8. Tantalum 1992

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CONTENTS

INTRODUCTION

This review is intended to cover the literature on the inorganic coordination chemistry of tantalum for the year 1992 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, 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. Also we have included aspects of the metallo-organic chemistry of tantalum only where there was sufficient cause to do so from the coordination point of view.

The review is based on coverage of *Chemical Abstracts* volumes 116 (July-Dec.), 117 and 118 (Jan-June).

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] and to the preceeding review of the coordination chemistry of niobium for 1992 [2].

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 over several years but certain areas are still under active investigation, such as the use of halide complexes of tantalum to advance aspects of separation science and spectrophotometric determinations of tantalum, as synthetic precursors and for vibrational studies. Some of these applications are described below.

The simultaneous spectrophotometric determination of tantalum has been examined in an analogous way to that of niobium, exloiting the colour development between *o*-hydroxyhydroquinonephthalein and niobium or tantalum in the presence of hexadecyltrimethylammonium chloride in strong acid media [3]. In a similar vein, a spectrophotometric method for determining tantalum, based on the extraction of its ternary complex with pyrogallol and mepazine hydrochloride from an H_2SO_4 acid medium into chloroform has been reported [4].

A simple, one-step preparation of $[MF_n(SO_3F)_{5-n}]$ (M = Nb, Ta; n > 3) has been reported. The procedure involves the oxidation of the metal M by $S_2O_6F_2$ in the presence of the corresponding MF_5 at room temperature and leads to colourless viscous liquids. Of the resulting products, $[MF_n(SO_3F)_{5-n}]$ (M = Nb, Ta; n > 3) can be distilled *in vacuo* without decomposition. The preparation of $[TaF_3(SO_3F)_2]$ is also described [5].

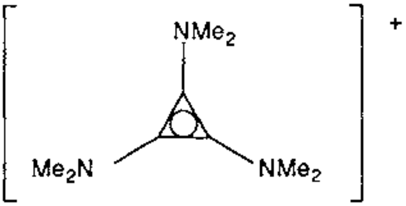
The compounds $K_2[NbOF_5.H_2O]$ and $K_2[TaF_7]$ were prepared through melting Nb_2O_5 and Ta_2O_5 with $KHF_2.2H_2O$, followed by recrystallisation [6]. The properties of both compounds towards hydrolysis were also examined. As temperature (from 250-550°C) and pressure (from 500 to 1500 bar) increase, the degree of hydrolysis of both $K_2[NbOF_5.H_2O]$ and $K_2[TaF_7]$ increases. Both the niobium and tantalum complexes are unstable in supercritical aqueous fluids. The degree of hydrolysis of both $K_2[NbOF_5.H_2O]$ and $K_2[TaF_7]$ decreases with increasing concentration of HF, independent of the concentration of NaF. The distribution coefficients of niobium and tantalum between granitic melt and the co-existing fluid phase are less than 0.15; *i.e.* most of the niobium and tantalum remain in the granitic melt. The distribution coefficient of tantalum is more dependent upon HF concentration than that of niobium [6].

The formation of complexes of tantalum(V) in NaCl/$AlCl_3$ melts at 175°C and 300°C have been studied by potentiometric and spectrophotometric methods [7]. The results at 175°C could, within the pCl range 1.13-*ca.* 4.5 and with tantalum(V) concentration in the range 0-0.3 M, best be explained by the equilibrium in equation (i), with a pK_a value (based on molar concentrations) of 3.89(4) and a solubility limit for tantalum of 0.087(9) M.

$$[TaCl_6]^- \rightleftharpoons TaCl_5 + Cl^- \qquad (i)$$

Equilibria involving Ta_2Cl_{10} could not be ruled out. UV-VIS spectra of pure $TaCl_5$ and $[TaCl_6]^-$ were difficult to obtain because of the formation of oxo-chloro species. The electrochemical reduction of tantalum(V) in $AlCl_3$-rich melts results in the formation of tantalum(IV) followed by dimerisation and reduction to Ta_6Cl_{14} and other tantalum clusters. No tantalum metal was observed to form during electrolysis [7].

Thermal vibrational amplitudes, determined from a single crystal X-ray study of monoclinic $K_2[TaF_7]$ at room temperature show similar characteristics to the neutron values for isomorphous $K_2[NbF_7]$ exhibiting considerable variations in anisotropies for the different fluorine atoms. These variations can be rationalised by using a combination of electron pair repulsion theory and crystal packing considerations [8].



(1)

Hexa-halo complexes of both niobium and tantalum have continued to be studied. In some cases it is the cation that has been of interest rather than the metal containing anion. Thus, 1,2,3-tris(dimethylamino)cyclopropenylium salts (1) of $[NbCl_6]^-$ and $[TaCl_6]^-$ were shown to be rhombohedral [9] and the complex, $[MePh_3P][TaF_6]$ contains a similar, octahedrally coordinated tantalate anion but in this case the lattice is monoclinic [10].

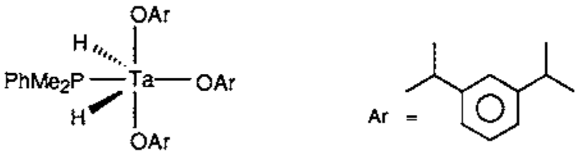
In the field of metallo-organic chemistry, the use of complexes of tantalum halides has continued to be a versatile one for the synthesis of a variety of complexes containing many different ligands. Thus, $[(\eta^5\text{-}C_5Me_5)TaCl_4]$ reacts with two equivalents of 2-butenyl Grignard reagent in thf to afford the tantalum butadiene complex, $[(\eta^5\text{-}C_5Me_5)TaCl_2(C_4H_6)]$. Similarly, reaction of $[(\eta^5\text{-}C_5Me_5)TaCl_4]$ with methylated allyl anions gave the corresponding diene complexes, $[(\eta^5\text{-}C_5Me_5)TaCl_2(\text{diene})]$ where diene = isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene [11]. In a similar fashion, the reaction of $[(\eta^5\text{-Cp})TaCl_4]$ (Cp = C_5Me_5, $C_5H_4SiMe_3$, $C_5H_3(SiMe_3)_2$) with Al_2Me_6 leads to $[(\eta^5\text{-Cp})TaCl_3Me]$ and $[(\eta^5\text{-Cp})TaCl_2Me_2]$ [12]. The structure of $[(\eta^5\text{-Cp})TaCl_2Me_2]$ has been determined by single crystal X-ray diffraction and shown to possess the expected four-legged piano stool type structure typical of mono-cyclopentadineyl systems [12]. The temperature dependence of the chemical shift difference of $\delta[CH_3 - CH_2D]$ has been used as evidence for the presence of agostic interactions between the methyl hydrogens and an electron-defficient metal centre [13]. In the case of the series of tantalum compounds, $[Ta(CH_2D)_nCl_{5-n}]$ (n

= 1-3), no temperature dependence was observed suggesting that, in the limits of the experimental protocol, no agostic interactions are present.

8.1.2 Complexes with group 16 donor ligands

As with niobium, most studies of ligands with group 16 donor atoms have concentrated on alkoxo and related systems.

Thus, $[Ta(O\text{-}2,6\text{-}Cy_2C_6H_3)_2H_3(PMe_2Ph)_2]$ acts as a catalyst precursor for hydrogenation of naphthalene and anthracene, at 90°C under 1200 psi H_2 for 24 h, to produce 1,2,3,4-tetrahydronaphthalene and 1,2,3,4-tetrahydroanthracene respectively with a small amount of the octahydro-product in the latter case [14]. The hydrogenation of naphthalene-d_8 and anthracene-d_{10} by $[Ta(O\text{-}2,6\text{-}Cy_2C_6H_3)_2H_3(PMe_2Ph)_2]$ produces tetrahydro-derivatives (by NMR spectroscopy) in which the hydrogen atoms introduced are all *cis*, thereby suggesting that hydrogenation occurs on the same face of the substrate [14].



(2)

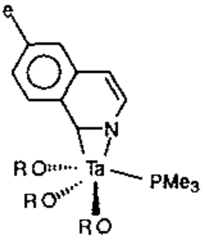
Compounds of the form $[Ta(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_3H_2L]$ (2) are prepared by reaction of $[Ta(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_3(CH_2C_6H_4Me)_2]$ with H_2 in the presence of tertiary phosphine ligands L [15]. The solid state structure of the PMe_2Ph derivative reveals a severely distorted geometry about the tantalum coordination sphere from the ideal octahedral. Hydrogenation of arylphosphines and other aromatic substrates is catalysed by these dihydride compounds in a similar fashion to the compounds $[Ta(O\text{-}2,6\text{-}Cy_2C_6H_3)_2H_3(PMe_2Ph)_2]$.

The compound $[TaCl(O\text{-}4\text{-}{}^tBuC_6H_4)_4]$ has been prepared by reaction of $TaCl_5$ and $HO\text{-}4\text{-}{}^tBuC_6H_4$ in a 1:4 stoichiometric ratio in benzene solvent under reflux and characterised by elemental analysis, molar conductance, molecular weight determinations, infrared, NMR spectral and mass spectrometric studies [16]. Reactions of $[TaCl(O\text{-}4\text{-}{}^tBuC_6H_4)_4]$ with approximately equimolar amounts of some aliphatic amines yield 1:1 addition compounds whereas with strong chloride ion acceptors, it behaves as a chloride donor indicating the formation of $[Ta(O\text{-}4\text{-}{}^tBuC_6H_4)_4][MCl_4]$ (M = Al, Fe, Sb).

In a related study, $[Ta(O\text{-}4\text{-}{}^tBuC_6H_4)_5]$, prepared by the reaction of $TaCl_5$ with $HO\text{-}4\text{-}{}^tBuC_6H_4$ (five equivalents) reacts with hydroxyl containing substrates containing labile protons (HL) such as benzoin, 2-hydroxyacetophenone and salicylaldehyde in 1:1 and 1:2 molar ratios to yield the six- and seven-coordinate compounds $[Ta(O\text{-}4\text{-}{}^tBuC_6H_4)_4L]$ and $[Ta(O\text{-}4\text{-}{}^tBuC_6H_4)_3L_2]$ respectively [17].

The reaction of $[Ta(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_3Cl_2(OEt_2)]$ with quinoline (quin) and 6-methylquinoline (6-Mquin) affords the adducts $[Ta(\eta^1\text{-}N\text{-quin})(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_3Cl_2]$ and $[Ta(\eta^1\text{-}N\text{-}6\text{-Mquin})(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_3Cl_2]$ [18]. Upon reduction of $[Ta(\eta^1\text{-}N\text{-quin})(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_3Cl_2]$ by two electrons, an η^1-*N*- to η^2-*N,C*-bonding mode rearrangement is effected and

[Ta(η^2-*N*,*C*-quin)(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_3$Cl$_2$] is isolated. Reduction of the complex [Ta(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_3$Cl$_2$(OEt$_2$)] in the presence of 6-Mquin, followed by addition of PMe$_3$, affords [Ta(η^1-*N*-6-Mquin)(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_3$(PMe$_3$)] (3) which has been characterised by single crystal X-ray diffraction. The structure of (3) reveals the disruption of heterocyclic aromaticity upon η^2-bonding.



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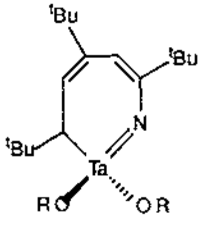

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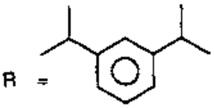
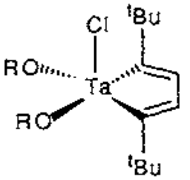


The η^2-pyridine complex [Ta(η^2-*N*,*C*-2,4,6-^{t}Bu$_3$C$_5$H$_2$)(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$Cl] reacts with LiBEt$_3$H to provide [Ta(=NC^{t}Bu=CHC^{t}Bu=CHCH^{t}Bu)(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$] (4), the product of [C-N] bond cleavage [18] whose crystal structure has been determined. The relevance of these discoveries to hydrodenitrogenation catalysis is discussed [18].



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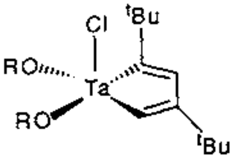

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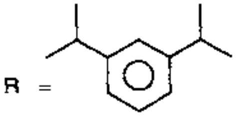
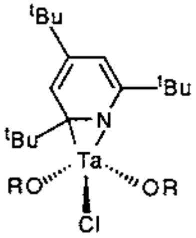


The kinetic product from reducing [Ta(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$Cl$_3$(OEt$_2$)] in the presence of ^{t}BuCCH is the α,α'-metallacyclopentadiene complex (5). Thermolysis of (5) produces the α,β'-isomer (6). Kinetic and mechanistic studies of the (5)-(6) isomerisation are presented which lead to the proposal that the rearrangement proceeds by the disruption of the metallacycle and the formation of an intermediate tantalum(V) metallacyclopropene adduct, followed by its reaction with free ^{t}BuCCH to reform the metallacycle. An X-ray crystal structure of (5) reveals a trigonal bipyramidal structure in the solid state with the metallacyclic Cα-atoms occupying equatorial sites. Compound (6), (but not (5)), engages in cycloaddition chemistry with ^{t}BuCCH to afford the η^6-arene complex [Ta(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$Cl(η^6-1,3,5-C$_6$H$_3$^{t}Bu$_3$)] which can be alkylated with MeMgBr to afford the methyl complex [Ta(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$Me(η^6-1,3,5-C$_6$H$_3$^{t}Bu$_3$)] (7) [19]. The arene ligand in (7) exhibits a diene-diyl distortion and thus resembles a purported intermediate in the [2 + 2 + 2] cycloaddition of alkynes, the 7-metallanorbornadiene. Compound (5), (but not (6)), forms adducts with thf and ^{t}BuCN. The adduct from reaction with the latter reagent undergoes a cycloaddition reaction upon warming to room temperature to afford (8) which has been studied by single crystal X-ray diffraction.

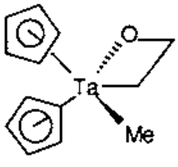


(8)

The η^2-pyridine ligand in (8) is severely distorted and spectroscopic and electrochemical studies reveal that the metal is in a higher effective oxidation state than the metal in the η^6-arene complex [19].

Facile nucleophilic attack on coordinated carboxylate ligands has been reported. Complexes of tantalum(V) react rapidly with amines and amino acid esters to give the corresponding amides. $[Ta(\eta^5\text{-}C_5H_5)]$-amino acid carboxylate complexes have been prepared and reacted with free amino acid esters to give dipeptides in good yields and with high stereochemical purity [20]. Thus, reaction of $[Ta(\eta^5\text{-}C_5H_5)Cl_4]$ with Ac-ala-OH gave the tantalum carboxylate complex $[Ta(\eta^5\text{-}C_5H_5)Cl_3(\text{Ac-ala-O})]$, which was reacted *in situ* with H-phe-OMe.HCl And N-methyl morpholine at -14°C to give Ac-ala-phe-OMe in 85% yield and 0.3% racemisation.

Thin films of Ta_2O_5 with an orthorhombic structure were grown on quartz and silicon (100) substrates at 600-700°C under reduced pressure of 5 Torr by metallo-organic chemical vapour deposition (MOCVD). The complexes $[Ta(OEt)_5]$ and $[Ta(O\text{-}2,6\text{-}Me_2C_6H_3)_4Cl]$ were used as the source materials and were compared with each other with respect to deposition behaviour, crystal structure and orientation of the Ta_2O_5 films. When $[Ta(O\text{-}2,6\text{-}Me_2C_6H_3)_4Cl]$ was used, fine (111) orientated films of Ta_2O_5 were obtained on quartz and silicon (100) substrates at 625-675°C [21].



(9)

The addition of CH_2O to $[Ta(\eta^5\text{-}C_5H_5)_2(CH_2)CH_3]$ has been studied from a molecular orbital point of view [22]. Two possible isomers of the product (9), *O-anti* and *O-syn* are analysed. The *anti*-isomer is suggested to be the more stable because it possess the more stable tantalum-carbon bonds. Steric hinderance of the $(\eta^5\text{-}C_5H_5)$ rings may result in the initial formation of the anti-isomer. In terms of the mechanisms of interconversion it is noted that both Berry pseudo-rotations and turnstile rotations are both high energy processes. Methyl migration via one of the $(\eta^5\text{-}C_5H_5)$ rings is a possible pathway from energetic and bonding considerations. This reaction path is found to be base catalysed. The possibility of an acid catalysed heterolysis of the [Ta-O] bond is discussed. A direct oxygen abstraction pathway is compared to one involving the formation of the tantalaoxetanes (9). An initial, weak coordination of the epoxide through the oxygen atom is suggested. A concerted elimination of the alkene from this precursor is a non-activated process, opposed to a path that involves formation of tantalaoxetanes by an insertion oftantalum into a [C-O] bond of the epoxide [22].

The synthesis of highly pure dipivaloylmethane (HDPM) chekates of tantalum(V) have been investigated. The chelates were synthesised by reaction of the ligands with $TaCl_5$ using anhydrous solvents under an atmosphere of high purity argon [23]. The compound [Ta(DPM)$_4$Cl] was synthesised as a new source material for the preparation of Ta_2O_5 thin films by MOCVD techniques. [Ta(DPM)$_4$Cl] has been characterised by MOCVD elemental analysis, FT-infrared, ^{1}H and ^{13}C NMR spectroscopies and TG-DTA. Vapourisation of impurities was not found by thermogravimetry. [Ta(DPM)$_4$Cl] vapourised at 220-360°C without residue and proved to be superior in volatility and purity as an MOCVD source material [23].

The complex [Ta(η^5-C_5Me_5)Cl_3(*O-O*)] (*O-O* is either chloride or a didentate oxygen donor such as a carboxylic, sulfonic or phosphonic acid) exhibit fluid solution luminescence at room temperature which is ligand-to-metal, (η^5-C_5Me_5)-to-Ta charge transfer in nature. Excited state lifetimes at room temperature range from 0.9 to 8.1 μs, while emission quantum yields in CH_2Cl_2 vary from 0.0019 to 0.16 [24]. An energy gap law relation is observed for six complexes. From the observed one-electron potential for [Ta(η^5-C_5Me_5)Cl_4] of -0.77 V (vs SCE) and the observed emission energy, the excited state can be shown to be a potent oxidant [24].

A sequence of metathesis reactions has been investigated by Gibson and co-workers. Oxo (M=O), imido (M=NR) and alkylidine (M=CHR) exchange reactions occur readily between the coordinatively unsaturated centres of [MQ_2X_2] (M = Mo, W; Q = O, NR, CHR'; X = O^{t}Bu; R = 2,6-^{i}Pr$_2$C$_6$H$_3$; R' = CMe$_2$Ph, ^{t}Bu) and [Ta(η^5-C$_5$R"$_5$)QX$_2$] (Q = NR, CHR'; X = Cl, O^{t}Bu; R" = H, Me) [25].

The syntheses of the complexes, [Ta(η^5-C_5Me_5)$_2$(O)H], [Ta(η^5-C_5Me_5)$_2$(NH)H] and [Ta(η^5-C_5Me_5)$_2$(NPh)H] from [Ta(η^5-C_5Me_5)$_2$(CH$_2$)H] and the solid state structures of [Ta(η^5-C_5Me_5)$_2$(O)H] and [Ta(η^5-C_5Me_5)$_2$(NPh)H] have been reported [26]. These are formally eighteen-electron complexes with the oxo and imido ligands donating only one pair of π-electrons to the tantalum centre in each case. Since these ligands commonly donate both pairs of π-electrons to transition metal centres, at issue are the [Ta-N] and [Ta-O] bond orders. The single crystal X-ray diffraction study of [Ta(η^5-C_5Me_5)$_2$(NPh)H] reveals a linear [Ta-N-C] unit, a feature which is accomodated on both electronic and steric grounds. The [Ta-N] and [Ta-O] bonds are intermediate in length between those expected for double and triple bonds and the ν(Ta=O) of [Ta(η^5-C_5Me_5)$_2$(O)H] is coniderably less than for other metal-oxo compounds. Thus, the [Ta-N] and [Ta-O] bond orders for these two compounds are anomolously low [26].

In the area of sulfur-based ligands, the complex Ta(S)(η^2-SCNEt$_2$)(η^2-S$_2$CNEt$_2$)$_2$ has been prepared from the reaction of NaS$_2$CNEt$_2$ with Ta$_2$Cl$_6$(tht)$_3$ in an analogous manner to the niobium system. It is presumed that the niobium and tantalum complexes are isostructural, the niobium derivative having been studies by X-ray diffraction [2]. The coordination sphere consists of a single sulfur atom, two chelating dithiacarbamate (dtc) ligands and one thiocarbamyl ligand bound through both carbon and sulfur. The resulting structure is a seven-coordinate pentagonal bipyramid with the sulfur atom and one of the sulfur atoms of the dtc ligands occupying polar positions. The formation of the sulfur and thiocarbamyl ligands is presumed to result from oxidative addition of one of the C-S bonds to the metal centre in the (III) oxidation state with concomitant cleavage of the dimeric structure of the precursor complex. A dimeric compound with bridging tridentate dtc ligands is proposed as a necessary intermediate for the oxidative addition reaction to occur [27].

The reaction of $[Nb(\eta^5\text{-}C_5H_4{}^tBu)_2H_3]$ with sulfur to form, ultimately, the polysulfide complex, $[Nb_2(\eta^5\text{-}C_5H_4{}^tBu)_4S_9]$ has been described in the previous review of niobium chemistry [2]. $[Ta(\eta^5\text{-}C_5H_4{}^tBu)S_2H]$ has been synthesised in a related reaction and structurally investigated [28]. Despite the problematic location of the hydrogen atom during X-ray characterisation, the complex contains an $M(\eta^2\text{-}S_2)$ core to which an H group is attatched. $[Ta(\eta^5\text{-}C_5H_4{}^tBu)S_2H]$ is the first known tantalocene sulfide. It readily loses sulfur upon reaction with PR_3 (R = Ph, OMe) and methyl iodide to afford two complexes which, although not fully characterised, contain the [Ta=S] moiety [28].

8.1.3 Complexes with group 15 donor ligands

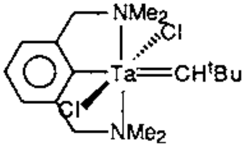
With few exceptions, the majority of complexes of tantalum(V) containing donor ligands from group 15 are nitrogen based. As with niobium, this is rationalised on the basis of matching the hard acid tantalum(V) with the harder base nitrogen.

Thus, we have already mentioned the studies on $[Ta(\eta^5\text{-}C_5Me_5)_2(NH)H]$ and $[Ta(\eta^5\text{-}C_5Me_5)_2(NPh)H]$ [26] and the metathesis exchange reactions between the coordinatively unsaturated centres of $[MQ_2X_2]$ (M = Mo, W; Q = O, NR, CHR'; X = O^tBu; R = $2,6\text{-}{}^iPr_2C_6H_3$; R' = CMe_2Ph, ^tBu) and $[Ta(\eta^5\text{-}C_5R''_5)(NR)X_2]$ (X = Cl, O^tBu) [25]. The tantalum imido complex $[Li(thf)_2]_2[Ta(NMes)_3(NHMes)]$ (Mes = $2,4,6\text{-}Me_3C_6H_2$) has been prepared by reaction of $[Ta(NEt_2)_2Cl_3]_2$ with excess LiNHMes in an analogous procedure to that reported for the niobium system [29]. Similarly, the complex $[Ta(\eta^5\text{-}C_5Me_5)(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)Cl_2]$ has been ontained upon treatment of $[Ta(\eta^5\text{-}C_5Me_5)Cl_4]$ with two equivalents of $(Me_3Si)HN\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ in chlorocarbon solvent [30].

The mixed imido-amido complex $[Ta(=NSiMe_2H)(N(SiHMe_2)_2)_3]$ has been formed *via* the reaction of $LiN(SiHMe_2)_2$ and $TaCl_5$. It was noted that, in both the above complex and its niobium analogue, no decomposition *via* β-hydrogen elimination or abstraction was observed [31].

The complex $[Ta(NPPh_3)_4][TaCl_6]$ has been prepared by the reaction of $TaCl_5$ with $Me_3SiN{=}PPh_3$ in CH_3CN solvent and characterised by infrared spectroscopy and X-ray diffraction [32]. In the cation, the tantalum atoms are surrounded in a distorted tetrahedral fashion by the four nitrogen atoms of the phosphiniminato ligands. The [Ta=N] and [P=N] distances are in accord with double bonds.

The potentially terdentate, monoanionic aryldiamine ligand $[2,6\text{-}(NMe_2CH_2)C_6H_3]^-$ (L^-) provides an excellent tool for the study of tantalum-centred alkylidine reactivity [33]. Transmetallation of $[TaCl_3(CH^tBu)(thf)_2]$ with $^1/_2$ LiL_2 affords the alkylidine complex $[TaCl_2(L)(CH^tBu)]$ (**10**) in 90% yield. The hexacoordinate tantalum centre in (**10**) has an irregular ligand array in which the aryldiamine ligand adopts a new pseudo-facial *N,C,N*-coordination mode. A Wittig type reaction of the alkylidine complex (**10**) with acetone or benzaldehyde affords the complex $[TaCl_2\{2,6\text{-}(NMe_2CH_2)C_6H_3\}(\mu\text{-}O)_2]$ **(11)** in virtually quantitative yield. A similar reaction of **(10)** with PhCH=NR affords $[TaCl_2\{2,6\text{-}(NMe_2CH_2)C_6H_3\}(NR)]$ (R = Me, $SiMe_3$). Complex **(11)** is a dimer with bridging oxo-groups and a distorted pentagonal bipyramidal array around the tantalum atom [33]. Reaction of **(10)** with ethene or propene gives a rearrangement reaction that affords alkene adducts $[TaCl_2[2,6\text{-}(NMe_2CH_2)C_6H_3](H_2C{=}CHR)]$ (R = $CH_2{}^tBu$ **(12)** and Me respectively). The structure of **(12)** is a distorted pentagonal bipyramid. The chirality of the coordinated alkene determines the conformation of both five membered [Ta-C-C-N] chelate rings. NMR spectroscopic experiments show the alkene complexes to be rigid in solution; the bonding of the alkene to the metal centre being best described as resulting in a metallacyclopropane unit [33].



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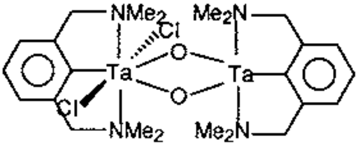

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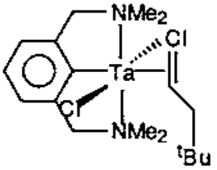


(12)

^{14}N and ^{15}N spectroscopic studies of imido ligands have been made [34] for 37 complexes of tantalum, molydenum, tungsten, rhenium and osmium, including bent imido ligands (NR), with evidence of bent-linear fluxionality in solution in concert with an alkoxo ligand or a second imido ligand. A striking difference between diazenido (N=NR) or nitrosyl ligands is the small difference in nitrogen chemical shift for linear and bent imido ligands, the latter appearing across the full range for imido groups of the metals studied (R = H, Me, Et, ^nBu, $CH_2{}^tBu$, aryl, $SiMe_3$) in complexes with coordination numbers ranging from 4 to 7, and with OR, Cl, F, NHR, $N(SiMe_3)_2$, S_2CNEt_2, PR_3, diphosphine or oxo co-ligands. This range, δ_N –90 to +156 ppm resembles that of linear ligating nitrogen in N_2 and NO ligands; the shielding is higher than in nitrides with low energy $n(N)\text{-}\pi^*$ paramagnetic circulations and lower than in bridging imides and amides. The deshielding on bending is much smaller than for N=NR or NO ligands because the imido LUMO's, mainly $\pi^*(MN)$ and $\sigma^*(MN)$ are higher lying than the $\pi^*(NN)$ and $\pi^*(NO)$ LUMO's. Another difference in the imido ligand system is the close parallelism of the metal and nitrogen shielding, both of which increase with $(\sigma + \pi)$-acceptor ability of the co-ligands (increasing the ligand field splitting). In the $[WCl_4(4\text{-}X\text{-}NC_6H_4)(thf)]$ series, similarly, the nitrogen shielding increases in the sequence X = OMe < Me < H < F < Cl < NO_2, with increase in the $(\sigma + \pi)$ acceptor ability of the aromatic group. The overall pattern of the imido shielding, including the periodicity of the meta dependence (the shielding increases down the group of the metal but decrease across the two) thus resebles that of other π-donor ligands such as oxo, fluoro but differs from that of π-acceptor nitrogen ligands such as N_2, N=NR or NO [34].

Where phosphorus based ligands are concerned, there have been few examples with tantalum(V) systems. We have mentioned above the complexes $[Ta(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_3H_2L]$ **(2)** (L = phosphine) and $[Ta(O\text{-}2,6\text{-}Cy_2C_6H_3)_2H_3(PMe_2Ph)_2]$ [15] and $[Ta(\eta^1\text{-}N\text{-}6\text{-}Mquin)(O\text{-}2,6\text{-}$

$^{i}Pr_2C_6H_3)_3(PMe_3)]$ (**3**) [18]. The complex $[Ta(\eta^5-C_5H_5)H_2L][PF_6]$ (L = $P(OMe)_3$, PMe_2Ph) is the first transition metal hydride system showing quantum mechanical exchange coupling [35]. The experimental J_{HH} coupling constant varies between 76.1 Hz (293 K) and 12.5 Hz (178 K) for L = $P(OMe)_3$ and between 15.6 Hz (310 K) and 4.6 Hz (193 K) for L = PMe_2Ph. NMR spectroscopic data on these two compounds provide confirmation of the proposed mechanism, explaining exchange coupling in these systems, and give access to the magnetic scalar coupling constants which are of the same sign as the exchange coupling ones (*ca.* 11 Hz for L = $P(OMe)_3$ and 4.6 Hz for L = PMe_2Ph).

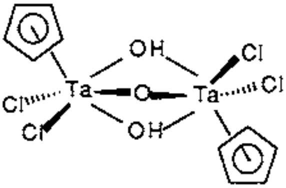
8.1.4 Complexes with other donor ligands

Of note in this particular section is the reaction of $TaCl_5$ and $Li_2C_2B_9H_{11}$ in toluene solvent which affords the complex $[Ta(C_2B_9H_{11})Cl_3]$ for which molecular mass measurements in benzene solution indicate a monomer [36]. A single crystal X-ray diffraction study reveals a distorted octahedral three-legged piano stool similar to many half-sandwich systems. Reaction of $[Ta(C_2B_9H_{11})Cl_3]$ with $Tl(C_5H_4Me)$ in CH_2Cl_2 solvent yields the bent metallocene-type complex, $[Ta(C_2B_9H_{11})(\eta^5-C_5H_4Me)Cl_2]$. X-ray diffraction reveals this complex to possess a distorted tetrahedral structure as expected by analogy to isolobal group 4 metallocenes. Reaction of $[Ta(\eta^5-C_5H_5)Cl_4]$ with $Li_2C_2B_9H_{11}$ yields $[Ta(C_2B_9H_{11})(\eta^5-C_5H_5)Cl_2]$ whilst alkylation of $[Ta(C_2B_9H_{11})Cl_3]$ with MeMgBr yields $[Ta(C_2B_9H_{11})Me_3]$. Similarly, alkylation of $[Ta(C_2B_9H_{11})(\eta^5-C_5H_4Me)Cl_2]$, under the same conditions, affords $[Ta(C_2B_9H_{11})(\eta^5-C_5H_4Me)Me_2]$ [36].

8.2 LOWER OXIDATION STATES OF TANTALUM

8.2.1 Complexes with group 17 donor ligands

Air oxidation of the tantalum(III) chloro complex $[Ta(\eta^5-C_5Me_5)(CO)_2Cl_2(thf)]$, either as a solid or in solution, gives a 38% yield of $[\{Ta(\eta^5-C_5Me_5)Cl_2\}_2(\mu-O)(\mu-OH)_2]$ (**13**). A single crystal X-ray structure determination has been performed [37].

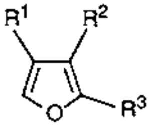


(13)

8.2.2 Complexes with group 16 donor ligands

The reduction of systems such as $[Ta(O-2,6-^{i}Pr_2C_6H_3)_2Cl_3(OEt_2)]$ in the presence of $^{t}BuCCH$ [19] and of $[Ta(\eta^1-N\text{-quin})(O-2,6-^{i}Pr_2C_6H_3)_3Cl_2]$ by two electrons [18] has been alluded to in section 8.2.

A variety of 2,3,4-trisubstituted furans of the form (**14**) (R^1 = n-$C_{10}H_{21}$, n-C_5H_{11}, C_6H_{11}, Me_3C, Me_3Si, Me_3CSiMe_2; R^2 = H, C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}, n-$C_{10}H_{21}$, Ph; R^3 = n-C_3H_7, n-C_5H_{11}, n-C_8H_{17}) have been prepared by treatment of low-valent tantalum alkyne complexes, prepared by reaction of the alkyne with the product of reducing $TaCl_5$ with zinc in benzene solvent in the presence of dimethoxyethane (dme), with aldehydes R^3CHO followed by addition of isocyanides in dme:benzene:thf (1:1:1) solvent. The regioselectivity of the reaction depends on the steric bulk of the substituents on the acetylenes [38]. 4-Me_3Si-substituted furans are produced exclusively when trialkylsilyl acetylenes are employed.



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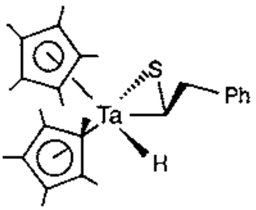


(15)

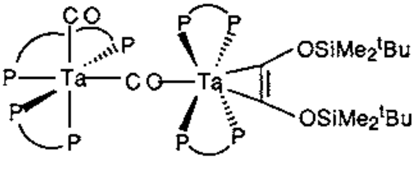
The complexes $[Ta(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}SCHR)H]$ (R = H, Ph, $PhCH_2$, $^tBuCH_2$) have been prepared by treating precursors to $[Ta(\eta^5\text{-}C_5Me_5)_2R']$ (*e.g.* $[Ta(\eta^5\text{-}C_5Me_5)_2(=C=CH_2)H]$ for R' = $=C=CH_2$) with the appropriate thiol RCH_2SH [39]. A single crystal X-ray diffraction study of $[Ta(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}SCHCH_2Ph)H]$ (**15**) has been reported [40]. Oxidative addition of the S–H bond leads to the unstable tantalum(V) derivatives $[Ta(\eta^5\text{-}C_5Me_5)_2R'(H)(SCH_2R)]$. Reductive elimination of R'H is facile forming $[Ta(\eta^5\text{-}C_5Me_5)_2(SCH_2R)]$ which undergoes β-hydrogen elimination to afford $[Ta(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}SCHR)H]$. These thioaldehyde complexes are in rapid equilibrium with the corresponding sixteen-electron thiolate species $[Ta(\eta^5\text{-}C_5Me_5)_2(SCH_2R)]$ through a β-hydrogen migratory insertion/elimination process. When heated, $[Ta(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}SCHR)H]$ rearranges to the thermodynamically favoured tautomer $[Ta(\eta^5\text{-}C_5Me_5)_2(S)(CH_2R)]$. An inverse deuterium isotope effect observed for $[Ta(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}SCY_2)Y]$ (Y = H, D) of k_H/k_D = 0.72(3) at 138°C is indicative of a stepwise process involving fast pre-equilibrium of $[Ta(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}SCY_2)Y]$ with $[Ta(\eta^5\text{-}C_5Me_5)_2(SCY_3)]$ and rate-determining α-CY_3 elimination of $[Ta(\eta^5\text{-}C_5Me_5)_2(S)(CY_3)]$. Derivatives of thioformylphenethyl hydride have been prepared from the *erythro*- and *threo*-phenethyl-d_2-mercaptan PhCHDCHDSH to elucidate the mechanism of alkyl transfer [39]. The migration proceeds with >85% retention of stereochemistry at carbon for the migrating phenethyl-d_2-group. The sulfido-methyl complex $[Ta(\eta^5\text{-}C_5Me_5)_2(S)(CH_3)]$ is hydrogenated under forcing conditions to afford methane and $[Ta(\eta^5\text{-}C_5Me_5)_2(S)H]$, but this product resists final hydrogenation to $[Ta(\eta^5\text{-}C_5Me_5)_2H_3]$ and H_2S.

8.2.3 Complexes with group 15 donor ligands

The novel, reduced metal complex $[Ta(\eta^1\text{-}N\text{-}6\text{-}Mquin)(O\text{-}2,6\text{-}^iPr_2C_6H_3)_3(PMe_3)]$ (3) containing both nitrogen and phosphorus species has been mentioned above [18] as well as the novel η^2-pyridine complex (8) [19].

In the area of phosphorus based ligands, hydrogenation of the alkylidine bridged dimer $[(CB)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CB)_2]$ (CB-H = 9H-carbazole) in the presence of PMe_2Ph leads to the green, hexahydride compound $[(CB)(PMe_2Ph)_2(H)Ta(\mu\text{-}H)_4Ta(H)(PMe_2Ph)_2(CB)]$ which contains a [Ta-Ta] distance of 2.5359(4)Å and [Ta-N] (carbazole) distance of 2.184(4)Å [41].

Reaction of $Na[Ta(CO)_2(dmpe)_2]$ (dmpe = bis(dimethylphosphino)ethane) with one equivalent of Me_3SiCl yields initially the siloxycarbyne species $[Ta(dmpe)_2(CO)(COSiMe_3)]$ which converts, in the presence of NaCl, to the carbon monoxide bridged complex $[(dmpe)_2(CO)Ta(CO)Ta(Me_3SiOCCOSiMe_3)(dmpe)_2]$. A single crystal X-ray diffraction study has been performed on the $^tBuMe_2$ analogue **(16)** [42]. The carbonyl bridge is nearly linear, the [Ta-C-O] and [C-O-Ta] angles being 169 and 166° respectively. An analogous CO-bridged dimetallic complex $[(dmpe)_2(CO)Ta(CO)Zr(\eta^5\text{-}C_5Me_5)_2Cl]$ was prepared by the reaction of $Na[Ta(CO)_2(dmpe)_2]$ with one equivalent of $[Zr(\eta^5\text{-}C_5Me_5)_2Cl_2]$ and was also structurally characterised. A mechanism for the formation of these CO-bridged species is proposed. Both complexes react with two equivalents of Me_3SiCl to afford the known coupled product $[Ta(Me_3SiOCCOSiMe_3)(dmpe)_2Cl]$ [42]. Along similar lines, reduction of the compound $[Ta(CNR)(CO)(dmpe)_2Cl]$ with 40% Na/Hg followed by addition of Me_3SiCl resulted in reductive coupling of the CO and RNC functions to afford $[Ta\{(Me_3Si)(Me)NCCOSiMe_3\}(dmpe)_2Cl]$ [43]. An X-ray crystal structure determination on the niobium derivative confirmed the presence of the unusual RR'NCCOR acetylene ligand. The reductive coupling proceeds as for coupling of two CO two RNC functions. Addition of aqueous acid to $[Ta\{(Me_3Si)(Me)NCCOSiMe_3\}(dmpe)_2Cl]$ provided the first stabilised hydroxy(alkylamino)acetylene complex $[TaH(MeHNCCOH)(dmpe)_2Cl]Cl$ **(17)**, characterised by X-ray diffraction. Finally, reductive coupling of two isocyanide ligands in $[Ta(CNR)_2(dmpe)_2Cl]$ was accomplished demonstrating that all three possible combinations of CO and CNR ligands can be coupled reductively in reactions that use the same metal framework and generalised mechanism [43].



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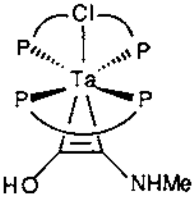

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Ultra-violet irradiation of $[Et_4N][Ta(CO)_6]$ in the presence of di- and tetradentate phosphines P_n yields $[Et_4N][Ta(CO)_4P_n]$. Ion exchange chromatography on silica gel affords the hydrido complexes $[TaH(CO)_4P_2]$ or $[TaH(CO)_3P_n]$ (n = 3, 4) which can be converted photochemically into $[TaH(CO)_2P_n]$ [44]. The solution structures are probably octahedral with a capping hydride ligand. Single crystal X-ray diffraction of $[TaH(CO)_2(dppe)_2]$ (dppe = bis(diphenylphosphino)ethane) reveals the presence of a pentagonal bipyramid with hydrogen, tantalum and the four phosphorus atoms in the pentagonal plane. Subsequently, 2-methyl-2-butene is "hydrotantalated" mainly in an anti-Markovnikov manner to yield the σ-alkyl complex

$[Ta(Me_2CH_2CHMe)(CO)_4P_2]$ ($P_2 = Ph_2PCH_2CH_2PEt_2$). The complexes, $[TaH(CO)_{4/3}P_n]$ react with pentafulvenes to form $[Ta(\eta^5\text{-}C_5H_4CHR_2)(CO)_2P_n]$ ($R_2 = Me_2, Ph_2, NMe_2 + H$,; $P_n = PhP(CH_2CH_2PPh_2)_2$). The chloride complexes $[TaCl(CO)_{6-n}P_n]$ have been prepared photochemically from $[Et_4N]Cl$ and $[TaH(CO)_4P_n]$ ($n = 4$; P_n = 2 x dppe) or reductive carbonylation in the presence of $MeP(CH_2CH_2CH_2PMe_2)_2$ with $TaCl_4$ [44].

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