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8. Tantalum

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CONTENTS

INTRODUCTION

This review is intended to cover the literature on the inorganic coordination chemistry of tantalum for the year 1991 and to be a companion monograph to the preceding one on niobium. To keep the review to a managable length, we have chosen to limit the study to low nuclearity inorganic coordination systems only; consequently several areas have had to be omitted. Specifically, the organic/organometallic chemistry of tantalum, high-nuclearity cluster chemistry (including polyoxometallates) and solid state and materials science have been excluded unless there was a strong reason to include them from an inorganic/coordination chemistry viewpoint.

This review is based on coverage of *Chemical Abstracts* from volumes 114 (July-Dec.), 115 and 116 (Jan.-June) repectively.

The layout of this review focuses on the different oxidation states of tantalum which range from +5 down to −2. However, as for niobium most compounds of tantalum in oxidation states lower than +5 are stabilised by carbon-based organic ligands and as such lie outside the scope of the present review. Consequently it has proven more efficient to separate the +5 oxidation state from the others since most studies in coordination chemistry have inevitably dealt with the former state. Within each main section the sub-sections are organised according to the nature of the coordinated ligands; halogens from group 17, chalcogens from group 16 and pnictogens from group 15. Within

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these broad boundaries however, there are areas of overlap when ligands from more than one group are present but these species will be covered in at least one of the relevant sections.

The readers' attention is directed to a comprehensive review of the coordination chemistry of niobium and tantalum for the years 1985-1987 especially for areas of cluster chemistry, solid state and material related science [1].

8.1 TANTALUM (V)

8.1.1 Complexes with group 17 donor ligands

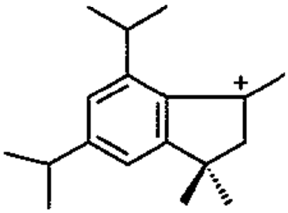
Like niobium(V), tantalum(V) is a hard Lewis acid and as such prefers to coordinate hard Lewis bases such as those from groups 15-17. Many of these complexes have been well studied but certain areas are still under active investigation, such as the use of halide complexes of tantalum to aid crystallinity, as synthetic precursors and for vibrational studies. Some of these applications are described below.

The vibrational frequencies of $[TaX_6]^-$ (X = F, Cl, Br, I) have been calculated in the same fashion as for analogous $[NbX_6]^-$ systems and shown to give good agreement with experimentally determined values [2].

Both niobium and tantalum fluorides and oxyfluorides have been synthesised under high temperature conditions from molten, stoichiometric mixtures of M_2O_5 (M = Nb, Ta) in NH_4HF_2 or $M'HF_2$ (M' = alkali metal) [3].

The hexahalo tantalate anions have proven particularly useful in their capacity to stabilise reactive or unusual cationic species in a similar way to hexahaloniobates. In this regard, the high thermodynamic stability and high crystallinity of $[TaX_6]^-$ systems make them ideally suited to this task. Thus, the novel complex $[C_3H_5N_2]^+[TaCl_6]^-$ has been studied by single-crystal X-ray diffraction and shown to be orthorhombic with the space group *Pnma*. As expected, the $[TaX_6]^-$ anion is octahedral with (Ta-Cl) distances ranging from 2.317 (3) Å to 2.362 (3) Å. The $[C_3H_5N_2]^+$ cation is the imidazolium cation which appears to interact with the tantalate anion *via* N-H and Cl-H bonds [4]. Moreover, there is cohesion between the layers due to the presence of normal van der Waals contacts. Another novel system involves tetramethyltetraselenafulvalenium fluorotantalate which contains the $[Ta_2F_{11}]^-$ anion [5]. The reactive cation, $[ClF_2]^+$ has been stabilised by combination with $[TaF_6]^-$, and $[NbF_6]^-$ [7]. The tantalum system is isostructural to that found for niobium [6].

The pentahalides of tantalum have continued to find use as synthetic precursors in both inorganic and organometallic chemistry but one remarkable and unexpected organic application involves the cleavage of C-C and C-H bonds in alkyl benzenes facilitated by the $TaCl_5$-CH_2Cl_2 system [8]. Thus, treatment of 1,3,5,-triisopropylbenzene with $TaCl_5$-CH_2Cl_2 affords the diisopropyltrimethylindan-1-yl cation (**1**) whereas treatment of both 1,2,4,5-tetramethylbenzene and 1,2,3,5,-tetramethylbenzene with the same tantalum solution affords the dihydroanthryl cation (**2**). Both cations crystallise with the octahedral $[TaCl_6]^-$ counterion and have been characterised by X-ray diffraction.



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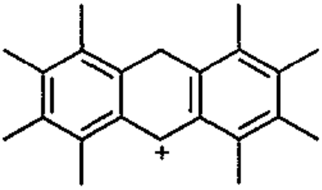


(2)

8.1.2 *Complexes with group 16 donor ligands*

As with niobium, the coordination chemistry of tantalum(V) is dominated by ligation with group 16 donor atoms, particularly oxygen. Again, as with niobium, the chemistry of the [Ta-O] and [Ta-OR] moieties has formed the basis of most study. Below, we discuss the various areas of tantalum(V) chemistry in the order (i) oxyhalide species, (ii) alkoxide compounds and (iii) sulfur compounds. By the very similar nature of niobium(V) and tantalum(V), several of the studies reported for niobium have been duplicated for tantalum [6].

Both high-temperature molten salt and low-temperature solution synthetic routes to oxyhalide species have been investigated. Thus, reaction of Ta_2O_5 with metal fluorides or oxides in NH_4HF_2 or $M'HF_2$ (M' = alkali metal) melts gives tantalum fluorides or oxyfluorides of alkali, alkaline earth or transition metals [3]. A more convenient, low-temperature solution route to thiohalides has been developed for both niobium and tantalum. In this strategy, the thermodynamic driving force for reaction is provided by the formation of HCl (or an adduct with a suitable nitrogen base) or Me_3SiCl. In addition to this, since the products of these reactions, thiohalides, are usually less soluble in common organic solvents than the starting materials there is an additional driving force provided by the precipitation of the product from solution [9]. Equations 1 and 2 illustrate this synthetic methodology [9], where X = Cl, Br.

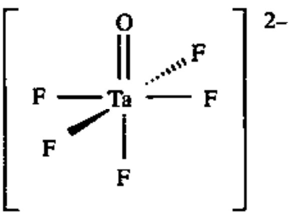
$$TaX_5 + H_2S \xrightarrow{CCl_4/CH_2Cl_2} Ta(S)X_3 \quad (1)$$

$$TaX_5 + (Me_3Si)_2S \xrightarrow{CCl_4/CH_2Cl_2} Ta(S)X_3 \quad (2)$$

The product thiohalides are also Lewis acids like the pentahalide starting materials and as such ae capable of coordinating Lewis bases such as halide donors, equation 3 [9]. The structures of mixed oxyhalides of tantalum such as $Ta(X)Cl_3$ have not been reported but are believed to be polymeric by analogy with niobium systems such as $[Nb(O)Cl_3]_n$ which are known to be linear, polymeric species.

$$Ta(S)Cl_3 + PPh_4Cl \xrightarrow{CH_2Cl_2} [PPh_4]_2[Ta(S)Cl_5].2CH_2Cl_2 \qquad (3)$$

The crystal structure of the complex, $[Et_3NH]_2[Ta(O)F_5]$ has been reported. It is monoclinic with the space group $P2_1/n$. The tantalum-containing anion has the expected pseudo-octahedral structure (3). Hydrogen-bonding exists between the $[Et_3NH]^+$ cation and $[Ta(O)F_5]^-$. This complex has been prepared by the evaporation of a mixture containing Ta_2O_5 in 38% HF in the presence of NEt_3 [10].



(3)

As found also with niobium, a variety of alkoxide complexes of tantalum have been prepared, many of them heteropolymetallic. In most cases however, characterisation has been provided only by elemental analysis, IR and UV-VIS spectroscopic data, magnetic studies and molecular weight measurements. Very few of these complicated polymetallic species have been studied by single-crystal X-ray diffraction. The complexes that have been reported are, $Ni[Al(O^tBu)_4][Ta(O^iPr)_6]$ [11], $[Ta(O^iPr)_6]Co[Al(O^tBu)_4]$ [12], the latter prepared as shown in equation 4.

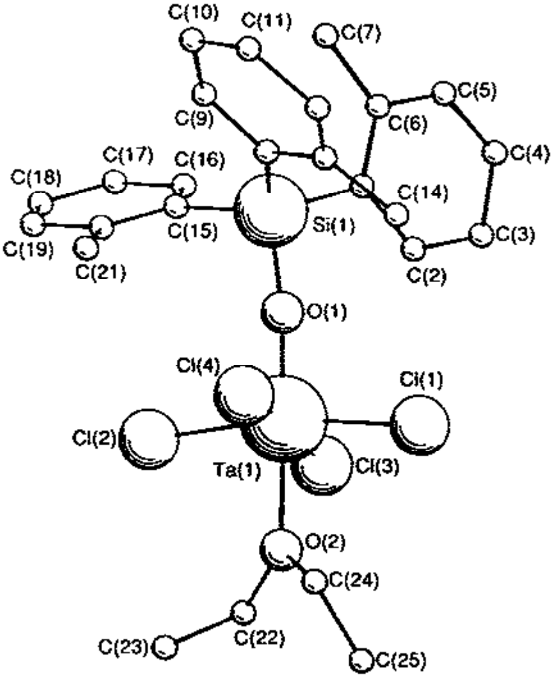
$$ClCo[Al(O^tBu)_4] + K[Ta(O^iPr)_6] \longrightarrow [Ta(O^iPr)_6]Co[Al(O^tBu)_4] + KCl \quad (4)$$

Reactions of $Ta(OEt)_5$ with salicylic acid hydrazide (H_2Sa) and anthranilic acid hydrazide (HAa) in different stoichiometric ratios in refluxing benzene gave $[Ta(OEt)_{6-2n}(Sa)_n]$ (n = 1, 2) and $[Ta(OEt)_{6-n}(Aa)_n]$ (n = 1-3) respectively in an analogous fashion to the reactions with niobium [13]. Subsequently, both $[Ta(O^tBu)_{6-2n}(Sa)_n]$ and $[Ta(O^tBu)_{5-n}(Aa)_n]$ were isolated by alcohol exchange reactions. Characterisation of each complex was provided, in each case by elemental analysis and IR and NMR spectroscopies.

As with niobium, the use of sterically demanding aryloxides in tantalum chemistry has permitted a variety of reactivities and structures; thus equations (5) and (6) illustrate some results with the bulky siloxide ligand, $[OSi(C_6H_4Me\text{-}2)]$ [14].

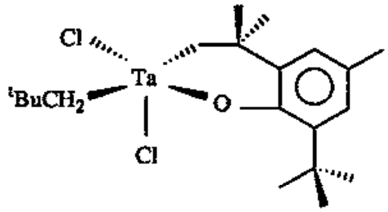
$$TaCl_5 + Li[OSi(C_6H_4Me\text{-}2)_3] \longrightarrow TaCl_4[OSi(C_6H_4Me\text{-}2)_3].1.5Et_2O \quad (5)$$

$$\begin{aligned} TaCl_4[OSi(C_6H_4Me\text{-}2)_3] + 3\,MeMgX \longrightarrow\ & TaMe_3Cl[OSi(C_6H_4Me\text{-}2)_3] \\ & + \\ & \{TaMe_3[OSi(C_6H_4Me\text{-}2)_3]\}_2 \\ & + \\ & TaMe_2Cl[OSi(C_6H_4Me\text{-}2)_3]_2 \quad (6) \end{aligned}$$



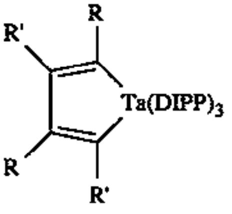
Crystal structure of $TaCl_4[OSi(C_6H_4Me\text{-}2)_3].1.5Et_2O$ (4).
Reproduced with permission from ref. 14.

The final product in equation 6 can also be prepared by reaction of $TaCl_3[OSi(C_6H_4Me\text{-}2)]_2$ with two equivalents of MeMgX (X = Cl, I) [14]. The crystal structure of $TaCl_4[OSi(C_6H_4Me\text{-}2)_3].1.5Et_2O$ has been reported (4), showing the complex to possess mutually *trans* aryloxide and ether ligands. The tantalum-oxygen distances are 1.812 (3) Å (siloxo) and 2.263 (3) Å (ether) respectively, and the tantalum-chlorine distances range from 2.328 to 2.356 (1) Å [15]. The theme of sterically-demanding aryloxide ligands is continued with the isolation and single-crystal X-ray structure of $Ta(CH_2C_6H_4\text{-}Me)_3(OC_6H_3Ph_2\text{-}2,6)_2$ [15]. This compound extrudes one equivalent of *p*-xylene when heated to 150°C to afford a cyclometallated product, from one of the ortho-phenyl substituents on the aryloxide ligand. Similar results were reported for the niobium analogue [15]. In a related system, it has been reported that reaction of $Ta(CH_2{}^tBu)_3Cl_2$ with $Li\text{-}O\text{-}2,6\text{-}{}^tBu_2C_6H_2Me$ in a 1:1 stoichiometric ratio affords either $Ta(CH_2{}^tBu)_2Cl_2(O\text{-}2,6\text{-}{}^tBu_2C_6H_2Me)$ by displacement of one neopentyl group or the cyclometallated product (5), in which one of the methyl groups of an ortho-^{t}Bu group has been metallated [16].



(5)

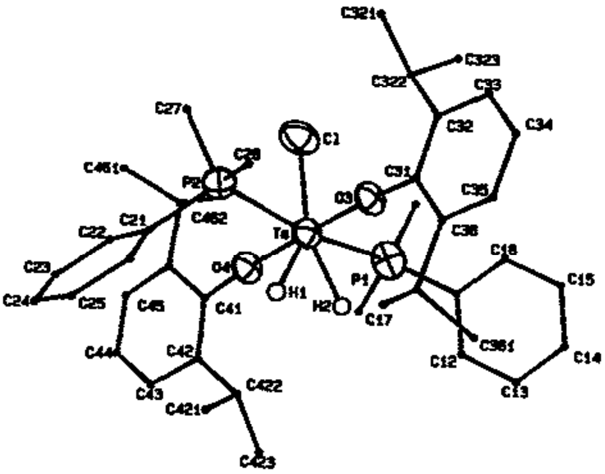
The stabilisation of unusual ligands *via* reductive coupling is a reaction that has considerable synthetic potential and one that has been investigated for a variety of early transition metals. Thus, $Ta(DIPP)_3Cl_2(OEt_2)$, where DIPP is the 2,6-diisopropylphenoxo group, is reduced by two electrons in the presence of the bulky alkynes PhCCPh and $Me_3SiCCMe$ to afford the pale yellow 1:1 adducts, $Ta(PhCCPh)(DIPP)_3$ and $Ta(Me_3SiCCMe)(DIPP)_3$ [17]. However, the reduction of $Ta(DIPP)_3Cl_2(OEt_2)$ in the presence of smaller internal alkynes such as EtCCEt or the terminal alkynes, Me_3SiCCH or ^{t}BuCCH affords the metallacyclopentadienes shown in the figure (6).



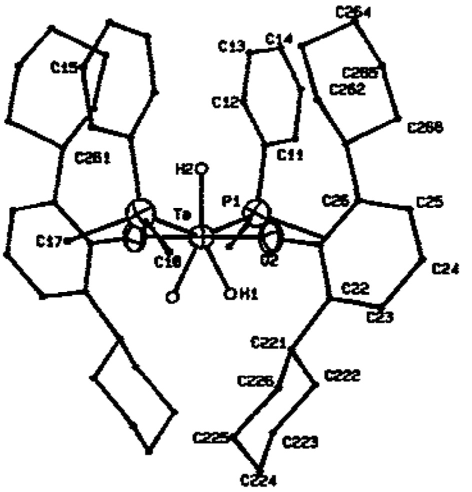
R = R' = Et; R = Me_3Si, ^{t}Bu; R' = H

(6)

The presence of large aryloxide ligands has also resulted in the isolation of rare and highly reactive mononuclear hydrido complexes. Thus, hydrogenation (1200 psi, 80°C) of cyclohexane



Crystal structure of Ta(DIPP)Cl(H)$_2$(PMe$_3$)$_2$ (7).
Reproduced with permission from ref. 18.



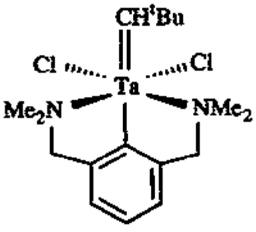
Crystal structure of Ta(O-2,6-Cy$_2$C$_6$H$_3$)$_2$(H)$_3$(PMe$_2$Ph)$_2$ (8).
Reproduced with permission from ref. 18.

solutions of $Ta(DIPP)_2Cl(CH_2SiMe_3)_2$ and $Ta(DIPP)_2(CH_2SiMe_3)_3$ in the presence of tertiary phosphines leads to $Ta(DIPP)_2Cl(H)_2L_2$ (L = PMe_3, PMe_2Ph, $PMePh_2$) and $Ta(DIPP)_2(H)_3(PMe_2Ph)_2$ in high yield [18]. Under the same conditions, the compounds $Ta(DPhP)_2(CH_2C_6H_4\text{-}Me)_3$ or $Ta(DPhP)_2(CH_2SiMe_3)_3$ (where DPhP = 2,6-diphenylphenoxide) form $Ta(O\text{-}2,6\text{-}Cy_2C_6H_3)_2(H)_3L_2$ (L = PMe_2Ph, $PMePh_2$) in which the diphenylphenoxide groups have undergone hydrogenation. The X-ray crystal structures of $Ta(DIPP)_2Cl(H)_2(PMe_3)_2$ (7) and $Ta(O\text{-}2,6\text{-}Cy_2C_6H_3)_2(H)_3(PMe_2Ph)_2$ (8) have also been reported in the same study. Both molecules adopt a pentagonal bi-pyramidal geometry in which the aryloxide ligands are in mutually *trans* positions. The two hydride ligands are *cis* in (7) while in (8) a crystallographically imposed two-fold axis of symmetry runs through a unique hydride within the pentagonal plane. The NMR spectroscopic properties of these seven-coordinate hydrides show the Ta-*H* group resonating at low field and the spectroscopic characteristics are consistent with a non-fluxional geometry on the NMR timescale at room temperature. In compound (8), exchange of the two chemically equivalent hydride ligands is slow leading to a AA'XX' (X = ^{31}P) spin system in the ^{1}H NMR spectrum. Analysis of this pattern allows quantification of the H-H, H-P and P-P coupling constants. In compound (8), the unique hydride displays a triplet of triplets pattern, the remaining two hydides constituting a complex multiplet. Furthermore, complex (8) acts as a catalyst precursor for the homogeneous hydrogenation of naphthalene to tetralin [18].

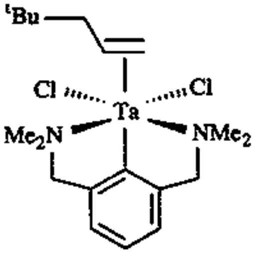
A few studies, primarily from the Mehrotra group, have dealt with sulfur containing ligands. Thus, the reactions of $Ta(O^{i}Pr)_5$ with $(RO)_2P(S)SH$ (R = Et, Pr, ^{i}Pr, ^{s}Bu, Ph) in equimolar ratios yield compounds of the form, $(^{i}PrO)_4Ta[S_2P(OR)_2]$ as hydrolyzable, yellow liquids which are soluble in common organic solvents and monomeric in freezing benzene [19]. Characterisation of these materials has been provided by molecular weight, spectral studies (NMR, IR) but no single-crystal X-ray diffraction studies have been carried out. The compounds are postulated to have chelating, bidentate $[S_2P(OR)_2]$ moieties [19]. In a related study, different dithiophosphate reagents have been used in which the OR groups on phosphorus are replaced by bridged diolato fragments such as in (OGO)P(S)SH where G = tetramethylene, 1,2-dimethylethylene, 2-dimethylpropylene and 2-diethylpropylene [20]. The products, $(^{i}PrO)_4Ta[S_2P(OGO)]$ have been characterised using standard methods are again postulated to be monomeric with bidentate $[S_2P(OGO)]$ moieties. The same group have also reported the isolation of analogous products, $TaCl_3[S_2P(OR)_2]_2$, from the reaction of $TaCl_5$ with $[(RO)_2PS_2]Na$ or $[(RO)_2PS_2][NH_4]$ (R = Ph, ^{i}Pr, ^{i}Bu) [21]. These complexes are reported to be orange-yellow viscous liquids which are soluble in common organic solvents and are moisture sensitive. For each compound a single ^{31}P NMR resonance is observed in the range, δ 77.6-86.8 ppm which is characteristic of dithiophosphates. No structural data were provided.

8.1.3 *Complexes with group 15 donor ligands*

Some rather unusual nitrogen-based ligands have been reported coordinated to tantalum. For example, the complex (9) has been synthesised as used as a precursor to organometallic complexes such as (10), formed *via* reaction of (9) with ethylene [22].



(**9**)

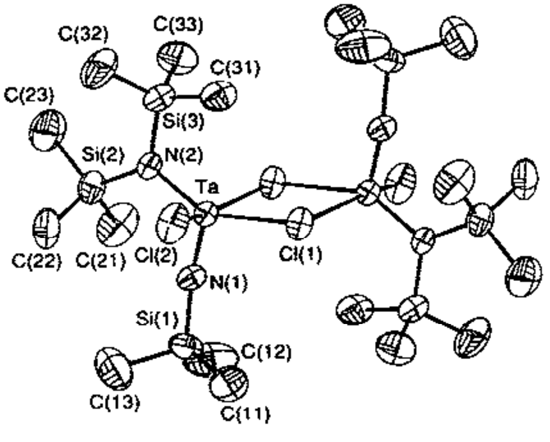


(**10**)

The reaction of $TaCl_5$ with EtNCO in acetonitrile solvent led to the formation of Ta[Et*N*C(O)N=CMeNEtC(O)Cl]Cl_4 [23], in which the organic ligand is coordinated to tantalum *via* the nitrogen atom in italics. This complex my subsequently be hydrolysed to afford 1,3-diethyl-6-methyl-[1H,3H]-1,3,5-triazine-2,4-dione and $TaCl_5$. This hydrolysis reaction is reversible.

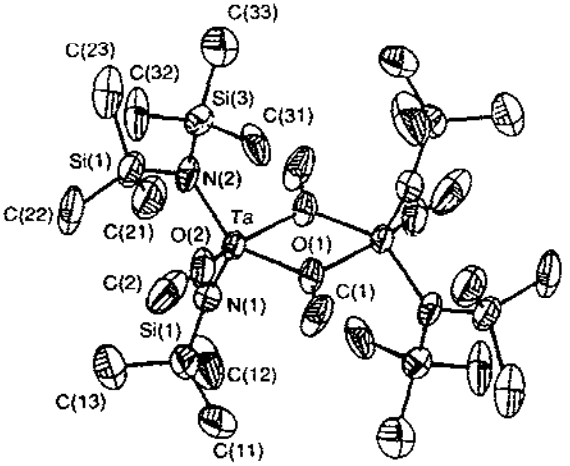
As with niobium(V), many studies have been reported concerning the chemistry of tantalum(V) with imido [=NR] ligands. An usual trimethylsilyl transfer reaction leads to the formation of a coordinated trimethylsilyl imido ligand (equation 7) [24].

$$Ta(O)Cl_3 + 3\,LiN(SiMe_3)_2 \xrightarrow{Et_2O} Ta[N(SiMe_3)_2]_2[NSiMe_3][OSiMe_3] \quad (7)$$



Crystal structure of [{Ta(μ-Cl)Cl(NSiMe$_3$)[N(SiMe$_3$)$_2$}$_2$] (**11**).
Reproduced with permission from ref. 25.

The product is isolated in only low (27%) yield. The niobium analogue is reported in the same paper. A variety of imido complexes of tantalum(V) have been prepared by Bradley and co-workers as illustrated in Scheme 1 [25]. Two of the complexes have been studied by X-ray crystallography. $[\{Ta(\mu\text{-}Cl)Cl(NSiMe_3)[N(SiMe_3)_2]\}_2]$ **(11)** and $[\{Ta(\mu\text{-}OMe)OMe(NSiMe_3)[N(SiMe_3)_2]\}_2]$ **(12)** both possess dimeric structures in which the tantalum atoms are each in distorted square-pyramidal configurations and the imido ligands occupy the axial positions. The very short $(Ta{=}NSiMe_3)$ separations of 1.755 (7) Å **(12)** and 1.777 (11) Å **(13)** respectively coupled with the near-linearity of the (Ta=N-Si) moieties sugest that the imido nitrogen atoms donate four electrons to the tantalum metal centre [25].



$[\{Ta(\mu\text{-}OMe)OMe(NSiMe_3)[N(SiMe_3)_2\}_2]$ **(12)**.
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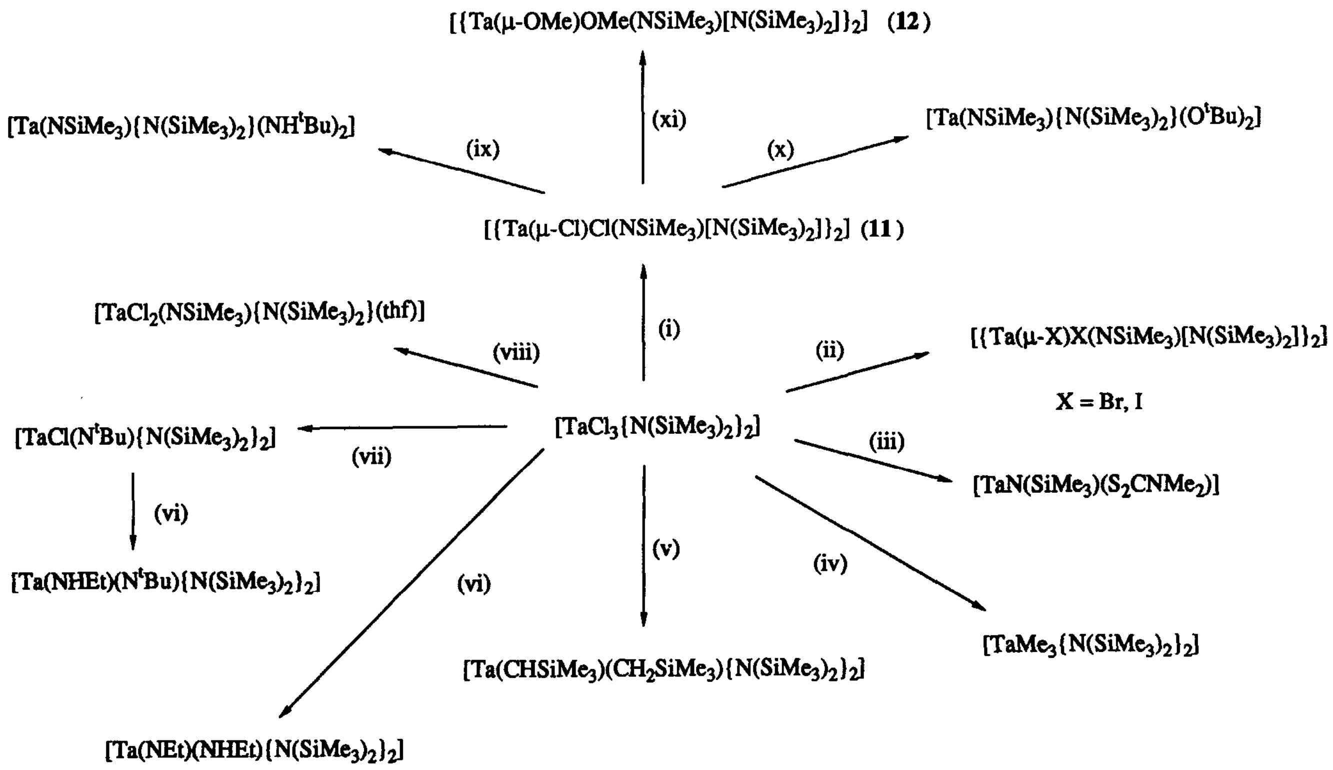
8.2 LOWER OXIDATION STATES OF TANTALUM

8.2.1 Complexes with group 17 donor ligands

Homoleptic halides of tantalum in lower oxidation states have continued to find use as starting materials for the synthesis of other low oxidation state complexes, particularly organometallic species as in equation 8 [26].

$$TaCl_4 + 4\,LiR \longrightarrow TaR_4 \qquad (8)$$

$(R = 2\text{-}MeC_6H_4,\ 2,5\text{-}Me_2C_6H_3)$



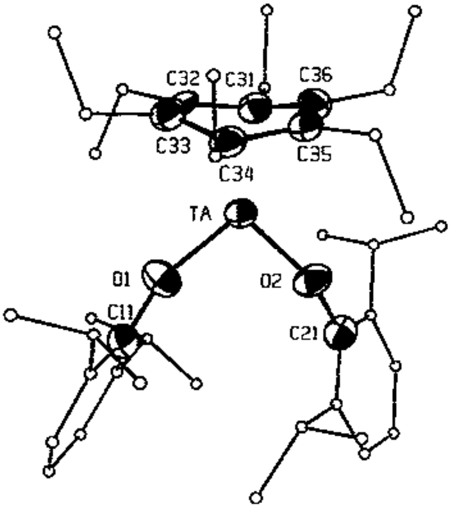
(i) heat; (ii) Me_3SiX; (iii) NaS_2CNMe_2; (iv) LiMe; (v) $LiCH_2SiMe_3$;
(vi) LiNHEt; (vii) $LiNH^tBu$; (viii) thf; (ix) $LiNH^tBu$; (x) LiO^tBu; (xi) LiOMe

Scheme 1

8.2.2 Complexes with group 16 donor ligands

The dissolution and subsequent evaporation of aliphatic alcoholic solutions of $[(Ta_6X_{12})(H_2O)_4X_2].4H_2O$ (X = Cl, Br) in a vacuum have resulted in complete exchange of the four coordinated water molecules and two terminal halide ligands by aliphatic alcohols forming insoluble, crystalline, diamagnetic clusters $[Ta_6X_{12}(ROH)_6]X_2$ (R = CH_3, C_2H_5, $CHMe_2$, CH_2CHMe_2) [27]. Spectral evidence indicates occupation of all octahedral coordination sites by aliphatic alcohol molecules.

As with niobium, the use of sterically demanding alkoxides and aryloxides has been used to stabilise low oxidation states and low coordination numbers at tantalum. Thus, $(\eta^6$-$C_6Me_6)Ta(DIPP)_2Cl$ (DIPP = 2,6-diisopropylphenoxide) undergoes a facile one-electron reduction in the presence of sodium amalgam to afford the complex $(\eta^6$-$C_6Me_6)Ta(DIPP)_2$ [28]. This is formally a complex of tantalum(II) and if the $(\eta^6$-$C_6Me_6)$ ligand is regarded as occupying a single coordinaton site then the tantalum atom is formally three coordinate, an unusually low coordination number for such an oxophilic and relatively large transition metal. The crystal structure of $(\eta^6$-$C_6Et_6)Ta(DIPP)_2$ (**13**) [28] confirms this low coordination number.



Crystal structure of $(\eta^6$-$C_6Et_6)Ta(DIPP)_2$ (**13**). Reproduced with permission from ref. 28.

The extremely bulky siloxide ligand SILOX ($^tBu_3SiO$-) has been used in the synthesis of low valent, low coordination number complexes of tanatalum [29]. Thus, $[Ta(SILOX)_3]$ reacts smoothly with olefins such as C_2H_4, C_2H_3Me, 1-butene and *cis*-2-butene to afford the 1:1 adducts [Ta(olefin)$(SILOX)_3$]. In the cases of the latter two olefins a competing cyclometallation process also produced $\{Ta[OSi_9(CMe_3)_2CMe_2CH_2](H)(SILOX)_2\}$. In concentrated benzene solution, $[Ta(SILOX)_3]$ trapped benzene to afford the novel, bridging complex $[Ta(SILOX)_3]_2[\mu$-

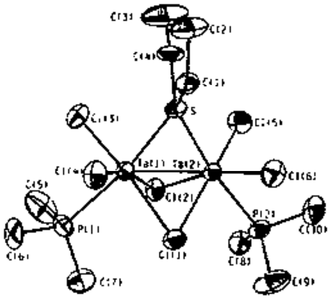
$\eta^2(1,2)$:$\eta^2(4,5)$-C_6H_6] in low (7%) yield along with the cyclometallated product above. Ethyne, 2-butyne and $F_3CC{\equiv}CCF_3$ reacted with [Ta(SILOX)$_3$] to afford [Ta(alkyne)(SILOX)$_3$]. Treatment of [Ta(SILOX)$_3$] with pyridine, 2-picoline, 2,6-lutidine, pyridazine (1,2-$N_2C_4H_4$), pyrimidine (1,3-$N_2C_4H_4$) provided the complexes, [Ta(SILOX)$_3$(η^2-NC_5H_5-*N*,*C*)], [Ta(SILOX)$_3$(η^2-6-NC_5H_4Me-*N*,*C*)], [Ta(SILOX)$_3$(η^2-2,6-$NC_5H_3Me_2$-*N*,*C*)], [Ta(SILOX)$_3$(η^2-$N_2C_4H_4$-*N*,*N*)] and [Ta(SILOX)$_3$(η^2-1,3-$N_2C_4H_4$-N^1,C^6)] respectively.Formation of these η^2 heterocyclic adducts is proposed to occur *via* nucleophilic attack by [Ta(SILOX)$_3$] at the LUMO (predominantly C=N π^*) of the substrate, a process consistent with the generation of the pyridyl-hydride complex, [Ta(SILOX)(H)($C_5H_2Me_2N$)] from 2,6-lutidine prior to equilibration. Molecular orbital calculations, in the extended Huckel mode, on η^1- and η^2-coordination forms of [Ta(SILOX)$_3$(NC_5H_5)] provide a rationale for the variation in pyridine ligation. Of critical importance are the four-electron repulsions between filled d_{z^2} orbitals on tantalum and the pyridine-nirtogen donor orbitals and the capability of pyridine to function as a good π-acceptor in the η^2-mode [29].

8.2.3 Complexes with group 15 donor ligands

Two coordination complexes have been characterised by single-crystal X-ray diffraction that contain tertiary phosphine ligands. [$Ta_2(\mu\text{-}Cl)_2Cl_4$(tht)($PMe_3)_2$] (**14**) was shown to possess the face-shared bioctahedral structure shown below in which two chlorine atoms and the tetrahydrothiophene ligands adopt bridging positions [30]. The (Ta-Ta) separation is 2.682 (3) Å, the (Ta-S) distance is 2.422 (6) Å and the (Ta-P) distance is 2.623 (8) Å. As expected, the terminal chlorine atoms are closer to tantalum than the bridging ones with $(Ta\text{-}Cl)_{terminal}$ of 2.375 (9) Å and $(Ta\text{-}Cl)_{bridge}$ of 2.502 (13) Å. The complex, [$Ta_4S_4Cl_8(PMe_3)_6$] (**15**) was produced in low yield (*ca.* 2%!) along with [$Ta_2S_2Cl_4(PMe_3)_4$] (20%) in the reaction of $TaCl_5$ with Li_2S and sodium amalgam in the presence of PMe_3 [31]. The crystal structure of (**15**) shows a tetranuclear tantalum compound comprising a central $Ta(\mu\text{-}S)_4Ta$ unit with *trans* [$Cl_2(PMe_3)_2$] sets of ligands on each end. To this are added two [$TaCl_2(PMe_3)$] units so that octahedral coordination is completed about each metal atom. The central (Ta-Ta) distance, at 2.891 (1) Å is consistent with a single bond. The other two, equivalent, (Ta-Ta) distances are significantly longer [3.091 (1) Å] but probably represent a bonding interaction.

The mechanism of formation of (**15**) and [$Ta_2S_2Cl_4(PMe_3)_4$] is not known although it is possible that (**15**) could be a precursor to, or condensation product of, the dinuclear compound (equation 9).

$$[Ta_4S_4Cl_8(PMe_3)_6] + 2\,PMe_3 \longrightarrow 2\,[Ta_2S_2Cl_4(PMe_3)_4] \qquad (9)$$



Crystal structure of [$Ta_2(\mu\text{-}Cl)_2Cl_4(tht)(PMe_3)_2$] (**14**).
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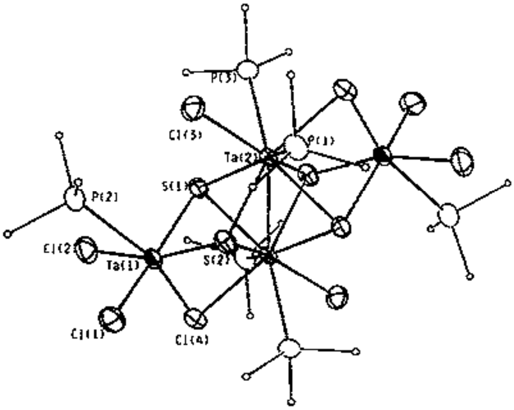

Crystal structure of [$Ta_4S_4Cl_8(PMe_3)_6$] (**15**).
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