JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 4
1984

$[TaCl(\mu\text{-}Cl)(NBu^t)(NHBU^t)(NH_2Bu^t)]_2$; a Tantalum(v) Complex containing Terminal Imido, Amido, and Amino Ligands

Tony C. Jones, Alastair J. Nielson,* and Clifford E. F. Rickard*

Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand

Imido complexes of niobium and tantalum(v) are prepared by the reaction of the pentachlorides with $Me_3SiNHBu^t$: with excess of t-butylamine, imido, amido, and amino ligands are formed about the same metal centre, as shown in an *X*-ray crystallographic study of the title complex.

Recently it was shown that imido complexes (MNR) of niobium and tantalum could be prepared by reaction of imines with neopentylidene complexes.[1] More simply, we believed that by analogy with high-valent metal–alkyl–alkylidene chemistry,[2] proton extraction from one of two co-ordinated primary amido groups $M(NHR)_2$, or base-promoted deprotoration of one primary amido group hydrogen [equations (1) and (2) respectively] might generate the required imido linkage.

$$MCl_3(NHR)_2 \longrightarrow MCl_3(NR) + RNH_2 \tag{1}$$

$$MCl_4(NHR) \xrightarrow{\text{base}} MCl_3(NR) + \text{base}\cdot HCl \tag{2}$$

When $Me_3SiNHBu^t$ (2 equiv.) was treated with M_2Cl_{10} (M = Nb, Ta) in benzene, Me_3SiCl was formed as well as a complex analysing as $[MCl_3(NHBu^t)_2]_n$ but which ^1H and ^{13}C n.m.r. spectra showed to be $[MCl_3(NBu^t)(NH_2Bu^t)]_n$ (**1**). One equivalent of $Me_3SiNHBu^t$ reacted with M_2Cl_{10} in the presence of 3 equivalents of PMe_3 to give $MCl_3(NBu^t)(PMe_3)_2$ (**2**) and PMe_3HCl. Complex (**2**) could also be prepared by the addition of PMe_3 to (**1**).

$[MCl_3(NBu^t)(NH_2Bu^t)]_n$ (**1**) $MCl_3(NBu^t)(PMe_3)_2$ (**2**)

$[MCl_2(NBu^t)(NHBu^t)(NH_2Bu^t)]_n$ (**3**)

On addition of an approximate 8-fold excess of Bu^tNH_2 to M_2Cl_{10} in benzene, 3 equivalents of Bu^tNH_3Cl were formed along with a benzene-soluble complex analysing as $[MCl_2(NHBu^t)_3]_n$ but shown to be $[MCl_2(NBu^t)(NHBu^t)(NH_2Bu^t)]_n$ (**3**) by the presence of 3 quaternary carbon resonances in the ^{13}C n.m.r. spectrum (for M = Ta, δ 66.6, 57.6, 53.2 p.p.m.) and amido and amino protons in the ^1H n.m.r. spectrum (for M = Ta, δ 3.4 and 10.2). The complex was also formed after the addition of Bu^tNH_2 to (**1**), which could not be obtained as an intermediate in the M_2Cl_{10}–t-butylamine reactions as they proceeded through to complex (**3**). Reaction of (**3**) with PMe_3 gave a complex which failed to give good analyses but which was shown by n.m.r. spectroscopy to be $MCl_2(NBu^t)(NHBu^t)(PMe_3)_2$. One equivalent of EtOH reacted with (**3**; M = Ta) to give the white complex, $[TaCl_2(NBu^t)(NH_2Bu^t)(\mu\text{-}OEt)]_2$ as characterised by an *X*-ray crystallographic analysis, to be reported elsewhere.[3]

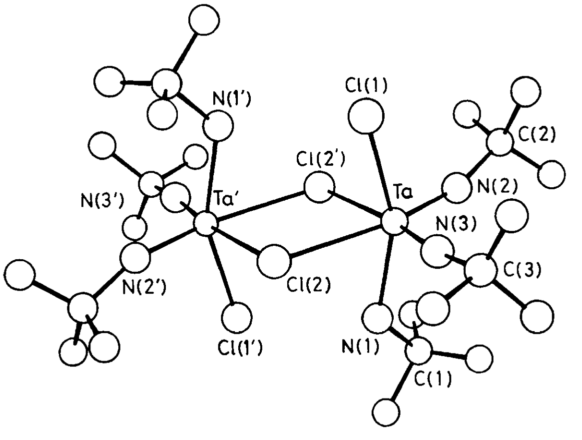

Figure 1. Molecular structure of $[TaCl(\mu\text{-}Cl)(NBu^t)(NHBu^t)(NH_2Bu^t)]_2$, (**3**; M = Ta). Important bond lengths (Å) and bond angles (°); Ta–Cl(1) 2.410(9), Ta–Cl(2) 2.66(1), Ta–Cl(2′) 2.687(9), Ta–N(1) 2.23(3), Ta–N(2) 1.86(3), Ta–N(3) 1.61(3); Ta–Cl(2)–Ta′ 103.2(3), Ta–N(1)–C(1) 126(2), Ta–N(2)–C(2) 160(2), Ta–N(3)–C(3) 169(2).

Crystal data for (**3**; M = Ta): $C_{24}H_{57}Cl_2N_6Ta_2$, $M = 936.52$, monoclinic, $a = 13.607(7)$, $b = 9.699(2)$, $c = 15.434(11)$ Å, $\beta = 109.27(6)°$, $U = 1936$ Å^3, space group $P2_1/c$, $Z = 2$, $D_c = 1.49$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 61.15$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å. Intensity data were recorded on a Nonius CAD4 diffractometer with Mo-K_α radiation, corrected for Lorentz, polarisation and absorption effects as well as decay of intensity due to crystal decomposition. The structure was solved from Patterson and electron density synthesis and refined by full-matrix least-squares, omitting hydrogens and with all but terminal carbons anisotropic, to an R_w value of 0.091 for 1062 reflections with $F_O > 3\sigma(F_O)$.†

The structure (Figure 1) shows (**3**; M = Ta) to be dimeric with nearly symmetrical chloro bridges, and terminal imido N(3), amido N(2), and amino N(1) ligands. The bond distances and angles for imido and amino ligands are close to those reported for similar metal–nitrogen bonds[4,5] indicative of 4- and 2-electron donors respectively. Of particular interest is the short Ta–amido nitrogen bond distance, 1.86(3) Å, and large Ta–N–C bond angle, 160(2)°. To obtain an 18 electron configuration in the complex this Ta–N bond must involve significant π-bonding which is reflected in the comparatively short bond distance and lengthening of the Ta–Cl bond [2.66(1) Å] *trans* to it. Calculation of the amido proton position at the present stage of refinement, assuming a C–N–H bond angle of 120°, indicates a close approach to the metal centre (Ta···H–N *ca.* 2.0 Å)‡ probably involving a 2-electron 3-centre bond and allowing pseudo-7-co-ordination about the metal.

Complex (**3**; M = Ta) thus shows analogies to metal–carbon multiple and single bonded d^0 transition metal complexes. Firstly, the formation of 3 types of metal–nitrogen bonding about the same metal centre (*cf.* alkylidyne, alkylidene, and alkyl groups in W^{VI}[8]) and secondly, close approach of an amido proton to the metal (*cf.* close approach of α-carbon proton in alkylidene[9] and alkyl complexes[10]).

Received, 21st September 1983; Com. 1247

---

† Consistent poor crystal quality and disorder in several t-butyl methyl carbons indicated by high thermal parameters have precluded further refinement of the structure.

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 requests should be accompanied by the full literature citation for this communication.

‡ To our knowledge the only other M(NH-alkyl) complex characterised by *X*-ray crystallography is (adamantyl-NH)$_2$Mo(OSiMe$_3$)$_4$ (ref. 6) [Mo–N bond length 2.057(3) Å] containing a large Mo–N–C angle of 150.8(3)°, attributed to steric factors or possible amido hydrogen bonding to oxygen. Modified extended Hückel calculations predicted an Mo–N–H angle of 77°. In phenylamido complexes M–N–C bond angles and M–N bond lengths are typically in the region of 136—140° and 2.0—2.2 Å respectively (ref. 7).

References

1 S. M. Rocklage and R. R. Schrock, *J. Am. Chem. Soc.*, 1980, **102**, 7808; 1982, **104**, 3077.

2 R. R. Schrock and J. P. Fellmann, *J. Am. Chem. Soc.*, 1978, **100**, 3359.

3 P. A. Bates, A. J. Nielson, and J. M. Waters, unpublished work.

4 W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 123.

5 A. J. Nielson and J. M. Waters, *Polyhedron*, 1982, **1**, 561.

6 W. A. Nugent and R. L. Harlow, *Inorg. Chem.*, 1980, **19**, 777.

7 K. W. Chiu, W. Wong, G. Wilkinson, A. M. R. Galas, and M. B. Hursthouse, *Polyhedron*, 1982, **1**, 37; P. A. Bates, A. J. Nielson, and J. M. Waters, unpublished work.

8 M. R. Churchill and W. J. Youngs, *J. Chem. Soc., Chem. Commun.*, 1979, 321.

9 M. R. Churchill and H. J. Wasserman, *Inorg. Chem.*, 1983, **22**, 1574 and references therein.

10 Z. Dawoodi, M. L. H. Green, V. S. B. Mtetwa, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1982, 802 and 1410.