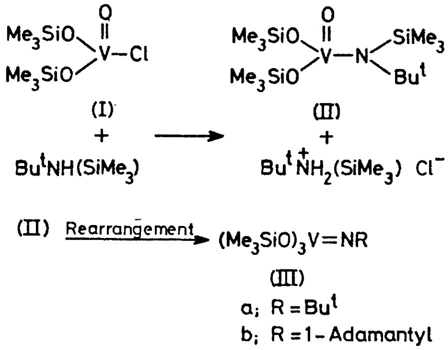
Stable First-row Transition Metal Alkylimido Complexes; *X*-Ray Crystal and Molecular Structure of *N*-(1-Adamantylimido)tris(trimethylsiloxy)-vanadium(v)

By WILLIAM A. NUGENT* and RICHARD L. HARLOW

(*Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware* 19898)

Summary The novel complexes $(Me_3SiO)_3V{=}NR$ (R = t-butyl or 1-adamantyl) have been prepared and characterized; the structure of the adamantyl derivative has been determined by *X*-ray crystallography.

THE preparation of multiply bonded alkylimido complexes has, in general, been restricted to the second and third row transition metals. Certain reactions of vanadium(v) have been suggested to afford alkylimido complexes but the thermal instability of the products precludes further characterization.[1] We now report the preparation of thermally stable vanadium(v) alkylimido complexes (III) and the *X*-ray crystal structure of (IIIb).



Reaction of the chlorovanadium complex (I)[2] with t-butyltrimethylsilylamine[3] in hexane at −78 °C is assumed to afford initially the amide intermediate (II).[4] On warming the red brown solution of (II) to room temperature it becomes bright yellow. Filtration to remove $Bu^tNH_2(SiMe_3)Cl$, distillation to remove the solvent, and recrystallization from hexamethyldisiloxane at −40 °C affords (*ca.* 80%) *N*-t-butylimidotris(trimethylsiloxy)vanadium (IIIa) as yellow sublimable needles, m.p. 55—56 °C; $\delta(C_6D_5CD_3)$ 0·25 (27H, s) and 1·22 (9H, s); *M* found (cryoscopic, *p*-xylene) 403, calc. 390. A nearly linear V–N–C arrangement in (IIIa) is indicated by its ^{51}V n.m.r. spectrum which is a 1 : 1 : 1 triplet due to coupling to ^{14}N (J = 95 Hz).[5] In contrast to the t-butylimido complexes of osmium,[6] (IIIa) does not react with hex-1-ene in pyridine (100 °C, 24 h).

Compound (IIIb) was prepared in an analogous manner but in very low yield using 1-adamantyltrimethylsilylamine. Reaction of excess of $Bu^tNH(SiMe_3)$ with Group 6 oxychlorides, MO_2Cl_2, allowed isolation of products of the type $(Me_3SiO)_2M(NBu^t)_2$ (M = Cr or Mo) in *ca.* 80% yield.

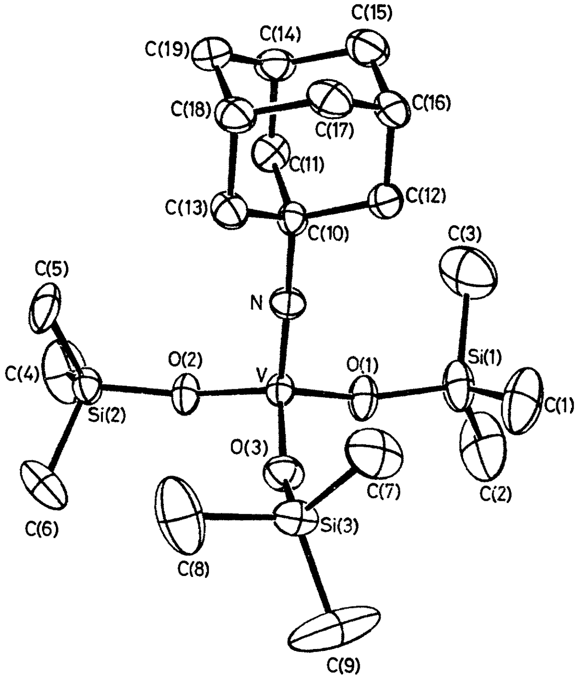


FIGURE. Structure of (IIIb). For the carbon atoms attached to Si(2) the drawing shows only the position of highest occupation. The adamantyl group adopts a staggered conformation relative to the three trimethylsiloxy groups; the O(1)–V–C(10)–C(13) torsion angle is −168·5°. Important bond distances and angles in the molecule are: V–N, 1·614(2); V–O(1), 1·766(2); V–O(2), 1·765(2); V–O(3), 1·762(2); N–C(10), 1·454(3); O(1)–Si(1), 1·612(2); O(2)–Si(2), 1·621(2); and O(3)–Si(3), 1·615(2) Å; ∠N–V–O(1), 109·1(1); ∠N–V–O(2), 110·0(1); ∠N–V–O(3), 109·2(1); ∠O(1)–V–O(2), 110·7(1); ∠O(1)–V–O(3), 109·3(1); ∠O(2)–V–O(3), 108·6(1); ∠V–N–C(10), 175·8(2); ∠V–O(1)–Si(1), 148·7(1); ∠V–O(2)–Si(2), 152·7(1); and ∠V–O(3)–Si(3), 154·1(1)°.

The *X*-ray crystal structure (Figure) of (IIIb) shows that the V–N bond length is extremely short [1·614(2) Å] and the V–N–C angle is nearly linear [175·8(2)°]. This confirms considerable triple-bond character in V≡NR. Thus it appears that even the smaller *d* orbitals of a first row transition metal will accommodate the effective π-donation from nitrogen required for such bonding.

Crystal data: $C_{19}H_{42}NO_3Si_3V$, M = 467·75, triclinic, space group $P\bar{1}$, with a = 10·736(4), b = 14·929(2), c = 9·931(2) Å, α = 92·93(1), β = 111·65(1), γ = 103·45(1)°, Z = 2, D_c = 1·09 g cm^{-3}; Mo-K_α radiation (λ = 0·71069 Å, μ = 5·1 cm^{-1}). Data were collected on a Syntex P3 diffractometer (to 2θ = 55°) using the ω-scan technique. The structure was solved by direct methods and refined by the full-matrix least-squares method. The methyl groups attached to Si(2) were disordered; occupation factors of 0·6 and 0·4 were assigned to atoms C(4)—C(6) and C(4)P—C(6)P, respectively. The positions of the hydrogen atoms on the adamantyl group were calculated (C–H = 1·00 Å) but not refined. The refinement of 271 variables (anisotropic thermal parameters for V, Si, O, N, and C) using 3391 reflections for which $I > 3{\cdot}0\sigma(I)$ yielded a conventional R index of 0·063. Several small peaks in the final difference Fourier (all $< 0{\cdot}31$ e Å^{-3}) suggested that the methyl groups attached to Si(1) and Si(3) are also partially disordered.†

(*Received*, 11*th December* 1978; *Com.* 1312.)

---

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] H. Burger, O. Smrekar, and U. Wannagat, *Monatsh.*, 1964, **95**, 292; A. Slawisch, *Z. anorg. Chem.*, 1970, **374**, 291; F. Becker, *J. Organometallic Chem.*, 1973, **51**, C9; A. F. Shihada, *Z. anorg. Chem.*, 1974, **408**, 9.

[2] M. Schmidt and H. Schmidbaur, *Angew. Chem.*, 1959, **71**, 220.

[3] R. M. Pike, *J. Org. Chem.*, 1961, **26**, 232.

[4] A rearrangement similar to that of (II) is reported for a phosphorus(V) trimethylsilylamide: R. H. Neilson, R. D. Jacobs, R. W. Scheirman, and J. C. Wilburn, *Inorg. Chem.*, 1978, **17**, 1880.

[5] *Cf.* M. Harman, D. W. A. Sharp, and J. M. Winfield, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 183.

[6] A. O. Chong, K. Oshima, and K. B. Sharpless, *J. Amer. Chem. Soc.*, 1977, **99**, 3420.