Unusual [2 + 2] Cycloaddition Adducts of an Imidovanadium Complex with Alkynes and Ethene: Conversion to η^3-1-Azaallyl and Ethenyl Complexes

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Summary: 2-Butyne displaces Et_2O *from (RNH)*-*(RN=)*$_2$*V*(OEt_2) *(**3**; R = t-Bu*$_3$*Si) at 25 °C to afford crystalline (RNH)(RN=)V{C(Me)=C(Me)N(R)} (**5a**), which undergoes ligand metalation to give complex **4a**. Thermolysis of (RNH)*$_2$*(RN=)VMe (**2a**) in the presence of alkynes also yields (RNH)(RN=)V{*η^1:η^3-$CH_2C(Me)_2$-*Si(t-Bu)*$_2$*NC(R′)CHR′} (R′ = Me (**4a**), Et (**4b**)); the X-ray structure of **4b** shows the first example of* η^3*-azaallyl coordination to a d*^{0} *transition metal. Ethene reacts reversibly with **3** to afford fluxional (RNH)(RN=)V{*CH_2-CH_2*N(R)} (**7a**), which slowly rearranges to (RNH)*$_2$-*(RN=)V(CH=*CH_2*) (**6a**), analogous to related complexes obtained from **2a** and 1-alkenes at 80 °C.*

Despite the wide utilization of imido ligands in high-oxidation-state complexes,[1-5] examples of the addition of hydrocarbon bonds to the M=NR bond have only recently been reported. Unsaturated substrates have shown either C—H activation[2] or cycloaddition reactivity[3] with imido ligands in coordinatively unsaturated complexes. In an attempt to extend the rich hydrocarbon activation chemistry exhibited by electrophilic d^0 metallocene complexes[6] to the poorly studied vanadium(V), we,[4] and others,[5] have utilized bulky electronegative ligands, particularly imido ligands,[4,5a-d] to synthesize robust hydrocarbylvanadium(V) complexes. Following Wolczanski's demonstration of C—H bond addition to the polar imido bond in transient RN=Zr(NHR)$_2$ (R = *t*-Bu$_3$Si),[2a] we have recently reported a first-row bis(imido) system, (RN=)$_2$V(NHR) (**1**), which activates alkanes, alkenes, benzene, and acetone to give (RNH)$_2$(RN=)VR′.[7] Unstable **1** is generated on thermolytic expulsion (80 °C) of methane from (RNH)$_2$(RN=)VMe (**2a**) and may be trapped as the labile Et_2O adduct **3**. We now report that the reaction of **3** with alkynes and ethene at 25 °C affords novel cycloaddition adducts, which cleanly rearrange to unusual C—H activation products.

Thermolysis of cyclohexane solutions of **2a** in the presence of 5–10 equiv of 2-butyne or 3-hexyne (80 °C, 16 h) affords quantitative yields of the red complexes **4a** and **4b**, respectively, which may be recrystallized from pentane solution. The same compounds are obtained under milder conditions by reaction of **3** with the alkynes for 16 h at 25 °C (vide infra). Elemental analyses are consistent with formation of a 1:1 adduct of **1** and alkyne, but ^{1}H, ^{13}C, and ^{51}V NMR spectroscopy[8] and a single-crystal X-ray structural study (for **4b**) show that simple cycloaddition or C—H activation products have not been obtained. The complexes contain a novel chelating ligand, showing unprecedented η^3-azaallyl coordination to a d^0 transition metal (Scheme I).

The X-ray structure of **4b** (Figures 1 and 2)[9] shows that the vanadium is coordinated by amido and imido ligands as well as an unusual {$CH_2C(Me)_2Si(t\text{-}Bu)_2NC(Et)CHEt$} ligand, bonded by V–alkyl and η^3-azaallyl interactions. The azaallyl fragment shows highly asymmetric η^3 coordination to vanadium, with the V–N(1) distance of 2.043(3) Å significantly less than the V–C(1) and –C(2) distances of 2.335(4) and 2.384(4) Å. The asymmetry in **4b** is

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[8] **4a**: ^{1}H NMR (C_6D_{12}) δ 9.3 (NH), 3.71 (C*H*Me), 2.79 (br, VCH_AH_B), 2.39 (br d, $^3J_{HH}$ = 10 Hz, VCH$_A$$H_B$), 2.21 ((NC(Me)), 1.82 (d, CH*Me*), 1.59 (C(Me_A)(Me_B)), 1.26, 1.20, 1.14, 1.09 (27H, 9H, 27H, 9H, CMe$_3$), Me$_B$ not observed; ^{13}C NMR (C_6D_{12}) δ 149.8 (*C*Me), 83.3 (d, $^1J_{CH}$ = 146 Hz, *C*HMe), 40.0 (*C*Me$_2$), 34.9 (NC(*Me*)), 31.8, 31.5 (9C, C*Me*$_3$), 31.4, 30.6 (3C, C*Me*$_3$), 25.4, 24.8 (3C, *C*Me$_3$), 24.8, 23.8 (1C, *C*Me$_3$), 21.6, 16.0 (C*Me*$_2$), V*C*H$_2$ and CH*Me* not observed. **4b**: ^{1}H NMR (C_6D_{12}) δ 9.3 (NH), 3.60 (C*H*Et), 3.0 (m, NC(CH_CH$_D$CH$_3$)), 2.8 (br, VCH_AH$_B$), 2.39 (br d, $^3J_{HH}$ = 9 Hz, VCH$_A$$H_B$), 2.23 (m, 2H, CH(C$H_2CH_3$)), 1.61 (C($Me_A$)(Me$_B$)), 1.26, 1.19, 1.15, 1.13 (27H, 9H, 27H, 9H, C*Me*$_3$), H_D and Me$_B$ not observed; ^{13}C NMR (C_6D_{12}) δ 155.2 (*C*Et), 92.2 (d, $^1J_{CH}$ = 146 Hz, *C*HEt), 40.0 (*C*Me$_2$), 35.0 (NC(*C*H$_2$CH$_3$)), 31.9, 31.7 (9C, C*Me*$_3$), 31.7, 31.6 (3C, C*Me*$_3$), 29.0 (1C, CH(*C*H$_2$CH$_3$)?), 25.5 (3C, *C*Me$_3$), 25.1 (1C, *C*Me$_3$?), 24.8 (3C, *C*Me$_3$), 24.3, 24.2 (1C, CH$_2$*C*H$_3$?), 22.8 (3C, *C*Me$_3$), 17.4, 13.9 (C*Me*$_2$), V*C*H$_2$ not observed.

[9] Crystal data for **4b**·0.5C_6H_{14}: $C_{45}H_{99}N_3Si_3V$, M_r = 817.5, monoclinic, space group $P2_1/n$ (No. 14), a = 13.837(2) Å, b = 17.078(2) Å, c = 21.456(2) Å, β = 90.62(2)°, V = 5071(2) Å^3, Z = 4, D_{exptl} = 1.07 g cm^{-3}, $F(000)$ = 1832 e, T = 200 K, graphite-monochromated Mo Kα radiation, λ = 0.710 69 Å, μ(Mo Kα) = 2.9 cm^{-1}; R = 0.056, R_w = 0.065, and S = 1.72 for 5302 independent absorption-corrected intensities with $I > 3\sigma(I)$ and $4 < 2\theta < 50°$.

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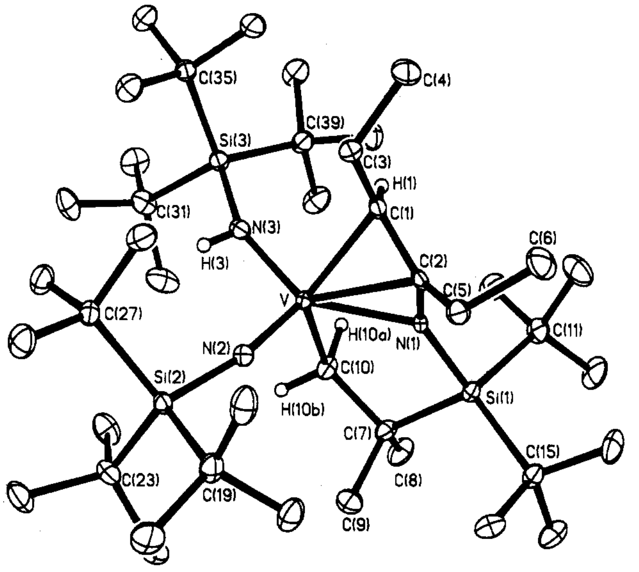


Figure 1. Molecular geometry of **4b** with 30% probability ellipsoids. Selected bond distances (Å): C(1)–C(2), 1.381(6); C(2)–N(1), 1.359(5).

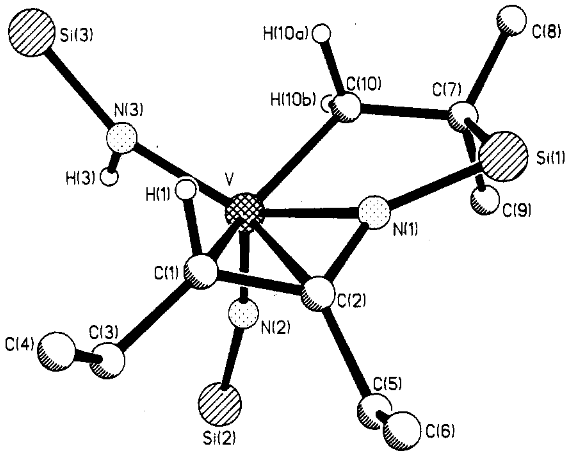
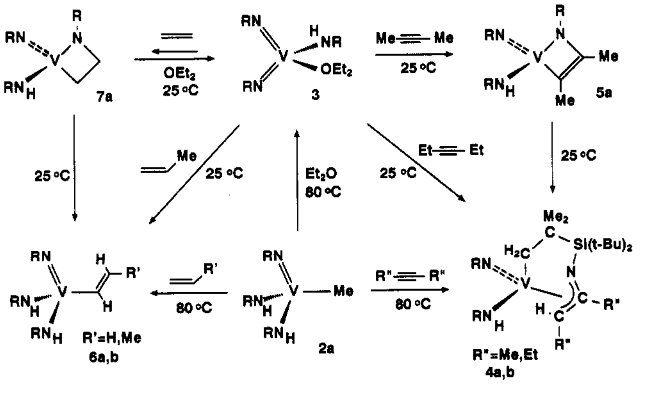


Figure 2. Alternative view of the structure of **4b**, with all *tert*-butyl atoms omitted.

Scheme I. Alkene and Alkyne Reactivity of Vanadium Complexes



reminiscent of bonding in Li$^+$–η^3-azaallyl complexes[10] but contrasts sharply with that in η^3-1-azaallyl complexes of less electrophilic transition metals,[11] with roughly similar M–C and M–N bond lengths. Rotation of the (anti-oriented) lone pair on nitrogen toward vanadium, facilitating lone-pair donation, is suggested by the apparent rotation of the syn substituent Si(1) away from the metal (torsion angle C(1)C(2)N(1)Si(1) is 155.0(5)°). However, the asymmetric azaallyl coordination and the near-planar nature of the geometry at N(1) (the sum of the bond angles at N(1) is 357.4°) may also partly reflect the geometrical constraints imposed by ligand chelation. The relatively long bonds from V to C(10)[4,12] and to the imido and the amido nitrogens[13] of 2.106(5), 1.676(3), and 1.883(4) Å, respectively, as well as the near-linearity of the imido group (V–N(2)–Si(2) = 169.4(2)°) and the large amido V–N(3)–Si(3) angle (156.8(2)°), may all reflect the steric crowding in the complex.[13c]

Observation of azaallyl *C*R, *C*HR, and C*H*R resonances for **4a** [and **4b**] at δ 149.8 [155.2], 83.3 [92.2] ($^1J_{CH}$ = 146 [144] Hz), and 3.71 [3.60] ppm, respectively, suggests that η^3 coordination of the fragment persists in solution. The similar locations of the ^{51}V NMR resonances (C_6D_{12}) of **4a** and **4b**, at δ 72.0 and 68.0 ppm, respectively, suggests that increased azaallyl bulk has little effect on the ligand coordination to crowded vanadium.

Careful ^{1}H NMR monitoring of the reaction at 25 °C of **3** with 2-butyne (3 equiv) in CD_2Cl_2 shows the gradual formation of free ether and a single intermediate, **5a**, which is converted cleanly to **4a** over 16 h. Cooling the solution containing **3**, **5a**, and **4a**, present as a 10%:55%:35% mixture (after 2 h, 25 °C), to −60 °C affords red crystals of analytically pure **5a**, which, on dissolution, are cleanly converted to **4a**. The 3-hexyne reaction proceeds via a similar, but unisolated, intermediate, **5b**. The NMR data for **5a**,[14] particularly the observation of two distinct ring methyl groups (^{1}H NMR, C_6D_{12}: δ 2.62, 2.59 ppm)[15] and three inequivalent Si-*t*-Bu$_3$ groups, is consistent with a static 2-azavanadacyclobutene structure (Scheme I),[3] rather than an η^2-alkyne structure. The driving force for the formation of **4a**, by *formal* transfer of a *tert*-butyl hydrogen in **5a** to the 4-carbon of the ring, may be the increase in the maximum electron-donating capacity of the 2− fragment, from six to eight electrons. Metalation of the ligand *tert*-butyl group is precedented by the formation of (RNH)(RN=)V{NSi(*t*-Bu)$_2$C(Me)$_2$CH$_2$} on decomposition of **1** at 80 °C.[7]

[2 + 2] cycloaddition reactions of imido ligands with alkenes, affording 2-azametallacyclobutane complexes,[16]

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(14) **5a**: ^{1}H NMR (C_6D_{12}) δ 7.55 (NH), 2.62, 2.59 (CMe), 1.27, 1.24, 1.07 (CMe$_3$); ^{13}C NMR (CD_2Cl_2, 0 °C) δ 31.3, 30.4, 30.2 (9C, CMe$_3$), 23.8 (6C, CMe$_3$), 22.6 (3C, CMe$_3$), solubility problems prevented observation of the *C*Me resonances.

(15) In CD_2Cl_2, the chemical shifts of the C*Me* resonances of **5a** show a slight temperature dependence, but there is no evidence for exchange broadening. At 25 °C, the resonances are accidentally coincident (δ 2.55 ppm) and at −80 °C are found at δ 2.55 and 2.49 ppm.

(16) [3 + 2] cycloaddition reactions of Os-bis(imido) fragments with alkenes have been reported: (a) Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420. (b) Schofield, M. H.; Kee, T. P.; Anhaus, J. T.; Schrock, R. R.; Johnson, K. H. *Inorg. Chem.* **1991**, *30*, 3595.

are unknown.[17] The reported synthesis of a variety of 2-oxametallacyclobutane derivatives,[18] in one case via reaction of an oxo ligand with an alkene,[18a] suggested that 2-azametallacyclobutane complexes might be accessible by reaction of alkenes with **3**, analogous to the formation of **5a**. Propene and ethene are cleanly activated at 25 °C on reaction with **3** in CD_2Cl_2, affording red crystalline alkenyl complexes **6b** and **6a** (Scheme I)[7,19] after 30 min and 2 days, respectively. C—H activation of $CH_2{=}CHR'$ by **2a** at 80 °C also affords alkenyl complexes **6** (Scheme I), but a crystalline product is obtained only for $CH_2{=}CH$-t-Bu.[7] ^1H NMR monitoring of the reaction of **3** with ethene shows the rapid formation ($t_{1/2}$ = 20 min) of another complex, **7a**, and free Et_2O, in an equilibrium reaction, followed by slow conversion to **6a**. The equilibrium **3** + $C_2H_4 \rightleftarrows$ **7a** + Et_2O may be displaced using high ethene pressures; the reaction of **3** in CD_2Cl_2 with 20 bar of ethene (2 h, 25 °C), followed by cooling to −70 °C, affords analytically pure red crystals of **7a**, which is a 1:1 adduct of **1** and ethene (Scheme I). Pure **7a** at 25 °C is cleanly converted to **6a** in the solid state, or in CD_2Cl_2 solution, with $t_{1/2}$ values of ca. 3 days and 6 h, respectively.

Complex **7a** has been further characterized by ^1H, ^{13}C, and ^{51}V NMR spectroscopy[20] as a fluxional 2-azavanadacyclobutane species.[17] Although **7a** in CD_2Cl_2 solution shows *single* ^1H (25 °C) and ^{13}C NMR resonances (−20 °C) for the $-CH_2CH_2-$ fragment at δ 3.22 and 48.3 ppm, respectively, the upfield location of the CH_2 resonances, which are greatly displaced from those of free C_2H_4 (^1H NMR, δ 5.44; ^{13}C NMR, 122.6 ppm), rules out η^2-ethene coordination, expected to be very weak for a d^0 metal.[21] The high $^1J_{CH}$ value of 149 Hz for the $-CH_2CH_2-$ fragment might be seen as evidence for sp^2 hybridization, but similar values have been observed in metallacyclobutane complexes.[22] The similar location of the ^{51}V NMR resonances (CD_2Cl_2) of **7a** and **5a** at δ −3 and −1 ppm, respectively, suggests that the complexes have related structures. However, facile ring breakup on the NMR time scale occurs only for **7a**. Thus, **7a** shows ^1H NMR resonances for two different nitrogen ligands in a 1:2 ratio, whereas **5a** shows three inequivalent nitrogen ligands. Furthermore, ethene displacement by THF is rapid for **7a** (<5 min, 25 °C), giving $(RNH)(RN{=})_2V(THF)$, while **5a** does not react with THF.

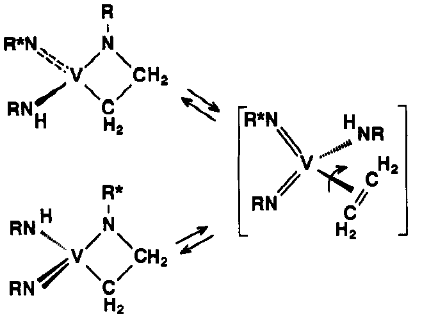

Figure 3. Proposed mechanism of enantiomer interconversion for complex **7a**.

Involvement of complete ethene dissociation from **7a** in the fluxional process which exchanges the environments of the $-CH_2CH_2-$ atoms, and of two of the nitrogen ligands, may be ruled out by the observation of a sharp resonance for free dissolved C_2H_4 (up to 0.1 equiv observed on dissolution of **7a**) in the presence of **7a**. Exchange of the two NR fragments may occur via breakup of the 2-azavanadacyclobutane ring in one enantiomer to give a transient η^2-ethene bis(imido) species, followed by ethene rotation, and re-formation of the 2-azavanadacyclobutane ring utilizing one or the other of the NR fragments (Figure 3). In the latter case, involving formation of the other enantiomer of **7a**, all the ethene hydrogens (as well as the carbons) may be exchanged, whereas simple ring breakup and re-formation with the same "imido" fragment exchanges only trans hydrogens (and the carbons). The remarkably facile nature of ring breakup in **7a** is illustrated by the fact that significant broadening of the CH_2 resonance occurs only at −90 °C (when a 2:1 pattern of *R*N resonances is still observed).[23]

Facile formation of the coordinatively unsaturated bis(imido) species **1** reflects the relief of steric crowding on extrusion of Et_2O from **3**. The unusual reactivity of **1** with alkenes and alkynes is probably related to high imido nitrogen nucleophilicity, resulting from competition for the available π-accepting orbitals at vanadium in the bis(imido) species.[7] Crowding in the 2-azavanadacyclobutane complex may explain the apparently facile (and reversible) extrusion of ethene and the instability of the analogous propene adduct; alkene extrusion from 2-oxametallacyclobutane rings has been reported.[18b–f] In contrast to **7a**, the ring in **5a** is static on the NMR time scale, and alkyne is not displaced by THF. Consistent with this, (reversible) alkyne extrusion from known 2-azametallacyclobutenes[3a] (and related oxa- and thiametallacyclobutenes)[24] occurs only on extended heating. Implication of **5a** as an intermediate in the formation of **4a** via (direct or indirect) hydrogen transfer from a t-Bu group to the ring 4-carbon therefore appears likely, whereas formation of C—H activation product **6a** presumably requires ring breakup in **7a**. This novel cycloaddition and C—H activation chemistry suggests that a wide range of unsaturated substrates should undergo similar reactions with **3** and related complexes.

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[18] 2-Oxametallacyclobutane complexes: (a) Day, V. W.; Klemperer, W. G.; Lockledge, S. P.; Main, D. J. *J. Am. Chem. Soc.* **1992**, *112*, 2031. (b) Whinnery, L. L.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *113*, 7575. (c) Bazan, G. C.; Schrock, R. R.; O'Regan, M. B. *Organometallics* **1991**, *10*, 1062. (d) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 3234. (e) Miyashita, A.; Ishida, J.; Nohira, H. *Tetrahedron Lett.* **1986**, *27*, 2127. (f) Ho, S. C.; Hentges, S.; Grubbs, R. H. *Organometallics* **1988**, *7*, 780. (g) Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *111*, 3079. (h) Zlota, A. A.; Frolow, F.; Milstein, D. *J. Am. Chem. Soc.* **1990**, *112*, 6411.

[19] **6a**: ^1H NMR (CD_2Cl_2) δ 9.2 (br, NH), 7.67 (dd, $^3J_{HH}$ = 18.4, 12.5 Hz, VCH═), 6.2, 5.7 (br, ═CH_2), 1.27, 1.19 (27H, 54H, CMe_3); ^{13}C NMR (CD_2Cl_2) δ 129.2 (t, $^1J_{CH}$ = 155 Hz, ═CH_2), 30.8, 30.5 (9C, 18C, C*Me*$_3$), 24.6, 23.2 (3C, 6C, *C*Me_3), V*C*H═ not observed; ^{51}V NMR (CD_2Cl_2) δ 66 ($\Delta\nu_{1/2}$ = 290 Hz).

[20] **7a**: ^1H NMR (CD_2Cl_2) δ 9.3 (NH), 3.22 (CH_2), 1.21, 1.10 (s, 54H, 27H, CMe_3); ^{13}C NMR (CD_2Cl_2, −20 °C) δ 48.3 (CH_2), 30.7, 30.1 (18C, 9C, C*Me*$_3$), 24.1, 23.2 (6C, 3C, *C*Me_3).

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Supplementary Material Available: Text giving full details of the preparation and characterization of the compounds and details of the structural characterization of **4b** and tables of the atomic coordinates, bond distances and angles, anisotropic displacement parameters, and hydrogen atomic parameters for **4b** (14 pages). Ordering information is given on any current masthead page.

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