The First Intramolecularly Co-ordinated Aryl Tantalum Compounds with Amine Donors: Synthesis and *X*-Ray Crystal Structure of $[\mathrm{Ta\{C_6H_4CH(R)NMe_2\text{-}2\}(CH_2Ph)_2Cl_2}]$(R = H, Me)

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$[\mathrm{Ta(CH_2Ph)_2Cl_3}]$ reacts with $[\mathrm{Zn\{C_6H_4CH(R)NMe_2\text{-}2\}_2}]$ (R = H, Me) to afford the new tantalum(v) complexes $[\mathrm{Ta\{C_6H_4CH(R)NMe_2\text{-}2\}(CH_2Ph)_2Cl_2}]$ in high yield; these complexes contain a five-membered $\overline{\mathrm{Ta–C–C–C–N}}$ chelate ring, in both the solid state and in solution, through intramolecular co-ordination of a trialkylamine ligand.

Chelating organic ligands are known to provide considerable stabilization of organometallic complexes of the early transition metals.[1] Considering the number of important processes in organotantalum chemistry, for instance C–H-activation[2] and alkene metathesis,[3] it is remarkable that the use of such ligands has not been applied to control the reactivity and stability of organotantalum compounds. We have investigated 2-[(dimethylamino)methyl]phenyl systems as appropriate chelating ligands for tantalum(v) and now report the synthesis and characterization of the first organotantalum compounds possessing intramolecular co-ordination with amine donors.

The reaction of $[\mathrm{Ta(CH_2Ph)_2Cl_3}]$[4] with $[\mathrm{Zn\{C_6H_4CH_2NMe_2\text{-}2\}_2}]$[5] (0.5 equiv.) at −78 °C in toluene–pentane (1 : 1) gave a dark red solution (and suspended $\mathrm{ZnCl_2}$) from which $[\mathrm{Ta\{C_6H_4CH_2NMe_2\text{-}2\}(CH_2Ph)_2Cl_2}]$ (**1a**) was isolated as a red powder in 72% yield. The related compound $[\mathrm{Ta\{C_6H_4CH(Me)NMe_2\text{-}2\}(CH_2Ph)_2Cl_2}]$ (**1b**) was prepared by a similar reaction of $[\mathrm{Ta(CH_2Ph)_2Cl_3}]$ with $[\mathrm{Zn\{C_6H_4CH(Me)NMe_2\text{-}2\}_2}]$[†] in $\mathrm{Et_2O}$ at −78 °C; yield: 70—75%. Both (**1a**) and (**1b**) can be handled at room temperature; (**1a**) decomposes at *ca.* 115 °C whereas the

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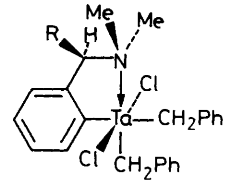
[†] The preparation of this new compound is similar to that of $[\mathrm{Zn\{C_6H_4CH_2NMe_2\text{-}2\}_2}]$ (see ref. 5); ^{1}H n.m.r. data (200.13 MHz, $\mathrm{C_6D_6}$) at 298 K for $[\mathrm{Zn\{(\mathit{R})\text{-}C_6H_4CH(Me)NMe_2\text{-}2\}_2}]$: δ 1.22 [6H, d, *J* 6.7 Hz, $\mathrm{C_6H_4CH(C\mathit{H}_3)}$], 1.96 (12H, s, $\mathrm{NCH_3}$), 3.14 (2H, q, *J* 6.7 Hz, $\mathrm{C_6H_4C\mathit{H}}$), 7.02—8.00 (8H, m, ArH).



[Ta{$C_6H_4CH(R)NMe_2$-2}$(CH_2Ph)_2Cl_2$]
(1a) R = H
(1b) R = Me (*R* and *R*/*S* enantiomers)

thermal stability of **(1b)** is already limited at 30 °C. They react readily with water and slowly decompose on contact with air but can be stored under nitrogen at −30 °C for months.

Compound **(1b)** contains a chiral benzylic carbon centre that is close to the inner co-ordination sphere of tantalum; **(1b)** has been prepared with *R* and *R*/*S* ligand combinations.

The ^1H n.m.r. spectra of compounds **(1a)** and **(1b)**‡ show an interesting temperature dependence and to aid interpretation of the spectroscopic data an *X*-ray structural analysis of one of these compounds was carried out. Suitable crystals of **(1a)** were obtained from a diethyl ether-layered tetrahydrofuran (THF) solution at −30 °C. The *X*-ray structure (Figure 1)§ shows the complex to be a mononuclear tantalum species that has a distorted octahedral geometry. In this complex there are two chlorine atoms occupying axial *trans* positions with two *cis*-positioned C-bonded benzyl ligands in the meridional plane. The co-ordination sphere is completed by the N donor atom and the *ipso* C atom of the chelating 2-[(dimethylamino)methyl]phenyl ligand; the resulting five-membered Ta–C–C–C–N ring is puckered. Of the several interesting features of this structure probably the most important is the rather small bite angle of the chelate ring [N(1)–Ta(1)–C(11) 69.7(4)°] that seems to be compensated for by a rather wide angle of 115.0(5)° between the two benzyl ligands. The distortions in the meridional plane (see Figure 2) are such that it is possible to use an alternative description of the structure based on a distorted trigonal arrangement of the organo groups around tantalum with 'supplementary' co-ordination of the N-donor substituent. The long tantalum–nitrogen bond length of 2.496(9) Å is similar to Sn–N bond lengths in organotin(IV) complexes with this type of chelating ligand.[6]

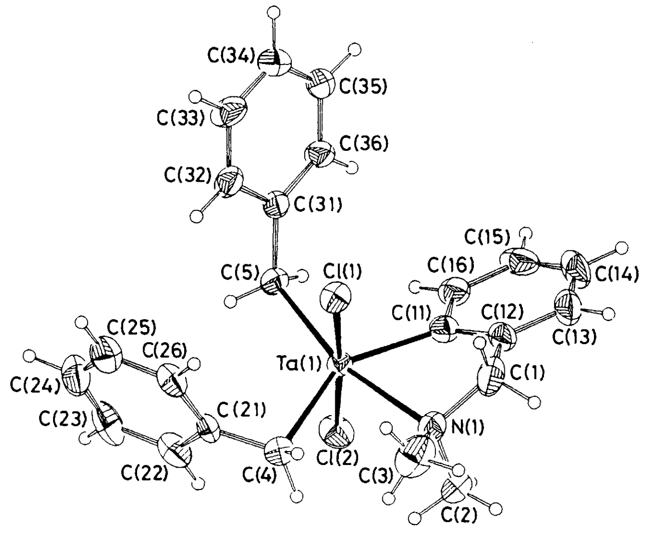


Figure 1. *X*-Ray structure of [Ta{$C_6H_4CH_2NMe_2$-2}$(CH_2Ph)_2Cl_2$] **(1a)**. ORTEP drawing with 30% probability ellipsoids. Selected bond lengths (Å) and angles (°) subtended at tantalum: Ta(1)–Cl(1), 2.312(3); Ta(1)–Cl(2), 2.335(3); Ta(1)–C(4), 2.187(1); Ta(1)–C(5), 2.236(1); Ta(1)–C(11), 2.154(1); Ta(1)–N(1), 2.496(9). Cl(1)–Ta(1)–Cl(2), 176.36(8); C(4)–Ta(1)–C(5), 115.0(5); C(5)–Ta(1)–C(11), 99.8(4); N(1)–Ta(1)–C(11), 69.7(4); N(1)–Ta(1)–C(4), 77.6(4).

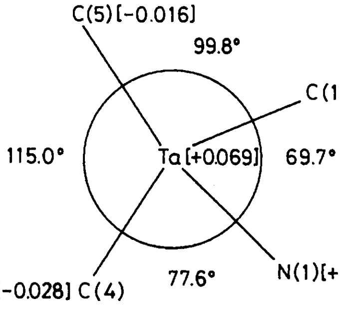


Figure 2. Projection [Cl(1)–Cl(2)] showing interligand angles (°) and deviations (Å) from the least-squares plane defined by Ta(1), C(4), C(5), and C(11).

The ^1H n.m.r. spectrum of **(1b)** (200.13 MHz, $CD_3C_6D_5$) at 213 K is in fact consistent with the solid state structure of **(1a)** with intramolecular co-ordination of the N-donor unit; there are patterns for two inequivalent benzyl ligands and the two methyl groups of the NMe_2 unit afford anisochronous resonances at δ 1.72 and 2.08. In the presence of the chiral centre these groups can only be diastereotopic when the nitrogen centre is a stable tetrahedral array on the n.m.r. time scale, *i.e.* when the nitrogen centre is co-ordinated to tantalum and inversion of configuration is blocked. Upon raising the temperature fluxionality becomes evident; the benzyl groups become equivalent whilst the two NMe_2 signals broaden and eventually coalesce at 333 K. A process which can render these two methyl groups homotopic is dissociation of the Ta–N bond since this allows pyramidal inversion at nitrogen and rotation around the CH(Me)–N bond (reco-ordination of the N-donor is optional). At this temperature **(1b)** decomposes slowly with loss of toluene. The corresponding ^1H n.m.r. spectra of **(1a)** reflect similar behaviour; at 213 K there are two distinct singlets for the benzyl α protons (δ 3.05 and 3.22) that coalesce at 238 K. From these data we can conclude that the underlying fluxionality of these compounds is restricted to a

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‡ ^1H n.m.r. data (200.13 MHz, $CD_3C_6D_5$), for **(1a)** at 294 K: δ 2.09 (6H, s, NCH_3), 3.14 (4H, s, CH_2Ph), 3.66 (2H, s, CH_2N), 6.65—8.07 (14H, m, ArH); for **(1a)** at 213 K: δ 1.89 (6H, s, NCH_3), 3.05 and 3.22 (4H, s, CH_2Ph), 3.46 (2H, s, CH_2N), 6.40—8.35 (14H, m, ArH); for **(1b)** at 294 K: δ 0.95 [3H, d, *J* 6.7 Hz, $C_6H_4CH(CH_3)$], 1.91 and 2.29 (6H, s, NCH_3), 3.23 (4H, s, CH_2Ph), 4.12 (1H, q, *J* 6.7 Hz, C_6H_4CH), 6.65—8.23 (14H, m, ArH); for **(1b)** at 213 K: δ 0.77 [3H, d, *J* 6.7 Hz, $C_6H_4CH(CH_3)$], 1.72 and 2.08 (6H, s, NCH_3), 2.85—3.61 (4H, m, CH_2Ph), 4.03 (1H, q, *J* 6.7 Hz, C_6H_4CH), 6.55—8.37 (14H, m, ArH).

§ *Crystal data* for **(1a)**: [Ta{$C_6H_4CH_2NMe_2$-2}$(CH_2Ph)_2Cl_2$], $C_{23}H_{26}Cl_2NTa$, *M* = 568.32, triclinic space group $P\bar{1}$, *a* = 9.055(2), *b* = 9.614(1), *c* = 13.910(3) Å, α = 72.93(1), β = 80.91(2), γ = 72.74(1)°, *U* = 1102.1(4) $Å^3$, *Z* = 2, D_c = 1.712 g cm^{-3}, μ(Mo-K_α) = 51.8 cm^{-1}. A block-shaped crystal (0.15 × 0.20 × 0.63 mm) of **(1a)**, mounted in a Lindemann glass capillary, was used for data collection on an Enraf-Nonius CAD-4F diffractometer with Zr-filtered Mo-K_α radiation (θ_{max} = 28°). The heavy atoms were located with routine Patterson techniques (SHELXS-86) and the remaining non-H atoms were found in subsequent difference Fourier maps. All H-atoms were introduced at calculated positions except those on C(4) and C(5) which were found in a difference Fourier map. Empirical absorption and extinction corrections were applied (DIFABS). Full-matrix least-squares refinement converged at a final *R* value of 0.049; R_w = 0.057; $w^{-1} = [\sigma^2(F) + 0.001363\,F^2]$ for 3427 unique reflections with $I \geq 2.5\sigma(I)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

scrambling process of the benzyl ligands that does not involve the axial chlorine ligands and that may be initiated by dissociation of the Ta–N bond.

These preliminary results clearly show that tantalum compounds with an intramolecularly co-ordinating N-donor ligand site are readily accessible. We are currently investigating the scope of our synthetic method with 8-(dimethylamino)-1-naphthyl and 2-(dimethylamino)benzyl ligands that likewise afford cyclometallated tantalum compounds but in which the chelate rings have different steric constraints; the thermal decomposition of these compounds involving C–H activation reactions is currently being studied.

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