Structure and Reactivity in the Group 5B t-Butylimido Complexes $(Me_2N)_3M{=}NBu^t$; *X*-Ray Crystal and Molecular Structure of *N*-t-Butylimidotris(dimethylamido)tantalum

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 $(Me_2N)_3M{=}NBu^t$ (M = Nb or Ta) contain a linear M=N–C unit and undergo reactions with electrophiles at the amido nitrogen; the structure of $(Me_2N)_3M{=}NBu^t$ has been determined by *X*-ray crystallography.

Bradley and his co-workers have reported[1] that treatment of $NbCl_5$ or $TaCl_5$ with lithium dialkylamides affords mixtures containing the unusual alkylimido species $(R_2N)_3M{=}NR$ in addition to $M(NR_2)_4$, $M(NR_2)_5$, and other products. We now report that treatment of freshly sublimed $TaCl_5$ with lithium dimethylamide and lithium t-butylamide [reaction (1)] yields, upon filtration, concentration, and cooling, *ca.* 40% of *N*-t-butylimidotris(dimethylamido)tantalum as white hexagonal plates:

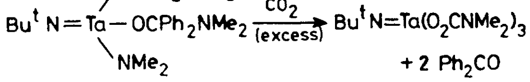
$$MCl_5 + 4LiNMe_2 + LiNHBu^t \rightarrow (Me_2N)_3M{=}NBu^t + 5LiCl + Me_2NH \quad (1)$$

(Ia), M = Ta
(Ib), M = Nb

(Ia), m.p. 68—69 °C; δ ($C_6D_5CD_3$) 1·43 (9H, s) and 3·20 (18H, s). The analogous reaction with $NbCl_5$ affords after sublimation *ca.* 20% of *N*-t-butylimidotris(dimethylamido)niobium as a yellow crystalline solid: (Ib), m.p. 58—60 °C; δ 1·39 (9H, s) and 3·16 (18H, s). Compound (Ia) [but not (Ib)] can also be prepared by direct aminolysis of the dimethylamide according to reaction (2).

$$Ta(NMe_2)_5 + Bu^tNH_2 \rightarrow (Ia) + 2Me_2NH \quad (2)$$

Compounds (Ia) and (Ib) do not react with hex-1-ene in benzene (80 °C; 24 h) but undergo the typical[2] reactions of the dialkylamide ligands with electrophiles (ROH, R_2CO, CO_2, CS_2, or RI). The insertion reaction with ketones is noteworthy both in its reversibility and sensitivity to steric restrictions. Thus (Ia) undergoes insertion by 1 or 2 [compound (II)] but not 3 equiv. of benzophenone. The ketone is then readily displaced by CO_2 [reaction (3)] to afford the carbamate complex. Reaction of (Ia) with an excess of benzaldehyde affords $PhCH{=}NBu^t$ but this product may arise from free t-butylamine produced by catalytic amounts of protic impurities.[3]



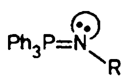
$$Bu^tN{=}Ta(OCPh_2NMe_2)_2(NMe_2) \xrightarrow[\text{(excess)}]{CO_2} Bu^tN{=}Ta(O_2CNMe_2)_3 + 2\,Ph_2CO \quad (3)$$

(II)

^{13}C N.m.r. studies and extended Hückel MO calculations suggest the presence of a linear M=N–C unit in (Ia) in which the electron density on N is intermediate between that in electrophilic[4] alkylimido species like (III) and nucleophilic[5] derivatives like (IV). Linearity was confirmed by an *X*-ray crystal structure determination (Figure) which also shows the longest known[6] M=N bond of 1·77 Å. Differences in structure and reactivity among these compounds apparently reflect increasing π donation from nitrogen into low-lying *d* orbitals (triple bond character) along the series (IV) < (Ia) < (III).

$$O_3Os{=}NBu^t$$

(III)



(IV)

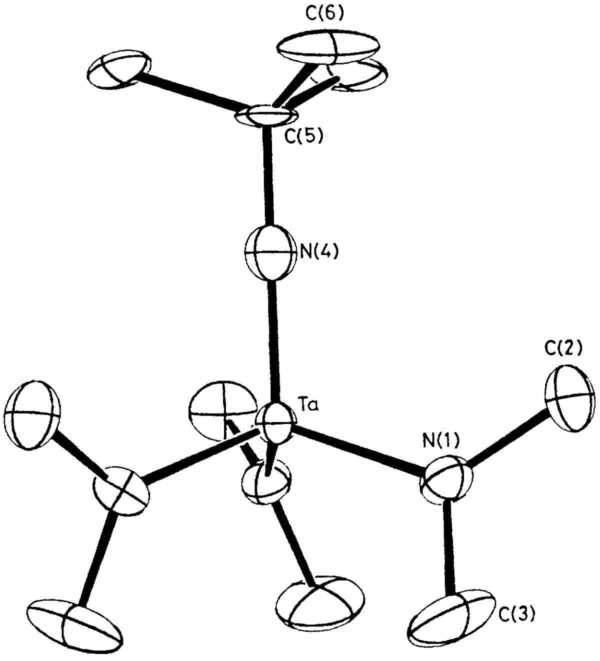


Figure. View of the molecule of $(Me_2N)_3M{=}NBu^t$ perpendicular to the 3-fold rotation axis containing atoms Ta, N(4), and C(5). For clarity, only the positions of highest occupation are shown. At the present stage of refinement, the important bond distances and angles are: Ta–N(1) 1·99(1), Ta–N(4) 1·77(2), N(1)–C(2) 1·48(2), N(1)–C(3) 1·51(3), N(4)–C(5) 1·42(2), C(5)–C(6) 1·61(3) Å; ∠N(1)–Ta–N(4) 108·0(4), N(1)–Ta–N(1) 110·9(3)°.

Crystal data: $C_{10}H_{27}N_4Ta$, M = 387·30, hexagonal, space group $R\bar{3}$, with a = 11·490(2) and c = 21·338(7) Å, Z = 6, D_c = 1·582 g cm^{-3}; Mo-K_α radiation (λ = 0·71073 Å), μ = 71·1 cm^{-1}. Data were collected by the Molecular Structure Corporation on an Enraf-Nonius CAD4 diffractometer (to 2θ = 55°). The structure was solved by the heavy-atom method which placed the Ta atom on a crystallographic 3-fold rotation axis. An electron-density map revealed the remaining atoms and also showed that the methyl groups of the NBu^t group were disordered about the 3-fold axis with occupation factors for C(6) and C(6)P of 0·6 and 0·4 respectively. After several cycles of least-squares refinement, a subsequent difference Fourier clearly showed that the Me$_2$N-groups were also disordered about the 3-fold axis with an occupancy-factor ratio of *ca.* 4 : 1. For 1017 reflections [$I > 3\,\sigma\,(I)$], the least-squares refinement of 58 variables [anisotropic thermal parameters for all atoms except N(1)P, C(2)P, and C(3)P] yielded a conventional R of 0·076. The isotropic thermal parameters for these three atoms were refined but the co-ordinates were fixed.†

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† 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.

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