Isolation and Structural Characterization of the Terminal Mesityl Azide Complex $V(N_3Mes)(I)(NRAr_F)_2$ and Its Conversion to a Vanadium(V) Imido Complex

Michael G. Fickes, William M. Davis, and
Christopher C. Cummins*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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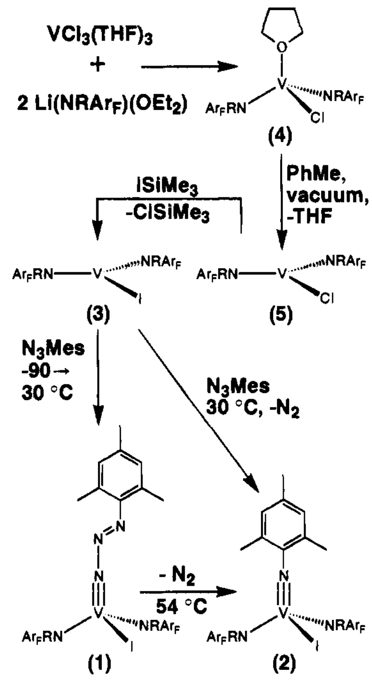
Transition metal imido complexes have risen to prominence among metal–ligand multiply bonded systems because of the diverse range of chemistry in which they participate.[1] One standard strategy for the synthesis of arylimido complexes is the reaction of an organic azide with a metal complex capable of undergoing 2e oxidation.[1] Although organoazide complexes have been proposed as intermediates prior to dinitrogen evolution,[2] it appears that none have previously been isolated and fully characterized. Herein we report the isolation and structural characterization of an unusually stable terminal mesityl azide complex, $V(N_3Mes)(I)(NRAr_F)_2$ (**1**; $R = C(CD_3)_2CH_3$, Ar_F = 2,5-C_6H_3FMe, Mes = 2,4,6-$C_6H_2Me_3$), in which the aryl azide moiety is best described as a "diazenylimido" ligand. The synthesis of **1** is presented along with preliminary mechanistic information regarding its conversion to the imido complex $V(NMes)(I)(NRAr_F)_2$ (**2**) at 54 °C.

The vanadium(III) complex $V(I)(NRAr_F)_2$ (**3**) was synthesized in three steps (Scheme 1). Slow addition of a THF solution of $Li(NRAr_F)(OEt_2)$[3] (7.484 mmol, 0.05 M) to a THF slurry of $VCl_3(THF)_3$ (3.743 mmol) led to the isolation of $V(THF)(Cl)(NRAr_F)_2$ (**4**) in 65% yield.[4] The THF-free species $V(Cl)(NRAr_F)_2$ (**5**) was obtained as a forest green crystalline solid in 92% yield by trituration with toluene.[5] $V(Cl)(NRAr_F)_2$ (**5**) exhibits a μ_{eff} of 2.60 μ_B in benzene-d_6, suggesting that the complex is probably not exclusively monomeric in hydrocarbon solvents.[6] For this reason, and because of the relatively low solubility of **5**, the chloride was replaced with iodide. A solution of $ISiMe_3$ (434 μL, 3.05 mmol) in ether was added to a stirred slurry of **5** (1.3697 g, 2.985 mmol) in 50 mL of cold (≅−100 °C) ether, leading to the isolation of $V(I)(NRAr_F)_2$ (**3**) in 88% yield after warming to 30 °C and recrystallization (pentane, −35 °C). Dark brown crystalline **3** has good solubility in hydrocarbon solvents and a μ_{eff} of 3.01 μ_B.[7]

A dark, yellow-brown solution of $V(I)(NRAr_F)_2$ (**3**, 2.1793 mmol) in ether was cooled to ca. −100 °C, whereupon it turned emerald green.[8] Dropwise addition of mesityl azide (2.231 mmol) as a 0.750 M solution in ether resulted in an immediate color change to reddish brown. After the magnetically-stirred reaction mixture had warmed to 30 °C, it was cooled to −35 °C to provide crystalline **1** in 79% isolated yield (three crops).[9] Because **1** was found to be diamagnetic, yet possessed ^{1}H, ^{13}C, ^{19}F, and ^{51}V NMR spectra completely different from those of imido **2** (see below), the structure of **1** was determined by X-ray diffraction.[10]

Scheme 1



The structure of $V(N_3Mes)(I)(NRAr_F)_2$ (**1**; Figure 1) is readily interpreted in terms of 2e reduction of the aryl azide concomitant with complexation of its terminal nitrogen atom. The complexed $MesN_3$ unit is best described as a "diazenylimido" ligand in that the V–N(1) distance for **1** (1.662(4) Å) is nearly as short as the corresponding distance (1.645(7) Å) for imido **2**. A pseudo-triple bond between V and N(1) is thereby indicated.[11] The nearly linear V–N(1)–N(2) angle for **1** (169.1(4)°) also compares well with the V–N–C angle (175.7(7)°) for **2**. A double bond between N(2) and N(3) is indicated by their 1.198(6) Å separation, which is slightly shorter than the corresponding distance (1.243(3) Å) in *trans*-azobenzene.[12] As is typical for aryl azo compounds, the mesityl ring in **1** is essentially coplanar with the plane defined by nitrogens 1, 2, and 3.[13]

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(1) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

(2) Hillhouse, G. L.; Haymore, B. L. *J. Am. Chem. Soc.* **1982**, *104*, 1537. Gambarotta, S.; Chiesi-Villa, Guastini, C. *J. Organomet. Chem.* **1984**, *270*, C49. Osborne, J. H.; Rheingold, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 7945. Antonelli, D. M.; Schaefer, W. P.; Parkin, G.; Bercaw, J. E. *J. Organomet. Chem.* **1993**, *462*, 213.

(3) The synthesis of $Li(NRAr_F)(OEt_2)$ is directly analogous to that reported for $Li(NRAr)(OEt_2)$ ($R = C(CD_3)_2CH_3$, Ar = 3,5-$C_6H_3Me_2$): Laplaza, C. E.; Davis, W. M.; Cummins, C. C. *Organometallics* **1995**, *14*, 577. Data specific to $Li(NRAr_F)(OEt_2)$ will be reported in due course.

(4) ^{2}H NMR (THF): 12.1 ($\Delta\nu_{1/2}$ = 29 Hz). Anal. Calcd for $C_{26}H_{26}ClD_{12}F_2N_2OV$: C, 58.80; H, 7.21; N, 5.27. Found: C, 58.86; H, 6.97; N, 5.14. Magnetism: $\mu_{eff} = 2.87\ \mu_B$ (C_6H_6, 28 °C). Crystal data: a = 10.608(3) Å, b = 15.162(3) Å, c = 16.713 (1) Å, β = 98.57(3)°, V = 2658(2) Å^3, space group $P2_1/c$, $Z = 4$, mol wt = 518.99 for $C_{26}H_{26}ClD_{12}N_2OV$, and d(calcd) = 1.297 g/cm^3; $R = 0.098$ and $R_w = 0.088$. $V(THF)(Cl)(NRAr_F)_2$ is a pseudotetrahedral monomer in the solid state and has a structure comparable to that suggested for $V(THF)(Cl)[N(SiMe_3)_2]_2$: Berno, P.; Minhas, R.; Hao, S. K.; Gambarotta, S. *Organometallics* **1994**, *13*, 1052.

(5) ^{2}H NMR (C_6H_6): 10.8 ($\Delta\nu_{1/2}$ = 60 Hz). Anal. Calcd for $C_{22}H_{18}ClD_{12}F_2N_2V$: C, 57.57; H, 6.59; N, 6.10. Found: C, 57.20; H, 6.47; N, 6.12. Magnetism: $\mu_{eff} = 2.60\ \mu_B$ (C_6H_6, 28 °C). Mp 168.5–169.5 °C.

(6) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169. Figgis, B. N.; Lewis, J. *Prog. Inorg. Chem.* **1964**, *6*, 37.

(7) ^{2}H NMR (C_6H_6): 20.0 ($\Delta\nu_{1/2}$ = 41 Hz). Anal. Calcd for $C_{22}H_{18}D_{12}F_2IN_2V$: C, 48.01; H, 5.49; N, 5.09. Found: C, 48.19; H, 5.61; N, 4.86. Mp 70–74 °C.

(8) Although the origin of this thermochromism is not yet clear, it may correlate with a reversible structural change. On cooling ether solutions of **3** to −85 °C we observe near-complete replacement of the ^{2}H NMR signal at 21.1 ppm by a new signal at 25.2 ppm. The color change to emerald green cannot be attributed solely to solvent coordination, since pentane solutions of **3** exhibit the same phenomenon upon cooling. Variable-temperature UV–vis experiments designed to further elucidate the thermochromic behavior of **3** are underway.

(9) ^{1}H NMR (C_6D_6): 7.54 (bs, Ar_F ortho), 6.73 (s, Mes meta), 6.38 (m, Ar_F meta and para), 2.53 (s, Mes *o*-Me), 2.05 (s, Mes *p*-Me), 1.96 (s, Ar_F-Me), 1.56 (s, $C(CD_3)_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 153.3 (d, J_{FC} = 247 Hz), 142.8 (s), 139.9 (s), 133.3 (s), 132.9 (bs), 132.0 (s), 130.6 (s), 130.2 (s), 129.6 (s), 116.3 (br), 69.6 (s), 33.6 (s), 33.2 (m), 21.4 (s), 20.5 (s), and 20.2 (s) ppm. ^{19}F NMR (C_6D_6): −114.60 (s, 2F, ArF). ^{51}V NMR(C_6D_6): 140.6 ($\Delta\nu_{1/2}$ = 470 Hz). Anal. Calcd for $C_{31}H_{29}D_{12}F_2IN_5V$: C, 52.32; H, 5.81; N, 9.84. Found: C, 52.44; H, 5.84; N, 9.77.

(10) Crystal data for **1**: a = 9.672(3) Å, b = 10.176(3) Å, c = 17.281(5) Å, α = 77.15(2)°, β = 83.99(3)°, γ = 89.70(2)°, V = 1649(2) Å^3, space group $P\bar{1}$, $Z = 2$, mol wt = 711.62 for $C_{31}H_{29}D_{12}F_2IN_5V$, and d(calcd) = 1.409 g/cm^3; $R = 0.038$ and $R_w = 0.043$.

(11) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

(12) Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 146. Traetteberg, M.; Hilmo, I.; Hagen, K. *J. Mol. Struct.* **1977**, *39*, 231.

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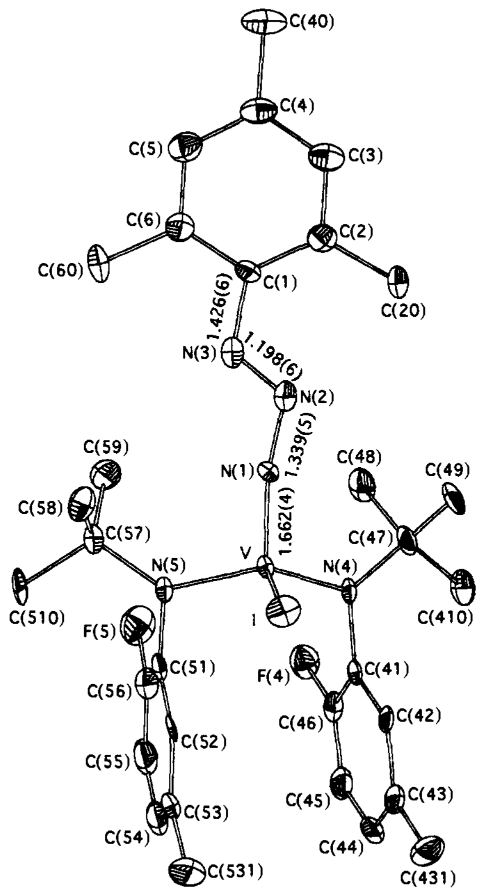

Figure 1. Structural diagram of V(N_3Mes)(I)(NRAr_F)$_2$ (**1**) showing the atom-labeling scheme and thermal ellipsoids at the 40% probability level. Selected bond distances (Å): V−I, 2.6188(8); V−N(1), 1.662(4); V−N(4), 1.851(4); V−N(5), 1.869(4); N(1)−N(2), 1.339(5); N(2)−N(3), 1.198(6); N(3)−C(1), 1.426(6). Selected bond angles (deg): I−V−N(1), 101.3(1); I−V−N(4), 113.6(1); I−V−N(5), 109.9(1); N(1)−V−N(4), 104.1(2); N(1)−V−N(5), 105.6(2); N(4)−V−N(5), 120.0(2); V−N(1)−N(2), 169.1(4); N(1)−N(2)−N(3), 116.6(4); N(2)−N(3)−C(1), 118.1 (4); V−N(4)−C(41), 110.7(3); V−N(4)−C(47), 131.9(3); C(41)−N(4)−C(47), 117.5(4); V−N(5)−C(51), 111.3(3); V−N(5)−C(57), 130.1(3); C(51)−N(5)−C(57), 118.6(4).

Although "diazenylimido" **1** is formally related to Staudinger phosphazides (R_3PNNNAr), it differs from them both structurally and in the kinetics of its N_2 extrusion upon heating. Structurally, phosphazides are found to be bent (115 ± 5°) rather than linear at N(1), and the π-system is more delocalized in phosphazides than in **1**.[14] Mechanistic studies have shown that phosphazides may eliminate N_2 in a unimolecular fashion, for which a cyclic transition state has been postulated.[14] In contrast, the **1** → **2** conversion with N_2 extrusion follows second-order kinetics at 54 °C.[15] This contrasts sharply with the observation, by Proulx and Bergman, that Cp_2Ta(N_3Ph)(CH_3) loses dinitrogen in a first-order manner.[16] A double-labeling experiment, in which equal amounts of V(N_3Ar)(I)(N[C(CH_3)$_3$]Ar_F)$_2$ (**6**, Ar = 2,6-$C_6H_3Me_2$)[17] and **1** were thermolyzed together (50 °C, 6 h, 4.2 mM in each component), gave clear evidence of crossover.[18] While our preliminary kinetic and labeling results are intriguing, more data are required in order to draw a firm conclusion regarding the mechanism of N_2 extrusion from **1**.[19]

The imido complex V(NMes)(I)(NRAr_F)$_2$ (**2**, Scheme 1) was also prepared directly by dropwise addition of mesityl azide (91.3 mg, 566 μmol) to a magnetically stirred solution of **3** (0.299 g, 543 μmol) in ether at 30 °C. The reaction mixture quickly became dark red, and effervescence was observed over 5 min. Removal of all volatile material, followed by extraction with pentane and cooling to −35 °C, gave diamagnetic **2** in 89% yield as dark red crystals.[20] ^{1}H NMR spectra of **2** are consistent with the presence of two isomers in a 6:1 ratio.[21] It is intriguing that treatment of **3** with MesN_3 at 30 °C gives imido **2** directly, since purified **1** is relatively stable at that temperature. Control experiments show that **3** is not a competent catalyst for N_2 extrusion from **1** at 30 °C, but it is possible that a trace catalyst for the **1** → **2** conversion is generated in situ in the 30 °C experiment. It is also possible that "diazenylimido" **1** is not an intermediate in the synthesis of imido **2** at 30 °C.[22]

In summary, we have established the structure of a rare organoazide complex of vanadium and have begun to delineate the conditions under which it extrudes dinitrogen to provide a structurally similar arylimido derivative. Future work will concentrate on the mechanism of N_2 extrusion from **1** and on other possible modes of reaction for this complex.

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Supplementary Material Available: Experimental details for the X-ray structure of V(N_3Mes)(I)(NRAr_F)$_2$ (**1**), tables of positional and thermal parameters, bond lengths and angles, and experimental details for collection of kinetic data and the double-labeling study (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(14) Gololobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1353.

(15) ^{19}F NMR; k = [6.3 ± 1.1] × 10^{-3} M^{-1} s^{-1}; six runs. The error limits on the rate constant are at the 95% confidence level. Rate constants obtained from the linear plots of 1/[1] versus time for each of the individual six runs were given a weight proportional to the reciprocal of their squared standard error. Accordingly, the reported rate is a weighted average of the six runs. The error in the rate constant is estimated as $\pm 2.571\sigma(\sum w_s)^{-0.5}$ where 2.571 is Student's t factor (95% confidence) for N = 6, σ is the standard deviation of the weighted mean, and $\sum w_s$ is the sum of the weights. Mortimer, R. G. *Mathematics for Physical Chemistry*; MacMillan: New York, 1981. Topping, J. *Errors of Observation and Their Treatment*; Reinhold: New York, 1957.

(16) Proulx, G.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 6382−6383.

(17) **6** was prepared analogously to **1** and, like **1**, was shown to decompose in a second-order fashion at 54 °C.

(18) Molecular ion clusters (EIMS analysis) having similar intensities were observed at 680/681, 671, 666/667, and 657 amu. This is the expected result for crossover because independent spectra of **2** and V(NAr)(I)(N[C(CH_3)$_3$]Ar_F)$_2$ (**7**) exhibited molecular ion clusters at 680/681 and 657 amu, respectively. See supplementary material for a detailed discussion of these EIMS data.

(19) Several potential mechanisms remain consistent with the data currently in hand. We hope to be able to "winnow the field" in a full paper to come.

(20) ^{1}H NMR (C_6D_6). Major isomer: 7.45 (d, J = 5.0 Hz, anilido *ortho*), 6.65 (bs, mesityl *meta*), 6.59 (bs, mesityl *meta*), 6.40 (t, J = 8.8 Hz, anilido aryl), 6.33 (m, anilido aryl), 3.15 (bs, mesityl *o*-Me), 2.86 (bs, mesityl *o*-Me), 2.04 (s, mesityl *p*-Me), 1.93 (s, anilido aryl Me), 1.38 (s, anilido *t*-BuMe), and 1.34 (bs, anilido *t*-BuMe-d_2 H) ppm. Minor isomer: 6.54 (s), 2.93 (bs), 2.05 (s), 2.02 (s), 1.40 (s), and 1.25 (s) ppm. ^{13}C{^{1}H] NMR ($CDCl_3$): 154.0 (d, J_{FC} = 24.6 Hz), 135.3 (small s), 134.8 (s), 134.5 (s), 134.3 (small bs), 134.2 (small bs), 132.8 (s), 129.8 (d, J_{FC} = 7 Hz), 128.6 (bd, J_{FC} = 23 Hz), 128.5 (d, J = 23 Hz), 116.09 (s), 115.9 (s), 69.8 (s), 31.5 (s), 30.9 (m), 22.51 (bs), 21.4 (s), 21.0 (small s), 20.4 (s), and 19.8 (bs) ppm. ^{19}F NMR (C_6D_6). Major isomer: −115.83 (s, 2F, ArF). Minor isomer: −116.35 (s) ppm. ^{51}V NMR(C_6D_6). Major isomer: 3.8 ($\Delta\nu_{1/2}$ = 752 Hz). Minor isomer: 29.4 (s). mp 188.5−192.5 °C. Anal. Calcd for $C_{31}H_{29}D_{12}F_2IN_3V$: C, 54.47; H, 6.04; N, 6.15. Found: C, 54.92; H, 6.14; N, 6.20. Crystal data: a = 13.878(4) Å, b = 15.323(3) Å, c = 14.901(4) Å, β = 92.055(13)°, V = 3166.8(13) Å^3, space group $P2(1)/n$, Z = 4, mol wt = 518.99 for $C_{31}H_{29}D_{12}F_2IN_3V$, and d(calcd) = 1.255 g/cm^3; R = 0.0698 and R_w = 0.1327. Imido **2** is a pseudotetrahedral monomer in the solid state.

(21) The X-ray structure of **2** shows that it is a crowded compound with a V(I)(NRAr_F)$_2$ core that is nearly superimposable on that of **1**. The nature of the isomerism, while not yet unambiguously resolved, probably involves V−N rotamers or N−Ar_F rotamers.

(22) We thank a reviewer for pointing out that the 30 °C experiment may involve interaction of V with the α-nitrogen of MesN_3, rather than the γ-nitrogen as required for the formation of **1**.