13}C ($\delta = 335$–259 ppm, $J_{CH} = 102$–63 Hz) NMR spectra, respectively.[11] Experimental J_{CH} coupling values were obtained by a ^{13}C undecoupled HMQC experiment. Likewise, the ^{51}V NMR chemical shifts are consistent with hard ligands having high electronegativities inducing an overall high shielding (e.g., **2**, $\delta = -24$ ppm; **3**, $\delta = -58$ ppm), while the less electronegative and more polarizable sulfide derivative **4** confers a pronounced deshielding effect ($\delta = 570$ ppm).[13,14]

The solid-state structures of **2**–**4** expose mononuclear V^V complexes bearing terminal neopentylidene ligands (V=C: 1.83–1.89 Å) as well as terminal diphenylmethylene hydrazido (**2**, V=N: 1.7091(14) Å),[15] oxo (**3**, V=O: 1.595(4) Å),[16] and sulfide groups (**4**, V=S: 2.0706(13) Å),[17] all of which are oriented in a *cis* configuration with the alkylidene motif given the meridional constraint imposed by the PNP ligand template (Figure 1). The distorted V=C-C angles imply an α-hydrogen agostic interaction taking place with the high-valent vanadium center, which correlates well with our measured alkylidene J_{CH} values.

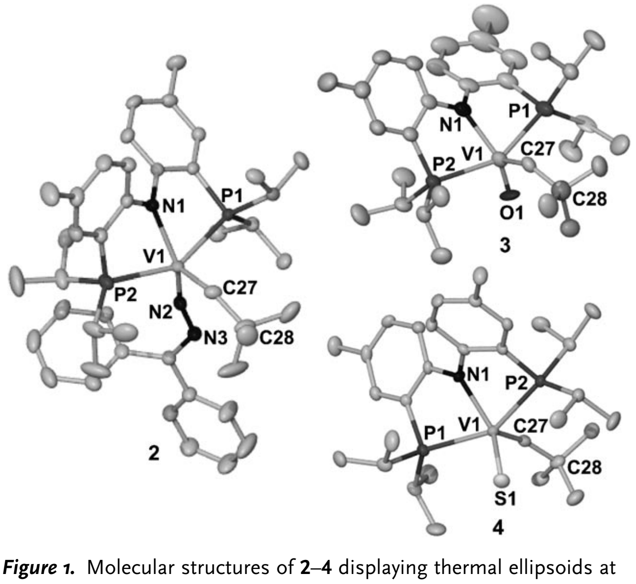

Figure 1. Molecular structures of **2**–**4** displaying thermal ellipsoids at the 50 % probability level. H-atoms have been excluded for clarity. Selected distances (in Å) and angles (in °): **2**: V1–C27 1.8246(18), V1–N1 2.1098(14), V1–N2 1.7091(14), V1–P1 2.4711(5), V1–P2 2.4554(6), N2–N3 1.3216(19); P1-V1-P2 149.127(19), V1-C27-C28 150.03(14). **3**: V1–C27 1.894(5), V1–N1 2.093(3), V1–O1 1.595(4), V1–P1 2.4811(10), V1–P2 2.4752(9); P1-V1-P2 152.28(4), V1-C27-C28 140.5(7). **4**: V1–C27 1.826(4), V1–N1 2.092(3), V1–S1 2.0706(13), V1–P1 2.4716(12), V1–P2 2.4768(12); P1-V1-P2 149.86(4), V1-C27-C28 155.2(3).

Sterics seem to play a critical role in the outcome of the reaction in that addition of the ylide Ph_3P=X (X = CHPh, NPh) to **1** provoked a very slow conversion over 48 h in toluene, under an atmosphere of N_2, to afford an alkylidene complex having a bridging, end-on dinitrogen unit, namely the compound [{(PNP)V(=CH*t*Bu)}$_2$(μ-N_2)] (**5**) shown in Scheme 1. The reaction likely operates from a putative V^{III} alkylidene intermediate [(PNP)V(=CH*t*Bu)(XY)] (**A**) (X = CHPh or NPh, Y = Ph_3P; **A**), which subsequently exchanges the coordinated ylide for N_2 to ultimately produce **5**. It is also possible that N_2 binds first without the ylide playing a role (see below). The initial steps en route to **2**–**4** are likely similar to those which we propose for complex **5**, but the substrates in the former cases are ultimately reduced to form terminal [(PNP)V^V(=CH*t*Bu)(=X)] complexes.

Complex **5** is a brown-colored diamagnetic material (^{51}V NMR: $\delta = -26$ ppm, $\Delta\nu_{1/2} = 1084$ Hz) that evinces a broad ^{15}N resonance at $\delta = 104$ ppm ($\Delta\nu_{1/2} = 517$ Hz) versus nitromethane referenced at $\delta = 0$ ppm. The enriched $^{15}N_2$ isotopologue of **1** is readily prepared with the appropriate ylide under an atmosphere of isotopically enriched $^{15}N_2$, thus indicating that the bridging N_2 unit originates from sequestration of atmospheric nitrogen. Complex **5** also reveals an intense and highly reduced symmetric ν_{NN} stretch in the Raman spectrum at 1370 cm^{-1}, a band blue shifted when compared to its isotopologue prepared with enriched $^{15}N_2$ (1325 cm^{-1}). The retention of the alkylidene unit from putative **A** is clearly evident from ^{13}C NMR ($\delta = 309.8$ ppm, $J_{CH} = 77$ Hz) and ^{1}H NMR spectroscopic data ($\delta = 10.2$ ppm).

It is important to note that complex **5** can also be formed under an N_2 atmosphere and without the ylide. Unfortunately, we have been unable to isolate the product resulting from the thermolysis of **1** in the absence of N_2. Likewise, when the resulting product(s) from the latter reaction are exposed to N_2, formation of **5** is not observed. Therefore, we propose that by first coordinating to **1**, the ylide or atmospheric nitrogen accelerates the α-hydrogen abstraction step. When solutions of **1** are heated to ca. 50 °C under an atmosphere of nitrogen, formation of **5** occurs over 3 days (80 % yield based on NMR).

Salient structural features for the vanadium alkylidene–dinitrogen dimer **5** are depicted in Figure 2. The structural data from a hexagonal single crystal reveals a terminal neopentylidene ligand having a short V=C bond of 1.863(4) Å and, as anticipated from the symmetric ν_{NN} and ^{15}N NMR data, a topologically linear μ-η^1:η^1-N_2 ligand bridging both vanadium centers. The V–N2 distance in **5** (1.757(3) Å)[18] is imide-like, suggesting that each metal center significantly backbonds to both nitrogen atoms composing the N_2 unit, and the VN_2V metrical parameters are comparable to other reduced dinitrogen complexes of vanadium.[19,20] In the structure of **5**, each {(PNP)V(=CH*t*Bu)(N)} fragment is related by symmetry, and its alkylidene functionalities are essentially orthogonal with respect to each other. The gross structural features of **5** closely resemble a Ta^V analogue prepared previously by Schrock by the two-electron reduction of a Ta^V alkylidene–dichloride precursor under an atmosphere of N_2.[21] The packing diagram of **5** (space group $R\bar{3}c$) also merits highlighting. In the unit cell, three large voids or channels along the N_2 vector are observed with dimensions

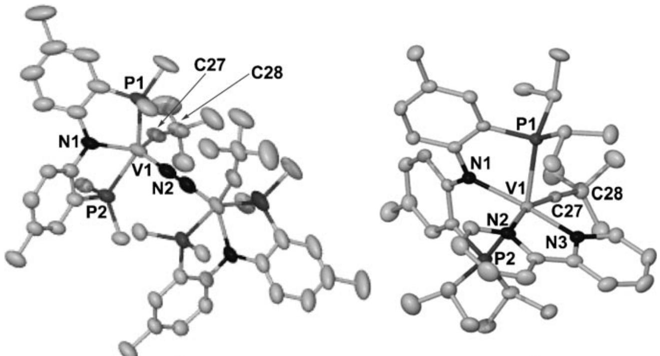

Figure 2. Molecular structures of **5** and **6** displaying thermal ellipsoids at the 50% probability level. H-atoms, isopropyl methyl groups on P (**5** only), and solvent (**5** only) have been excluded for clarity. Selected distances (in Å) and angles (in °): **5**: V1–C27 1.863(4), V1–N1 2.109(3), V1–N2 1.757(3), V1–P1 2.4567(11), V1–P2 2.4876(10), N2–N2′ 1.246(6); P1-V1-P2 149.94(4), V1-C27-C28 162.5(3). **6**: V1–C27 1.843(3), V1–N1 2.124(3), V1–N2 2.166(3), V1–N3 2.064(2), V1–P1 2.4788(9), V1–P2 2.4739(10); P1-V1-P2 152.58(3), V1-C27-C28 175.9(3).

3811.7 Å^3 per void, and located at (0,0,0) and symmetry related positions.[22] Such a feature translates into a remarkable volume of 11762.0 Å^3 (ca. 1/3) per unit cell in this honeycomb-type arrangement (Figure 3).[11,23] Notably, this type of architecture remains intact without solvent around thus behaving as a "porous" material. Further inspection of the aggregation between molecules reveals no significant interaction chemically intuitive for framework preassembly. Therefore, simple stacking of these molecules appears to dominate this unusual form of aggregation.

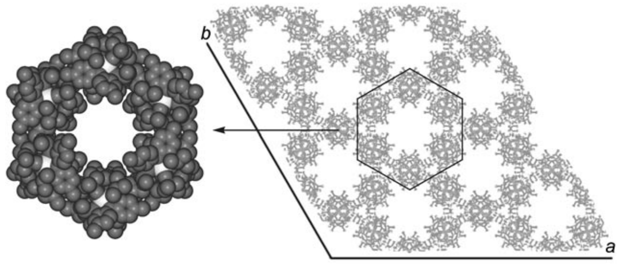

Figure 3. Packing plot of **5**, one channel (left) and 2×2 unit cells, view along the *c* axis (right) are shown. The uneven channels have an approximate solvent-accessible width of 12.4 Å.

Attempts to trap the elusive V^{III} alkylidene **A** were unsuccessful when π acids such as PR$_3$ were used with precursor **1**. Teuben and co-workers have reported a diamagnetic V^{III}–alkylidene species from treatment of the bisalkyl precursor [CpV(CH$_2$CMe$_3$)$_2$(PMe$_3$)] with the chelating diphosphine dmpe.[24] In our case, treatment of **1** with a bischelate such as bpy in toluene promoted a color change from green to blue, to ultimately afford a diamagnetic product as implied by its ^{51}V NMR spectrum centered at $\delta = 996$ ppm ($\Delta\nu_{1/2} = 581$ Hz). The ^{1}H and ^{13}C NMR spectra were consistent with a terminal alkylidene complex having a coordinated bpy ligand, namely the complex [(PNP)V(=CH*t*Bu)(bpy)] (**6**) depicted in Scheme 1. This result implies that formal oxidation of the metal center is not a strict requirement for α-hydrogen abstraction but coordination of a π acid to **1**.

For the solid-state structure of **6**,[25] the vanadium center is confined in a pseudo octahedral geometry where significant π backbonding between V^{III} and the bpy ligand has taken place when judged by the short V–N distances of 2.064(2) and 2.166(3) Å (Figure 2). The alkylidene unit (V=C, 1.843(3) Å) for **6** is virtually linear (175.9(3) Å) and oriented along the same plane defined by the bpy ligand. Linearity about the V=C-C unit is further manifested by the exceedingly low J_{CH} of 63 Hz for the alkylidene carbon. We strongly believe the distortion of the alkylidene ligand to be governed by the octahedral coordination environment of the vanadium ion.[1]

The reactivity of **1** has shown it to be a powerful two-electron reductant as well as convenient source of the V^V alkylidene fragment. Whether substrate binding precedes α-hydrogen abstraction along the two-electron process is questionable at this point given our inability to isolate the product from the thermolysis of **1** in the absence of a π base. Studies which shall further demonstrate the reactivity of the rare V^V alkylidene unit, as well as the mechanism to its formation, are currently underway and will be reported in due course.

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[15] Crystal data for **2**: $C_{44}H_{60}N_3P_2V$, $M_r = 743.83$, monoclinic, space group $P2_1/n$, $a = 9.9043(12)$, $b = 33.619(4)$, $c = 13.2774(16)$ Å, $\beta = 108.262(4)$, $Z = 4$, $\mu = 0.345\ \mathrm{mm^{-1}}$, $\mathrm{Mo_{K\alpha}} = 0.71073$ Å, $V = 4198.4(9)$ Å^3, $T = 140(2)$, $\rho_{calcd} = 1.177\ \mathrm{mg\,mm^{-3}}$, GoF on $F^2 = 0.930$, $R_1 = 3.39\,\%$ and $wR_2 = 8.86\,\%$ (F^2, all data). Data/restraints/parameters: 6464/102/447. Out of a total of 57137 reflections collected 8637 were unique and 6416 were observed ($R_{int} = 7.71\,\%$) with $I > 2\sigma I$ (red plate, $0.10 \times 0.10 \times 0.08$ mm, $26.43° \geq \theta \geq 2.02°$).[26]

[16] Crystal data for **3**: $C_{31}H_{51}NOP_2V \cdot 0.5\,C_5H_{10}$, $M_r = 601.67$, triclinic, space group $P\bar{1}$, $a = 10.6282(13)$, $b = 11.5935(13)$, $c = 14.7057(18)$ Å, $\alpha = 79.862(3)$, $\beta = 82.650(3)$, $\gamma = 76.213(3)°$, $Z = 2$, $\mu = 0.405\ \mathrm{mm^{-1}}$, $\mathrm{Mo_{K\alpha}} = 0.71073$ Å, $V = 1725.3(4)$ Å^3, $T = 150(2)$, $\rho_{calcd} = 1.158\ \mathrm{mg\,mm^{-3}}$, GoF on $F^2 = 1.033$, $R_1 = 5.46\,\%$ and $\mathrm{w}R_2 = 16.56\,\%$ (F^2, all data). Data/restraints/parameters: 7444/0/339. Out of a total of 25795 reflections collected 6464 were unique and 4685 were observed ($R_{int} = 5.13\,\%$) with $I > 2\sigma I$ (light-brown plate, $0.18 \times 0.10 \times 0.03$ mm, $1.41° \geq \theta \geq 25.60°$).[26]

[17] Crystal data for **4**: $C_{31}H_{50}NP_2SV$, $M_r = 581.66$, orthorhombic, space group $Pbca$, $a = 12.8505(5)$, $b = 14.1120(5)$, $c = 35.0506(13)$ Å, $Z = 8$, $\mu = 0.498\ \mathrm{mm^{-1}}$, $\mathrm{Mo_{K\alpha}} = 0.71073$ Å, $V = 6356.3(4)$ Å^3, $T = 150(2)$, $\rho_{calcd} = 1.216\ \mathrm{mg\,mm^{-3}}$, GoF on $F^2 = 1.061$, $R_1 = 6.41\,\%$ and $wR_2 = 17.93\,\%$ (F^2, all data). Data/restraints/parameters 8637/0/464. Out of a total of 55151 reflections collected 8061 were unique and 6549 were observed ($R_{int} = 6.66\,\%$) with $I > 2\sigma I$ (brown plate, $0.20 \times 0.20 \times 0.02$ mm, $25.17° \geq \theta \geq 1.16°$). Non-merohedrally twin with twin domain ratio 60:40. 180° rotation about 001 in reciprocal space, twin law by the rows: $-1\,0\,0$, $0\,-1\,0$, $0\,0.154\,1$.[26]

[18] Crystal data for **5**: $C_{62}H_{100}N_4P_4V_2$, $M_r = 1127.22$, hexagonal, space group $R\bar{3}c$, $a = b = 40.5424(13)$, $c = 26.567(2)$ Å, $Z = 18$, $\mu = 0.328\ \mathrm{mm^{-1}}$, $\mathrm{Mo_{K\alpha}} = 0.71073$ Å, $V = 37818(4)$ Å^3, $T = 130(2)$, $\rho_{calcd} = 0.891\ \mathrm{mg\,mm^{-3}}$, GoF on $F^2 = 1.100$, $R_1 = 6.03\,\%$ and $wR_2 = 18.82\,\%$ (F^2, all data). Data/restraints/parameters: 8061/0/339. Out of a total of 149303 reflections collected 7444 were unique and 5094 were observed ($R_{int} = 12.64\,\%$) with $I > 2\sigma I$ (brown block, $0.15 \times 0.08 \times 0.07$ mm, $25.04° \geq \theta \geq 1.92°$). Three large voids (channels) with 3811.7 Å^3 each, at 000 and symmetry related positions; that is 11762.0 Å^3 (or about 1/3) per unit cell.[26]

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[25] Crystal data for **6**: $C_{41}H_{58}N_3P_2V$, $M_r = 705.78$, monoclinic, space group $P2_1/n$, $a = 17.3797(10)$, $b = 11.5075(6)$, $c = 20.6650(12)$ Å, $\beta = 111.962(1)°$, $Z = 4$, $\mu = 0.374\ \mathrm{mm^{-1}}$, $\mathrm{Mo_{K\alpha}} = 0.71073$ Å, $V = 3833.0(4)$ Å^3, $T = 150(2)$, $\rho_{calcd} = 1.223\ \mathrm{mg\,mm^{-3}}$, GoF on $F^2 = 1.062$, $R_1 = 6.07\,\%$ and $wR_2 = 17.79\,\%$ (F^2, all data). Data/restraints/parameters 7304/0/441. Out of a total of 28455 reflections collected 7304 were unique and 5436 were observed ($R_{int} = 6.97\,\%$) with $I > 2\sigma I$ (dark brown block, $0.15 \times 0.12 \times 0.11$ mm, $25.84° \geq \theta \geq 2.06°$).[26]

[26] CCDC-670631 (**2**), CCDC-670632 (**3**), CCDC-670633 (**4**), CCDC-670634 (**5**), and CCDC-670635 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.