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The Preparation, Characterization and Crystal and Molecular Structure of Bis-(bis-trimethylsilylamido)-trichlorotantalum(V)

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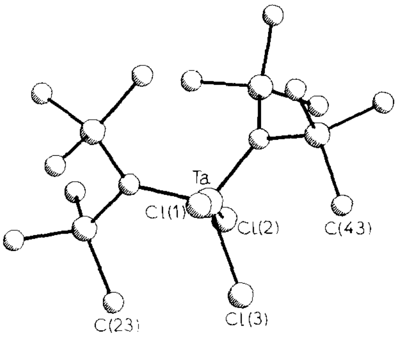
Previous work on the reactions of lithium bis-trimethylsilylamide with the tetrachlorides of Group IV metals [1] and thorium [2] showed that substitution of chlorine was restricted and the monochloride derivatives $MCl[N(SiMe_3)_2]_3$ were obtained [3]. In extending this work to Group V metal chlorides we have found that tantalum pentachloride undergoes only disubstitution with the formation of $TaCl_3[N(SiMe_3)_2]_2$ (pale orange crystals, m.p. 146–147 °C). The same product was obtained irrespective of the $LiN(SiMe_3)_2/TaCl_5$ mol ratio (between 1–5) in reactions carried out in pentane. Found Ta, 29.70; Cl, 17.46; N, 4.14; C, 23.31; H, 6.04; $TaCl_3[N(SiMe_3)_2]_2$ requires: Ta, 29.76; Cl, 17.49; N, 4.60; C, 23.68; H, 5.97%. The new compound was found to be monomeric in boiling benzene and in the mass spectrum gave a parent ion (m/e 606) and several fragment ions.

Assuming that steric hindrance is preventing further substitution of chlorine by the bulky silylamido ligand it seemed reasonable to expect a trigonal bipyramidal configuration of the monomer with the bulky ligands in the *trans* (axial) positions and chlorines in the equatorial positions. The room temperature ^1H n.m.r. spectrum supported this view (one singlet in C_6D_6, $\delta = 0.44$ p.p.m. rel. to T.M.S.) but on lowering the temperature line broadening and splitting showed that a different configuration must be present. Accordingly an X-ray single crystal structure determination was carried out.

Crystals obtained from pentane are orthorhombic with $a = 11.668(3)$, $b = 12.089(2)$ and $c = 17.095(4)$ Å, space group $P2_12_12_1$, $D_c = 1.57$ g cm^{-3}, $Z = 4$ and ν(Mo-Kα = 46.7 cm^{-1}.

Intensity data were recorded on a Nonius CAD4 diffractometer in our usual manner [4] using Mo-Kα radiation. Of the 3987 independent data measured, 3020 were considered observed ($I > 2\sigma(I)$) and used for structure solution (heavy atom method) and refinement (full matrix least squares). The R factor is currently 0.04 (all non-H atoms anisotropic).



The molecule is indeed found to have a trigonal bipyramidal structure but with the bulky silylamide groups occupying equatorial rather than axial sites (see Fig. 1). Distortions from regular geometry are clearly due to crowding by the silylamide ligands. Thus the axial Cl(1)–Ta–Cl(2) system is bent, with an angle of 168° due to short (~3.4–3.5 Å) $C_{Me}\cdots Cl$ contacts. Surprisingly however, the N(1)–Ta–N(2) angle in the equator, 115°, is much less than expected and probably results from the particular orientations of the $SiMe_3$ groups adopted which have a) produced short contacts (~3.5 Å) in the equatorial plane between two methyl groups (C(23), C(43) and Cl(3) and b) presumably minimised Me···Me repulsions between the silylamide ligands.

Bond lengths in the co-ordination sphere are also quite interesting. The two axial Ta–Cl lengths (2.362, 2.366(2) Å) are essentially equal and only slightly longer than the equatorial length (2.351(2) Å). The Ta–N distance of 1.928(7) and 1.933(7) Å are quite short and together with the fairly long Si–N distances of 1.785–1.826(7) Å are indicative of quite strong N→Ta pπ–dπ bonding. This result is entirely in keeping with the well established ability of tantalum(V) to form multiple bonds with nitrogen [5] and carbon [6] ligands. With this feature in mind, it is interesting to consider whether the choice of equatorial site by the silylamide ligands is related to the multiple bonding or whether these bulky ligands are in fact parallelling the behaviour of lone pairs in tbp structures. This aspect of the structure will be considered in detail in a future publication.

The infrared spectrum of $TaCl_3[N(SiMe_3)_2]_2$ (Nujol mull) showed bands typical of the silylamide ligand together with two Ta–N stretching frequencies (415 and 400 cm^{-1}) and two Ta–Cl bands (340 and 316 cm^{-1}) in accordance with the molecular structure. Further work on variable temperature n.m.r. spectra is in progress. Preliminary experiments involving niobium pentachloride and $LiN(SiMe_3)_2$ have shown that substitution of chlorine is accompanied by reduction to Nb(IV) species in contrast to the reactions involving tantalum pentachloride.

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Acknowledgments

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