The first intramolecularly co-ordinated aryl tantalum compounds with amine donors: synthesis and X-ray crystal structure of [Ta{C6H4CH(R)NMe2-2}(CH2Ph)2Cl2](R = H, Me)

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The First Intramolecularly Co-ordinated Aryl Tantalum Compounds with Amine Donors: Synthesis and X-Ray Crystal Structure of
\[ \text{[Ta\{C}_6\text{H}_4\text{CH}(\text{R})\text{NMe}_2\text{-2}\}\text{CH}_2\text{Ph}2\text{Cl}_2] (\text{R} = \text{H, Me}) \]

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[Ta(CH2Ph)2Cl3] reacts with [Zn(C6H4CH(R)NMe2-2)2] (R = H, Me) to afford the new tantalum(v) complexes [Ta{C6H4CH(R)NMe2-2}(CH2Ph)2Cl2] in high yield; these complexes contain a five-membered Ta-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-activation2 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 [Ta(CH2Ph)2Cl3]a with [Zn(C6H4CH2NMe2-2)2] (0.5 equiv.) at −78 °C in toluene-pentane (1:1) gave a dark red solution (and suspended ZnCl2) from which [Ta(C6H4CH2NMe2-2)(CH2Ph)2Cl2] (1a) was isolated as a red powder in 72% yield. The related compound [Ta(C6H4CH(Me)NMe2-2)(CH2Ph)2Cl2] (1b) was prepared by a similar reaction of [Ta(CH2Ph)2Cl3] with [Zn(C6H4CH(Me)NMe2-2)2] in Et2O at −78 °C; yield: 70−75%. Both (1a) and (1b) can be handled at room temperature; (1a) decomposes at ca. 115 °C whereas the

1H n.m.r. data (200.13 MHz, C6D6) at 298 K for [Zn((R)-C6H4CH(Me)NMe2-2)2]: δ 1.22 [6H, d, J 6.7 Hz, C6H4CH(CH3)], 1.96 (12H, s, NCH3), 3.14 (2H, q, J 6.7 Hz, C6H4CH), 7.02−8.00 (8H, m, ArH).
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 −50 °C. The X-ray structure (Figure 1) shows a distorted complex, similar to the mononuclear tantalum species that has a distorted octahedral geometry. In this complex there are two chlorine atoms occupying axial 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 TE-

[C6H4CH(R)NMe2-2(CH2Ph)2Cl2] (1a).

Figure 1. X-Ray structure of [Ta{C6H4CH(R)NMe2-2}2(CH2Ph)2Cl2] (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), 2.496(9); Ta(1)-C(5), 2.335(3); Ta(1)-N(1), 2.187(1); Ta(1)-N(6), 2.296(1); Ta(1)-C(11), 2.154(1); Ta(1)-Cl(1), 176.36(8); C(4)-Ta(1)-Cl(5), 115.0(5); C(5)-Ta(1)-C(11), 99.8(4); N(1)-Ta(1)-N(6), 69.7(4); N(1)-Ta(1)-C(11), 72.9(5).

Note: See Figure 2 for 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).

2.496(9) Å is similar to Sn-N bond lengths in organotin(v) complexes with this type of chelating ligand.6

The 1H n.m.r. spectrum of (1b) (200.13 MHz, CD3C6D4) 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 NMe2 atom 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 co-ordinated to tantalum and 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 NMe2 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
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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