2. Niobium and Tantalum 1993

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INTRODUCTION

This review is intended to cover the literature on the coordination chemistry of niobium and tantalum through the year 1993 as reflected in *Chemical Abstracts* volumes 118, 119 and 120. To keep the review within manageable length, we have chosen to limit the study, in a similar fashion to the 1992 review, to low nuclearity inorganic coordination systems only; consequently several areas have had to be omitted. Specifically, organic/organometallic systems have been omitted unless there was good reason on account of the non-carbon based components of the coordination sphere, high-nuclearity cluster chemistry (including polyoxometallates) and solid state and materials science have been excluded unless again there was a strong reason to include them from an inorganic/coordination chemistry viewpoint.

The layout of the review focuses on the different oxidation states of niobium and tantalum which range from +5 down to −2. However, most compounds in oxidation states lower than +5 are found to be stabilised by carbon-based organic ligands and consequently, many such compounds lie outside the scope of the present review. It has proven more efficient, from a presentational point of view, to separate the +5 oxidation state from the others since most coordination chemical studies 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, pnictogens from group 15 and ligands with other donor atoms. Within these broad boundaries however, there are areas of overlap where 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 covering the years 1985-1987 especially for areas of cluster chemistry, solid state and materials related science [1] and to the companion reviews of niobium and tantalum coordination chemistry for 1992 [2].

2.1 NIOBIUM(V) AND TANTALUM(V)

2.1.1 Complexes with group 17 donor ligands

As in many previous studies, the pentahalides of niobium and tantalum have found use as precursors to other derivatives of d^0 niobium and tantalum salts *via* reaction with suitably donating ligands. Thus, the reaction of $(EtO)_2P(=S)(OMe)$ (L) and $Ph_2P(=S)(OEt)$ (L') with MF_5 (M = Nb, Ta) has been studied by ^{19}F and ^1H NMR spectroscopy in dichloromethane (CH_2Cl_2) and acetonitrile (MeCN) solvents. The first stage of reaction occurs with coordination of the ligands to the MF_5 through the sulfur atoms with formation of octahedral MF_5L. After this, thione—thiol isomerisation of the coordinated ligands occurs as a result of which the oxygen atom becomes the donor atom. The rate of isomerisation involving the methoxy group is greater than that involving the ethoxy group [3]. A seven-coordinate intermediate is formed in which the ligands are coordinated to the central metal through sulfur and alkoxy oxygen atoms. If the solvent is not rigorously purified to remove dissolved oxygen, then besides the thione—thiol isomerisation, oxidation of the ligand occurs with separation of elemental sulfur. From a comparison of ^1H NMR chemical shifts of the uncoordinated and coordinated ligands and the values of the shift of the absorption bands of $\nu(P{=}O)$ in the IR spectra, conclusions are drawn on the greater acceptor capacity of NbF_5 with respect to TaF_5 toward the phosphoryl-containing ligands [3].

Along similar lines to the work above, highly pure $Nb(dpm)_2Cl_3$ [Hdpm = dipivaloylmethane] has been synthesised by the reaction of Hdpm with $NbCl_5$ using anhydrous solvents under an atmosphere of highly pure argon gas [4]. The formation of $Nb(dpm)_2Cl_3$ was confirmed using elemental analysis, FT—IR, ^1H and ^{13}C NMR and thermogravimetric-differential thermal analysis (TG—DTA). Vaporisation of impurities was not found to occur in the TG experiments. $Nb(dpm)_2Cl_3$ vaporised at 180—340°C without residue and is a promising new source material of metalloorganic chemical vapour deposition (MOCVD) for the preparation of photo-integrated circuit thin films [4].

The reaction of $[Ph_2P(=O)]_2C=CH_2$ (L) with PF_5 and TaF_5 has been studied by ^{31}P and ^{19}F NMR spectroscopies. The compounds $PF_5.L$, $[PF_5]_2.L$, $[PF_4.L][PF_6]$, $TaF_5.L$, $[TaF_4.L]^+$, *mer*-$Ta(O)F_3.L$ and $[TaF_3.L]_2O$ were reported to be formed [5].

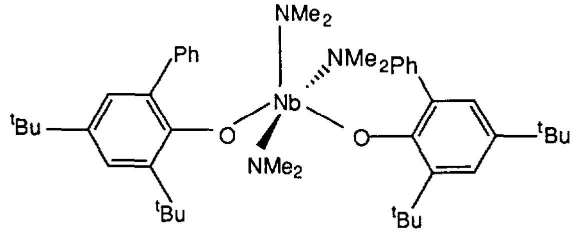
Spectroscopic studies on molten salt solutions continue to be a major feature of investigation for group 5 metal halides. Raman spectra have been obtained at temperatures in the range 375-650 K and pressures of up to four atmospheres from $GaCl_3$—$NbCl_5$ and $GaCl_3$—$TaCl_5$ binary mixtures in the liquid and vapour states. The data indicate formation of $NbGaCl_8$ and $TaGaCl_8$ liquid and vapour dinuclear addition complexes. The spectra were interpreted in terms of a C_{2v} configuration for the $MGaCl_8$ (M = Nb, Ta) molecules consisting of an MCl_6 octahedron sharing

2.1.2 Complexes with group 16 donor ligands

Since both niobium and tantalum are highly oxophilic metals, there is always a significant literature devoted to compounds in which these metals are bound to oxygen and to a lesser degree, sulfur. In most cases, the metal alkoxo and thiolato functions [M—XR] and the oxo or thio functions [M=X] (X = O, S) form the basic structural motifs with the ethereal dative bond [M—OR_2] being a feature of more loosely bound ether molecules as found in precursor compounds.

The aryloxo compound $TaCl_2(O\text{-}4\text{-}^tBuC_6H_4)_3$ was synthesised by reacting $TaCl_5$ with HO-4-$^tBuC_6H_4$ in a 1:3 molar ratio in dry C_6H_6 under reflux and was characterised by elemental analysis, conductance, IR, NMR and mass spectral studies. The reaction of $TaCl_2(O\text{-}4\text{-}^tBuC_6H_4)_3$ with equimolar amounts of hydroxy-containing substrates having labile protons (L) such as benzoin, 2-hydroxyacetophenone, salicylaldehyde in 1:1 molar ratio afforded the six-coordinate compounds $TaCl_2(O\text{-}4\text{-}^tBuC_6H_4)_3.L$ [9].

Aryloxo compounds have also been obtained from the reaction of dimethylamido complexes of titanium, tungsten and niobium with HO-2,4-^{t}Bu-6-Ph-C_6H_2. Three new mixed amido-aryloxo compounds were isolated $[Ti(O\text{-}2,4\text{-}^tBu\text{-}6\text{-}Ph\text{-}C_6H_2)_2(NMe_2)_2]$, $[Nb(O\text{-}2,4\text{-}^tBu\text{-}6\text{-}Ph\text{-}C_6H_2)_2(NMe_2)_3]$ (3) and $[W_2(O\text{-}2,4\text{-}^tBu\text{-}6\text{-}Ph\text{-}C_6H_2)_2(NMe_2)_4]$ and structurally characterised.



(3)

Compound 3 possesses a monomeric distorted trigonal bipyramidal geometry in which two of the amido ligands occupy mutually *trans* positions. The distortion from idealised geometry results from the opening up of the angle between the two formally equatorial aryloxo ligands to 144.9(1)° which is presumably a reflection of the steric interactions between these two bulky ligands. Indeed, the extent of this distortion is such that the molecule is beginning to approach a square-pyramidal geometry. The conformation of the amido groups in 3 is interesting since it can shed light on the possible contributions to $p\pi\text{-}d\pi$ bonding between the planar nitrogen atoms and the metal. The π-bonding of three NMe_2 groups arranged in a T-shape about a d^0 metal centre, as in 3, will be maximised with all three NC_2 propellers orientated mutually perpendicular thus allowing each nitrogen atom to donate into a different available metal *d*-orbital. However, in 3 this is not the case as the two mutually *trans* amides are parallel and the resulting competition for d-orbitals results in a significant lengthening of the Nb—N axial bonds [2.032(3) and 2.036(3)Å] over the corresponding equatorial distance [1.94(3)Å]. It is possible that steric effects are responsible for this or electronic effects due to competitive p-bonding between the metal and the aryloxo oxygen atoms.

Heating of these compounds for extended periods did not lead to cyclometallation of either the aryl or tert-butyl group of the aryloxo ligand [10].

The use of metal compounds containing sterically demanding aryloxo ligands as catalysts for the polymerisation of unsaturated organic substrates has been examined by the group of Nakamura [11]. Thus, the system comprising $WCl_n(O\text{-}2,6\text{-}Me_2C_6H_3)_{6-n}$ and EtMgBr (n = 1-4) has been examined as a catalyst for the polymerisation of 1-alkynes in toluene solvent at –20°C to +60°C for 24 h. The system $WCl_4(O\text{-}2,6\text{-}Me_2C_6H_3)_2/Et_3Al$ polymerised ^tBuCCH to a very high molecular weight polymer ($M_n > 2 \times 10^6$) with a narrow polydispersity index (M_w/M_n *ca.* 1.2). By increasing the number of aryloxo ligands, less bulky 1-alkynes were polymerised to high molecular weight polymers. Thus, 1-butyne gave an orange polymer with $M_n = 9.4 \times 10^4$ and $M_w/M_n = 3.5$. Similar results were obtained when the corresponding niobium and tantalum systems were examined [11].

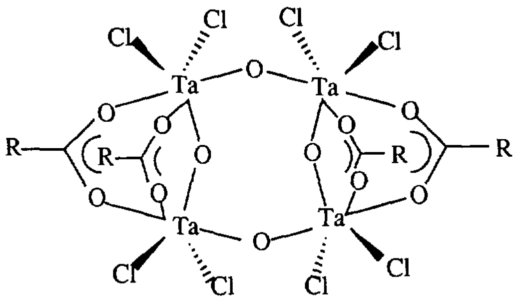
A variety of other mixed metal and mixed alkoxo compounds have been prepared by the Mehrotra group including $XSn\{Al(O^iPr)_4\}$, $XSn\{Zr_2(O^iPr)_9\}$, $XSn\{M(O^iPr)_6\}$, $\{Al(O^iPr)_4\}Sn\{Zr_2(O^iPr)_9\}$ and $\{Nb(O^iPr)_6\}Sn\{Ta(O^iPr)_6\}$ (X= Cl, O^iPr, O^tBu; M = Nb, Ta). These compounds were characterised by elemental analysis, molecular weight measurements and multinuclear (^1H, ^{13}C, ^{27}Al and ^{119}Sn) NMR analyses [12]. In a similar fashion, the compounds $Cl_{4-n}Sn\{M(O^iPr)_6\}_n$ (M = Nb, Ta; n = 1-3) have been synthesised by the reactions of $SnCl_4$ with an appropriate salt $K\{M(O^iPr)_6\}$ in the necessary molar ratios. These chloro precursors were then used to obtain $(RO)_2Sn\{M(O^iPr)_6\}_2$ (R = Me, ^iPr), $\{Ta(O^iPr)_6\}_2Sn\{Nb(O^iPr)_6\}_2$ and $\{Al(O^iPr)_4\}_4ClSn\{Nb(O^iPr)_6\}_2$ by halide atom replacement with the appropriate potassium alkoxide salt. Characterisation of these compounds was provided by elemental and alkoxo group analysis, IR, molecular weights and multinuclear (^1H, ^{13}C, ^{27}Al and ^{119}Sn) NMR spectroscopic analyses [13]. A variety of other mixed metal alkoxo systems based on tert-butoxide have been characterised using the same techniques by the same research group. Some examples include $FeCl_2\{Al(OBu^t)_4\}_2$, $Fe(OBu^t)_2\{Al(OBu^t)_4\}_2$, $Fe\{Al(OBu^t)_4\}\{Nb(O^iPr)_6\}_2$ and $Fe\{Al(OBu^t)_4\}_2\{Nb(O^iPr)_6\}$ which were synthesised by metathetical reactions. Alcoholysis of $Fe\{Al(OBu^t)_4\}_2\{Nb(O^iPr)_6\}$ with an excess of MeOH and ^tBuOH produces $Fe\{Al(OMe)_4\}_2\{Nb(OMe)_6\}$ and $Fe\{Al(OBu^t)_4\}_2\{Nb(O^iPr)_2(OBu^t)_4\}$ respectively [14].

$$MCl_5 + PPh_3 + R^1R^2CO \longrightarrow [R^1R^2C(PPh_3)OMCl_4]Cl \qquad (2)$$

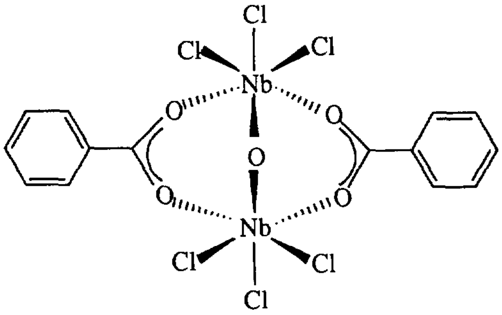
$$(M = Nb, Ta)$$

The formation of the [M—O] bond *via* the interaction of metal halides and tertiary phosphines with carbonyl substrates has been reported [15]. This reaction (2) is a form of phosphonium ion formation and bears a remarkable resemblance to the Pudovik and Abramov reactions of organophosphorus chemistry [16]. Thus, treatment of aldehydes and ketones with one mole equivalent of a Lewis acid such as $TiCl_4$, $NbCl_5$ or $TaCl_5$ and one mole equivalent of PPh_3 affords the derivatives $[R^1CH(PPh_2R^2)OMCl_n]Cl$ and $[R^1R^2C(PPh_2R^2)OMCl_n]Cl$ (M = Nb, Ta; n = 4; R^1 = various organic groups; R^2 = Ph) as air and moisture sensitive solids [15]. On the basis of NMR spectroscopic studies, some of the adducts obtained from aldehydes exist in solution as mixtures of isomers or oligomers whereas the ketone derivatives are in equilibrium with free ketone and $NbCl_5.PPh_3$.

As well as alcohols, carboxylic acids have been used as a versatile source of the [M—O] bond. Thus, it was found that the products from the interaction of MCl_5 (M = Nb, Ta) with RCO_2H (R = Ph, 4-MeC_6H_4, 4-FC_6H_4) included $\{[TaCl_2(\mu\text{-}O)(O_2CC_6H_4Me\text{-}4)]_4\}$ (4) which contains a $[Ta_4O_4]$ core, $[NbCl_3(O_2CR)_2(\mu\text{-}O)]$ and $[TaCl_4(O_2CR)]$ [17]. In a similar fashion, reaction of $NbCl_5$ with aryl carboxylic acids yields the oxo-niobium carboxylates $[NbCl_3(O_2CR)_2(\mu\text{-}O)]$ [R = Ph (5), 4-MeC_6H_4, 2-MeC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 2-FC_6H_4, 2-ClC_6H_4, 2-BrC_6H_4, 2,6-$Me_2C_6H_3$] [18]. A single crystal X-ray analysis of the benzoate derivative (5) shows a μ-oxo-bis(μ-carboxylato)dimetal core in which each niobium atom is in a distorted octahedral environment, the other three sites on each metal being occupied by chlorine atoms. Spectroscopic data suggest similar structures for the remaining derivatives.

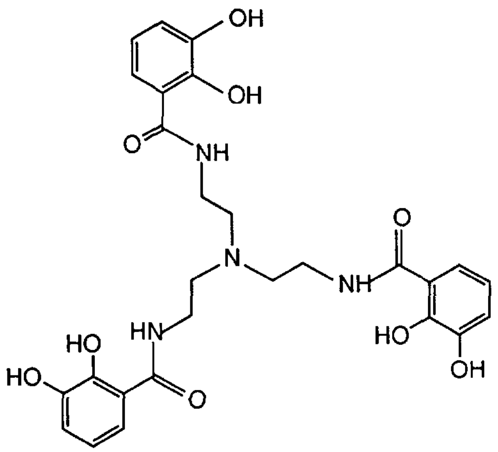


(4) R = 4-MeC_6H_4



(5)

The preparation and crystal structure of Nb(HTRENCAM).DMSO [H_6TRENCAM = hexadentate tris(catecholamide) (6)] has been reported, revealing a cavitand-like arrangement of the three catecholamide groups with the protonated non-binding nitrogen atom directed inwards to the niobium atom. The geometry around the niobium atom (shaded) resembles a distorted mono-capped trigonal antiprism (7) [19].



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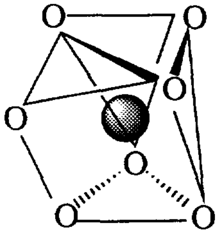


(7)

The use of sterically demanding alkoxo ligands has continued to provide a rich seam of chemistry, especially in the field of low coordinate metal species containing *d*-electrons. Such low-coordinate metal centres are particularly susceptible towards oxidation addition and cyclisation reactions with enormous potential for the manipulation of both saturated and unsaturated organic substrates and indeed, as model systems for the investigation of mechanistic features of important industrial reactions such as the Fischer-Tropsch process. The reduction of $Ta(SILOX)_3Cl_2$ (SILOX $= {}^tBu_3SiO$-) with Na/Hg in thf under H_2 afforded $Ta(SILOX)_3H_2$ [(**8**); 43%]. Compound (**8**) underwent a thermal cyclometallation to $TaH(SILOX)_2OSi^tBu_2CMe_2CH_2$ (**9**) but was reconstituted by treatment with H_2 (6 days, 3 atm). Treatment of (**8**) with C_2H_4, neat CCl_4 and MeI in diethylether generated $Ta(SILOX)_3HEt$ (63%), $Ta(SILOX)_3HCl$ (63%) and $Ta(SILOX)_3HI$ (62%) respectively. Reduction of $Ta(SILOX)_3HI$ with Na/Hg in thf produced a ring-opened thf compound $[(SILOX)_3TaH]_2[\mu{:}\eta\text{-}(CH_2)_3O]$ (58%). Photolysis of $Ta(SILOX)_2Cl_2CH_2Ph$ gave $[(SILOX)_2TaCl]_2(\mu\text{-}H)_2$, C_7H_8 and a trace of dibenzyl. Reduction of $Ta(SILOX)_2Cl_3$ with Na/Hg under 1 atm. H_2 over the course of 15 days yielded an unbridged D_{2d} dimer $[(SILOX)_2TaH_2]_2$ (83%) which possessed a [Ta—Ta] single bond with a length of 2.720(4)Å by single crystal X-ray diffraction [20]. Subsequent exposure of $[(SILOX)_2TaH_2]_2$ to 2 equivalents of HCl, 1 equiv. O_2 and 1 equiv. Me_3NO provided $[(SILOX)_2TaCl]_2(\mu\text{-}H)_2$ (78%), $[(SILOX)_2TaH]_2(\mu\text{-}O)_2$ [(**10**); 95%] and $[(SILOX)_2TaH]_2(\mu\text{-}H)_2(\mu\text{-}O)$ [(**11**); 67%)]. Derivatisation of (**10**) with C_2H_4 gave $[(SILOX)_2TaEt]_2(\mu\text{-}O)_2$ (39%). Compound (**11**) exists as a mixture of two C_2 symmetric isomers; the hydrides of one isomer exchanged with an energy barrier of ΔG *ca.* 8 kcal mol^{-1} whilst those of the other isomer exchanged coincidentally with isomeric interconversion (an energy barrier of ΔG *ca.* 11 kcal mol^{-1} was measured). Dihydride (**8**) undergoes σ-bond metathesis with D_2 forming initially $Ta(SILOX)_3HD$ and the exchange of (**8**) with hydrogen was measured directly using spin saturation transfer techniques. Carbonylation of (**8**) and $Ta(SILOX)_3HEt$ afforded η^2-aldehyde complexes of the general form $Ta(SILOX)_3(\eta\text{-}RCHO)$. Treatment of $[(SILOX)_2TaCl]_2(\mu\text{-}H)_2$ with CO yielded $[(SILOX)_2TaCl]_2(\mu\text{-}H)(\mu{:}\eta^2{:}\eta^2\text{-}CHO)$ [**(12)**; 56%)] whilst exposure of dimeric $[(SILOX)_2TaH_2]_2$ to 1 equivalent of CO afforded $[(SILOX)_2TaH]_2(\mu\text{-}CH_2)(\mu\text{-}O)$ [**(13)**; 67%). Subsequently, $[(SILOX)_2TaH]_2(\mu{:}\eta^2{:}\eta^2\text{-}CHO)(\mu{:}\eta^1{:}\eta^2\text{-}CH_2O)[Ta(SILOX)_2]$ **(14)** was isolated in 55% yield and converted to $[Ta(SILOX)_2]_2(\mu\text{-}O)_2(\eta\text{-}CHMe)$ [**(15)**; 61%)]. The sequence $[(SILOX)_2TaH_2]_2$ + CO going to **(13)** then **(14)** then **(15)** exhibits the critical bond breaking and the C—H and C—C bond making events of the Fischer-Tropsch (F-T) process. Extended exposure of $[(SILOX)_2TaH_2]_2$ or **(14)** to 1 atm. CO provided $[(SILOX)_2Ta]_2(\mu{:}\eta^1{:}\eta^1\text{-}CH{=}CHO)(\mu{:}\eta^1{:}\eta^2\text{-}CH_2O)(\mu\text{-}O)$ (**16**; 50%). Carbonylation of $[(SILOX)_2TaH]_2(\mu\text{-}O)_2$ **(10)** generated $[(SILOX)_2Ta]_2(\mu\text{-}O)_2(\mu\text{-}CH_2O)$ as the major product (70-90%), while treatment of **(11)** with CO afforded first $[(SILOX)_2TaH]_2(\mu\text{-}O)_2[TaMe(SILOX)]$ (90%) and then $[(SILOX)_2Ta]_2(\mu\text{-}O)_2(\mu\text{-}MeCHO)$ (90%). ^{13}CO labelling studies were used to follow the **(13)**-**(15)**-**(16)** conversions, thus providing a basis for mechanistic interpretation. Dimeric structures allow oxygenated fragments to remain coordinated to two tantalum atoms throughout the sequence. Insertion into [Ta—H] bonds may initiate each carbonylation process. Stereochemical consequences of SILOX ligation are discussed in relation to the structures and dynamics of the dinuclears, while the electrophilic tantalum centres are important in H/D exchange and carbonylation chemistry. The carbonylation chemistry underscores three critical points regarding the F-T process: (i) hydride transfer to CO is a reasonable alternative to CO dissociation; (ii) adsorbed hydrocarbyl and oxygenate fragments are related by reversible C—O bond breaking and bond making events; (iii) oxygenate and hydrocarbyl adsorbates can be removed protolytically, akin to hydrogenation [20].

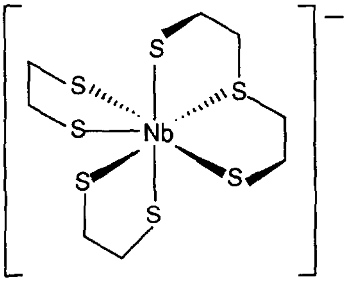
Metal-oxo species are again well represented. $CsBCO_6$ (B = Sb, Nb, Ta; C = Te, Mo, W, U) have been prepared from $CsNO_3$ and the respective metal oxides or $UO_2(NO_3)_2.6H_2O$ by the ceramic method. All of the compounds have a perovskite structure except $CsNbUO_6$ which is monoclinic, space group $P2_1/c$, $Z = 4$ [21].

A number of derivatives in which the metal contains a formal [M=O] unit have been reported. Thus $Nb(O)Cl_3.L$ (L = PMe_3, $PMePh_2$, PPh_3, PEt_3), $Nb(O)Cl_3.(Ph_2PCH_2CH_2PPh_2)$ and $Nb(O)Cl_3(PMe_2Ph)_3$ were prepared by reaction of either $[Nb(O)Cl_3]_n$ or $Nb(O)Cl_3(thf)_2$ with a stoichiometric amount of the phosphine in CH_2Cl_2 solvent. The influence of the different ligand fields on the IR stretching frequency of the metal-oxo unit was discussed in terms of the geometry of the complex and the stereo-electronic properties of the attendant ligands. Thus, the more phosphines attached to the metal and the more electron-donating the phosphorus centre, so the lower the [Nb=O] stretching frequency [22]. On the basis of similarities in the IR and other spectral data, it was envisaged that $Nb(O)Cl_3(PMe_2Ph)_3$ possessed a similar monocapped trigonal anti-prismatic geometry to $Nb(O)Cl_3(PMe_3)_3$ but there was no evidence for the former existing in different, apparently isomeric, forms unlike the latter.

Moving to ligands based on sulfur donor atoms, aspects of the coordination chemistry of dithiophosphates have been examined. Thus, $M(O^iPr)_3[S_2P(OR)_2]_2$ (M = Nb, Ta; R = Pr, ^{i}Pr, ^{i}Bu, Ph) were prepared by reacting $MCl_2(O^iPr)_3$ with the requisite molar ratio of Na or $NH_4[S_2P(OR)_2]$ in thf solvent. The monomeric products are viscous liquids which are soluble in common organic solvents and highly susceptible to hydrolysis; they have been characterised by IR and NMR spectroscopies which indicate a didentate mode of attachment of the dithiophosphato groups to the metal [23].

A number of transition metal complexes containing ligands based on the 1-substituted-2-tetrazoline-5-thione scaffold (**17**) have been reported including complexes of niobium and tantalum. These complexes have been characterised using elemental analysis, conductance measurements, IR and UV-VIS spectral studies. The Ph, 3-MeC_6H_4, 4-MeC_6H_4 and 4-ClC_6H_4 derivatives of 1-substituted-2-tetrazoline-5-thione are coordinated through the thione tautomeric form with VO_2^+, MoO_2^{2+}, WO_2^{2+} and ZrO^{2+} species but interact *via* the thiol form in the cases of Nb^{5+} and Ta^{5+} resulting in deprotonation of the thiol. The metal-ligand vibrations in the far-IR region have also been examined [24].

A facile [C—S] bond cleavage reaction has been reported to take place in the reaction between $NbCl_5$ and 3 equivalents of Li(TPDT) (H_2TPDT = 3-thiapentane-1,5-pentanedithiol) followed by a cation exchange with Ph_4PBr to afford, $(Ph_4P)[Nb(S)(EDT)(TPDT)]$, $(Ph_4P)[Nb(EDT)_2(TPDT)]$ [(**18**); H_2EDT = 1,2-ethanedithiol] and $(Ph_4P)[Nb(O)(EDT)(TPDT)]$ [25]. The crystal structure of (**18**) is also reported (monoclinic, space group $P2_1/c$, $a = 14.031(2)$, $b = 9.140(2)$, $c = 28.030(4)$ Å; $\beta = 107.28(1)°$ and $Z = 4$) and is found to contain a seven coordinate mixed dithiolate complex anion (shown below), in which the primary coordination sphere of the niobium centre is composed solely of sulfur donor atoms with a distorted pentagonal-bipyramidal geometry.

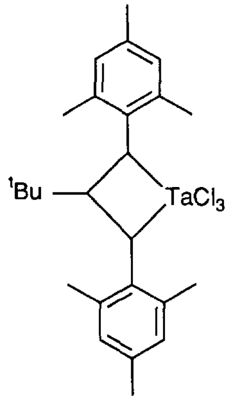


(**18**) Hydrogens omitted for clarity

2.1.3 Complexes with group 15 donor ligands

Because of the highly electrophilic nature of niobium and tantalum, most studies in this field have focused on ligands containing electronegative nitrogen donor atoms.

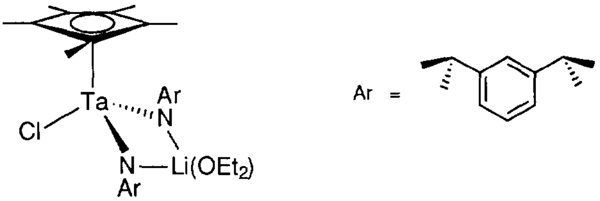
The complex $Ta(=CH^tBu)Cl_3(thf)_2$ is one such precursor compound which adds iminoboranes $^tBuB{=}NMes$ in a 1:2 molar ratio to afford the cyclobutane compound (**19**) [26].



(19)

As in previous years, amido [M—NR_2] and imido [M=NR] compounds have formed the bulk of niobium and tantalum systems studied with group 15 donor ligands.

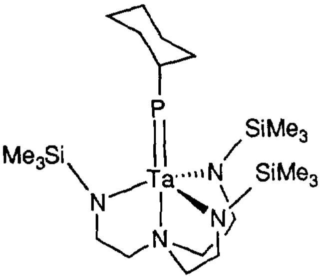
The reaction of Cp^*TaCl_4 (Cp^* = C_5Me_5) with 2 equivalents of LiNHAr (Ar = 2,6-$^iPr_2C_6H_3$) in thf solvent affords the imido compound $Cp^*Ta(NAr)Cl_2$. Upon reaction of Cp^*TaCl_4 with 4 equivalents of LiNHAr in diethylether solvent the isolated product is $[Cp^*Ta(NAr)_2Cl][LiOEt_2]$ **(20)** [27]. The corresponding thf adduct is obtained when reaction is performed in thf solvent or when $Cp^*Ta(NAr)Cl_2$ is reacted with 2 equivalents of LiNHAr in thf solvent. A single crystal X-ray diffraction study on **(20)** reveals a $[LiOEt_2]^+$ moiety bridging the imido nitrogens. In solution, the two tantalum-bound imido groups are equivalent with restricted rotation about the [Ta—N—C_{ipso}] bonds implying an intact $[LiOEt_2]^+$ bridge. The compound $Cp^*Ta(NAr)(NEt_2)Cl$ (prepared from $Ta(NAr)(NEt_2)Cl_2(thf)_2$ and $LiCp^*$ reacts slowly with LiNHAr in refluxing thf to afford $[Cp^*Ta(NAr)_2Cl][Li(thf)]$.



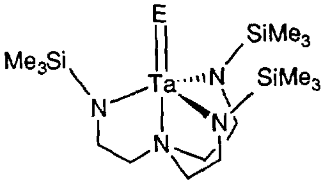
(20)

Multidentate ligands have proved a popular theme for study. Thus, it has been reported by Schrock and co-workers that $TaCl_5$ reacts with $Li_3(N_3N)$ [(N_3N) = $(Me_3SiNCH_2CH_2CH_2)_3N$] to give $Ta(N_3N)Cl_2$ which reacted with LiPHR (R = Ph, Cy, ^{t}Bu) in Et_2O to give $Ta(=PR)(N_3N)$ **(21)**. Aldehydes react with **(21)** to afford $Ta(=O)(N_3N)$ and RP=CHR' (R = R' = ^{t}Bu; R = Ph, ^{t}Bu, R' = ferrocenyl, Fc; R = R' = Ph) [28]. The phosphaalkene ^{t}BuP=CHFc dimerises to the corresponding

1,3-diphosphetan. Cyclopentadiene adds to unstable PhP=CHFc to afford the Diels-Alder adduct. Compound (**21**) (R = cyclohexyl) has been examined by X-ray crystallography and is found to be orthorhombic, space group $Pna2_1$, with $Z = 4$, $a = 19.754(2)$, $b = 11.862(1)$, $c = 12.993(1)$ Å.

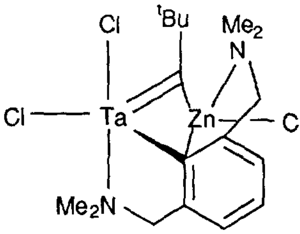


(**21**)



E = Se (**22**); Te (**23**)

Along similar lines, Arnold and co-workers have independently examined the same systems in relation to their interactions with group 16 donor ligands. Thus, $TaCl_5$ reacted with $(HN)_3N$ in Et_2O to give $Ta(N_3N)Cl_2$, which reacted subsequently with $(thf)_2LiESi(SiMe_3)_3$ (E = S, Se, Te) at −78°C to afford $Ta(=E)(N_3N)$. Both $Ta(N_3N)Cl_2$ and $Ta(=E)(N_3N)$ were characterised by IR, Raman, ^1H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$, $^{125}Te\{^1H\}$ NMR and mass spectroscopic techniques. $Ta(=Se)(N_3N)$ (**22**) is orthorhombic and $Ta(=Te)(N_3N)$ (**23**) monoclinic, both compounds possessing the same distorted trigonal bipyramidal geometry as compound (**21**) with the selenium and tellurium atoms in axial positions with respect to the tertiary nitrogen atoms [29].



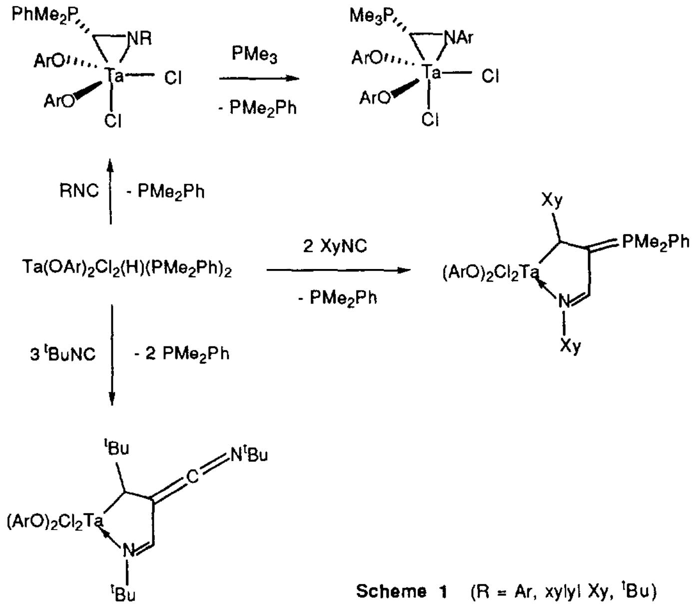
(24)

The 1:1 reaction of $TaCl_2[2,6\text{-}(Me_2NCH_2)_2C_6H_3](CH^tBu)$ with $^tBuCH_2ZnCl$ affords the dimetallic compound (**24**) in high yield. The five-coordinate tantalum metal centre has a coordination geometry between trigonal bipyramidal and square pyramidal, whilst the zinc centre has a distorted tetrahedral ligand array. The alkylidyne function and the aryl ipso-carbon bridge between the zinc and tantalum centres. The p-orbital at C_{ipso} of the aryldiamine ligand forms a 2-electron bond to the zinc centre, thus functioning as an 8-electron donor. The reaction of (**24**) with tmen at

60°C leads to elimination of $ZnCl_3$ and the formation of (**25**); which results from an alkylidyne-mediated activation reaction of a methyl C—H bond in a dimethylamino group [30]. In the presence of $[Pd(2\text{-}Me_2NCH_2C_6H_4)(\mu\text{-}X)]_2$ (X = Cl, I), the reaction of (**25**) with tmen appears to generate $TaCl_2[2\text{-}Me_2NCH_2C_6H_3](C^tBu)[2,6\text{-}(Me_2NCH_2)_2C_6H_3]$ and as such, is an unanticipated, new palladium-mediated alkylidyne functionalisation reaction.

The addition of $TaCl_2Me_3$ to 2 equivalents of $LiNHSiR_3$ (R = ^{t}Bu) in hexane solvent results in the liberation of methane and isolation of $Ta(=NSi^tR_3)(NHSiR_3)Me_2$ (**26**) in 63% yield [31]. Thermolysis of (**26**) in benzene resulted in disproportionation but in pyridine and thf solvents, $Ta(=NSi^tR_3)_2L_2Me$ (L = pyridine 68%; thf 13%) and methane were produced. The bis-adduct is considered to form *via* a 1,2-elimination of methane from $Ta(=NSi^tR_3)(NHSiR_3)Me_2py$ which is obtained from (**26**) and pyridine at 25°C. ^1H and ^{13}C NMR spectra of the bis-adduct indicated equivalent pyridine ligands but a single crystal X-ray structure determination revealed trigonal bipyramidal pseudo-C_S stereoisomer with an axial methyl group and equatorial imido ligands that reflects the steric requirements of the bulky $R_3SiN=$ units. Rather long [Ta=N] distances [1.810(13) and 1.819(13)Å] support electronic arguments suggesting that the imides donate a maximum of 6-electrons to the metal centre. Addition of $TaCl_5$ to 4 equivalents of $LiNHSiR_3$ in Et_2O at −78°C afforded $Ta(=NSi^tR_3)(NHSiR_3)_2Cl$ and R_3SiNH_2. Alkylation of $Ta(=NSi^tR_3)(NHSiR_3)_2Cl$ with $AlMe_3$ in hexane, PhLi in Et_2O/hexane, $PhCH_2K$ in toluene and RCH_2Li in Et_2O provided $Ta(=NSi^tR_3)(NHSiR_3)_2R$ (R = Me 78%; Ph 64%; CH_2Ph 51%; CH_2R 39%). Addition of R_3SiNH_2 or R_3SiOH to (**26**) yielded $Ta(=NSi^tR_3)(NHSiR_3)_2Me$ or $Ta(=NSi^tR_3)(OSiR_3)_2Me$ (52%) and methane. Thermolysis of $Ta(=NSi^tR_3)(NHSiR_3)_2R$ effected 1,2-RH elimination to form transient $Ta(=NSiR_3)(NHSiR_3)_2$ which is capable of adding one C—H bond across one imido linkage. Ground state information was obtained *via* the approach to equilibrium of $Ta(=NSi^tR_3)(NHSiR_3)_2Ph$ and CH_4 but observation of a ditantalum species $[(R_3SiNH)_2Ta(=NSiR_3)]_2(\mu\text{:}\eta^1,\eta^1\text{-}1,4\text{-}C_6H_4)$ complicated the measurements. Simulation of the approach to equilibrium yielded rate constants consistent with the previously measured 1,2-RH-elimination rates and showed that $Ta(=NSi^tR_3)(NHSiR_3)_2R$ possessed relatively similar ground state free energies. Equilibration of $Ta(=NSi^tR_3)(NHSiR_3)_2CH_2Ph$ to the aryl complex $Ta(=NSi^tR_3)(NHSiR_3)_2C_6H_4Me$ in toluene at 182° gave similar results. The data portray differing 1,2-RH-elimination rates that result from significant transition state energy differences, ruling out a late transition state despite a rough correlation of rate with the C—H bond strength of the eliminated alkane/arene. The implications of these measurements, including the possibility of d^0-alkane or arene complexes as intermediates and differences in [Ta—C] bond strengths are discussed in great detail [31].

Among the studies with niobium(V) and tantalum(V) and phosphorus donor ligands other than the phosphinidine species (**21**), it has been reported that $Ta(OAr)_2Cl_2(H)(PMe_2Ph)_2$ (HOAr = 2,6-diisopropylphenol) reacts with 1, 2 or 3 equivalents of organic isocyanides to produce a sequence of organometallic products resulting from the initial insertion into the [Ta—H] bond and subsequent coupling reactions [32]. These products contain a number of unusual nitrogen based ligands as illustrated in Scheme 1.



Scheme 1 (R = Ar, xylyl Xy, ᵗBu)

2.2 LOWER OXIDATION STATES OF NIOBIUM AND TANTALUM

2.2.1 *Complexes with group 17 donor ligands*

The study of solutions of $[(Ta_6X_{12})(H_2O)_4X_2].4H_2O$ (X = Cl, Br) in methanol-H_4/methanol-D_4 (1:5 v/v) by ^1H NMR spectroscopy has been reported. Within the region 3.7—3.8 ppm, the spectra reveal a complex multiplet characteristic of methyl groups in coordinated methanol [33]. The ten resonances observed in the bromo system can be assigned to the nine species, including *cis* and *trans* isomers, which can be formed in the substitution series $[(Ta_6X_{12})(H_2O)_{6-x}(MeOH)_x]^{2+}$ with $1 < x < 6$. A model for predicting the chemical shift and intensity of each methyl resonance in the series was derived for the case where H_2O and MeOH compete on an equal basis for the six terminal coordination sites of the Ta_6Br_{12} cluster unit. The ^1H NMR spectrum of $[(Ta_6Cl_{12})(H_2O)_4Cl_2].4H_2O$ in methanol changes slowly with time and achieves the equilibrium condition after *ca.* three days. This spectrum is more complicated because of competition of Cl^-, along with H_2O and MeOH, for the terminal coordination sites. This is supported by specific conductance data in methanol and quantitative detection of free chloride ions using ^{35}Cl NMR spectroscopy [33].

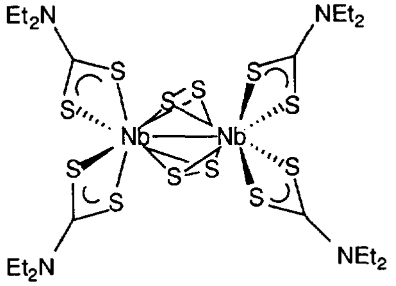
2.2.2 *Complexes with group 16 donor ligands*

Since a decrease in metal oxidation state commonly results in a lowered electrophilicity, the lower oxidation states of niobium and tantalum tend to be stabilised more by the lower congeners of group 16 rather than by oxygen. Nevertheless, an oxochloroniobium(IV) complex has been isolated by zinc reduction of $NbCl_5$ in concentrated HCl solution. The product, an extremely moisture and oxygen sensitive intense blue solid, was assigned a dimeric structure $(H_3O)^+{}_2[Nb_2O_2Cl_6]$ based on elemental analysis, IR, UV-VIS spectroscopy as well as magnetic and conductimetric measurements [34].

In the area of surface oxo-bound organometallics, the reduced metal species has been shown to have important catalytic applications. New niobium dimers on four different kinds of silica (SiO_2), prepared by the reaction between $[Nb(\eta^5\text{-}C_5H_5)(H)\text{-}\mu\text{-}(\eta^5;\eta^1\text{-}C_5H_4)]_2$ and surface hydroxo functions followed by chemical treatments, have been found to have different structures with different bond distances and coordination numbers associated with the [Nb—Nb] bond [35]. These results have been gained by EXAFS analysis. Subsequently, it was found that these niobium dimers are active in the dehydration of ethanol; indeed, the activity appears to be selective for this alcohol. The rate constant for ethene formation was found to be influenced by adsorbate-adsorbate or niobium-niobium interactions. The ratio of rate constants for intra- and intermolecular dehydration was also controlled by changing the niobium structures. On a SiO_2 surface, the direct niobium-niobium bond was not observed while the dimeric structure with bridging oxygen was formed after exposure to ethanol at 523 K. Probably, on this catalyst, ethanol dehydration proceeds in conjunction with the formation and breaking cycles of the niobium-niobium bond [35, 36].

Turning to sulfur chemistry, tantalum sulfide cluster ions ($Ta_nS_m^+$; $n < 9$; $m < 30$) have been produced by direct laser ablation of a mixture of tantalum and sulfur powders, and have been studied with a tandem time-of-flight mass spectrometry. The tantalum sulfide clusters in maximum abundance were found to be $[Ta_nS_{2n+7}]^+$ (n = 1-9) detected in the first stage mass spectra. The main dissociation path of the UV-photolysis (248 nm) of tantalum sulfide ions is a sequential S_2 loss. For cluster ions with $n > 3$, the photolysis yields $Ta_3S_4^+$ or $Ta_4S_6^+$ as the major product [37].

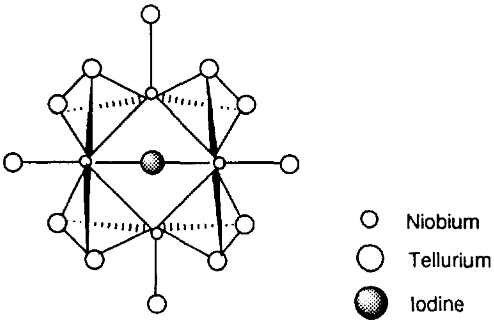
Continuing on the theme of sulfur clusters, the dimeric species $Cs_4Nb_2S_4(NCS)_8$ has been reacted with NaS_2CNEt_2 in water to afford the compound $Nb_2S_4(S_2CNEt_2)_4$ (**27**) which has been shown to crystallise in the monoclinic system, space group *C2/m*, *a* = 21.181(8), *b* = 6.958(1), *c* = 16.623(6) Å; *β* = 133.95(2)°; Z = 2 [38]. The compound contains the $[Nb_2(\mu^2\text{-}S_2)_2]^{4+}$ core in which the metal ions are in the formal +4 oxidation state, the remaining valency resulting in the formation of a [Nb—Nb] bond with a distance of 2.890(2) Å. The dithiocarbamate ligands, $[S_2CNEt_2]$ coordinate in a didentate fashion and along with the S_2^{2-} ligands form a distorted square antiprismatic geometrical arrangement around each niobium atom.



(27)

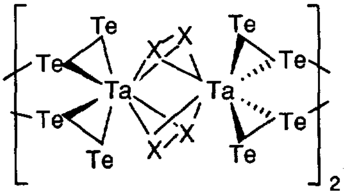
A multi-unit system based on niobium sulfide clusters and containing $[MS_4]^{3-}$; $FeCl_2$; NaSEt (M = V, Nb) has been shown to undergo heteronuclear self-assembly in MeCN solvent to afford the clusters, $[V_2Fe_6S_8(SEt)_9]^{3-}$, $[Nb_2Fe_6S_8(SEt)_9]^{3-}$ and $[Nb_2Fe_6S_8(SEt)_9]^{5-}$ which were isolated as Et_3NH^+ salts [39]. These clusters have the triply-bridged double cubane stereochemistry $\{[MFe_3S_4(SEt)_3]_2(\mu\text{-}SEt)_3\}^{3-}$, as demonstrated for the M = V cluster by single-crystal X-ray diffraction. These clusters, together with others previously reported, form a set $[M_2Fe_6S_8(SEt)_9]^{3-}$ whose members (M = V, Nb, Mo, W, Re) possess the same charge, identical ligands and essentially congruent structures with only small metric differences. This condition permits the examination of changes in heterometal on cluster properties. Redox potentials for the reversible couples $\{M_2Fe_6S_8(SEt)_9]^{3-/4-}$ and $[M_2Fe_6S_8(SEt)_9]^{4-/5-}$ decrease in the order M = V < Nb = Mo < W = Re. Reductions become more difficult as the ferrous character of the core increases. Redox reactions are accompanied by changes in electron density that largely occur in Fe_3S_4 cluster portions. The concept of cuboidal Fe_3S_4 as a cluster ligand is considered in terms of isomer shifts of heterometal clusters. The shifts of the majority of such clusters are close to those protein-bound $[Fe_3S_4]^{0/1-}$, providing an apparent definition of oxidation states. Isotropic shifts of ligands at iron sites provide a convenient indicator of the ground spin state of the clusters. Cubane-type MFe_3S_4 clusters are of renewed interest in view of the occurrence of the cuboidal cluster fragment $MoFe_3S_3$ in the co-factor of nitrogenase. The possible relation of these results to the FeMo-co-factor and the FeV-co-factor of nitrogenase is noted [39]. If the co-factor of vanadium containing nitrogenase has an analogous structure, properties derived from the heterometal cuboidal fragment may be influenced by vanadium in a manner similar to that for the cubane-type clusters.

After sulfur, tellurium ligands have been best represented in the lower valent coordination chemistry of niobium and tantalum. Thus, a new infinite-chain niobium telluride iodide has been prepared by reaction of the elements at 893 K. $Nb_4(Te_2)_4Te_4I$ (**28**) is monoclinic, space group *C2/c*, with $a = 21.957(5)$, $b = 6.147(3)$, $c = 19.925(4)$Å and $\beta = 122.40(1)°$. Compound (**28**) represents a new, one-dimensional structure type. The structure consists of infinite chains of $Nb_4(Te_2)_4Te_4I$ which are formed by the tetra-nuclear butterfly cluster units shown below and in which iodine atoms bridge different cluster units [40].



(**28**)

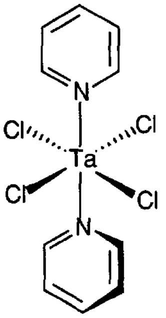
The complex $[Ta(Te_2)_2]_4[PtI_6]I_2$ (**29**) was synthesised from the elements at 680°C and its crystal structure determined; space group $P1$, $a = 16.831(1)$, $b = 17.740(1)$, $c = 19.018(1)$Å and $\alpha = 93.57$, $\beta = 94.08$, $\gamma = 102.09°$. The structure of this quasi-one-dimensional compound consists of $[Ta(Te_2)_2]$ chains separated by $[PtI_6]$ groups and iodine atoms [41] such that the tantalum atoms adopt a square prismatic geometry as illustrated below. A formal oxidation state assignment $[(Ta^{5+})(Te_2^{2-})_2]_4[(Pt^{4+})(I^-)_6](I^-)_2$ indicates that semi-conducting properties are to be expected for this material.



(29) (X = Te)

2.2.3 Complexes with group 15 donor ligands

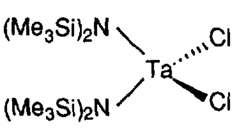
Among the lower oxidation states, the most common have been +3 or +4 with nitrogen or phosphorus donor ligands. Thus, the single crystal X-ray analysis of $TaCl_4py_2$ [(**30**); py = C_5H_5N] has been reported [42]. The compound was found to be monomeric with a distorted octahedral geometry in which the two pyridine ligands occupy mutually *trans* positions. It is suggested that the observed structure may be due to a combination of steric and electronic factors.



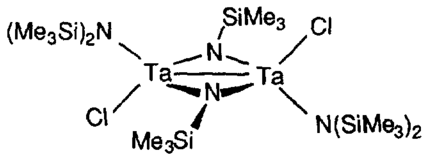
(30)

Lower valent complexes of tantalum have been demonstrated to be useful models for homogeneous hydrogenation catalysts. It has been demonstrated that an $\eta^1(N)$—$\eta^2(N,C)$ bonding rearrangement of quinoline occurs upon reducing quinoline adducts of d^0-Ta(V) to the formal d^2-Ta(III) oxidation state and that $\eta^2(N,C)$ coordination allows selective hydrogenation of the heterocyclic ring. In addition, the $\eta^2(N,C)$ coordination mode renders the C_α of a substituted pyridine substrate susceptible to nucleophilic attack resulting in C—N bond cleavage. This demonstration of C—N bond scission affords a more fundamental understanding of one way to cleave C—N bonds in hydrogenation catalysis. One feature of this reduced oxidation state tantalum system is that, in contrast to osmium η^2-pyridine systems such as $[(\eta^2\text{-}C,C\text{-}2,6\text{-}Me_2C_5H_3N)Os(NH_3)_5]^{2+}$, the tantalum system binds heterocycles only in the $\eta^2(N,C)$ mode in the d^2-electronic configuration, thereby disrupting the aromaticity of the heterocyclic ring only [43].

The syntheses and crystal structures of a number of monomeric tantalum(IV) amido halide and dimeric tantalum(IV) imido halide complexes have been reported by Hoffman and co-workers [44]. $Ta[N(SiMe_3)_2]_2Cl_3$ was reduced by Na/Hg to afford $Ta[N(SiMe_3)_2]_2Cl_2$ (**31**). $Ta(NSiMe_3)[N(SiMe_3)_2]Cl_2$ was reduced under analogous conditions to give $\{Ta(\mu\text{-}NSiMe_3)[N(SiMe_3)_2]Cl\}_2$ (**32**). Both compounds (**31**) and (**32**) have been characterised by single crystal X-ray diffraction analyses where it was found that (**31**) possesses a severely distorted tetrahedral geometry whilst (**32**) has an edge-shared tetrahedral structure with a tantalum-tantalum separation of 2.621(1)Å [44].



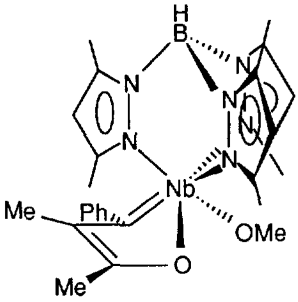
(**31**)



(**32**)

A number of other amido complexes of group 5 metals in lower oxidation states have been reported by the same group, including $Nb[N(SiMe_3)_2]_2Cl_2$ and $Nb(NPh)_4$, both of which possess tetrahedral geometries, the former being isostructural to the tantalum analogue (**31**) [45].

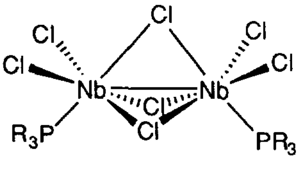
Treatment of $Tp'NbCl_2(PhCCR')$ [R' = Me, Et; Tp' = hydrido tris(3,5-dimethylpyrazolylborato)] with NaOMe gives good yields of the corresponding chiral chloro-methoxo derivatives, Tp'NbCl(OMe)(PhCCR'). The methyl and phenyl-methoxo complexes, Tp'NbR''(OMe)(PhCCR') (R' = Me, R'' = Me; R' = Et, R'' = Me; R' = Et, R'' = Ph) are obtained in high yields upon reaction of either Tp'NbCl(OMe)(PhCCR') (R' = Me, Et) with MeLi or PhLi respectively [46]. Due to the resultant chirality at the niobium atom, the ethyl groups in these complexes give rise to AMX_3 type ^1H NMR spin systems although in some of the complexes, deceptively simple spectra can be observed regardless of solvent or temperature even though rotation about the [Nb—Ph] bond can be frozen out. The complexes, Tp'NbR''(OMe)(PhCCR') (R' = Me, R'' = Me; R' = Et, R'' = Me; R' = Et, R'' = Ph) react with CO to form five-membered oxoniobacycles $Tp'Nb(OMe)[\eta^2\text{-}C(Ph)C(R)C(Me)O]$ [R = Me (**33**); Et] and $Tp'Nb(OMe)[\eta^2\text{-}C(Ph)C(Et)C(Ph)O]$ respectively from regioselective coupling of the coordinated alkyne with an acyl or benzoyl group. A single crystal X-ray diffraction study has confirmed the structure of (**33**), wherein the metallacycle is folded in an envelope conformation about the C_α—O axis with the C_α—Nb—O triangle constituting the flap. Examination of metric parameters within the ring and comparison with related complexes indicate that an analogy between the oxoniobacycle and the bonding description for a metallacyclopentatriene is appropriate [46].



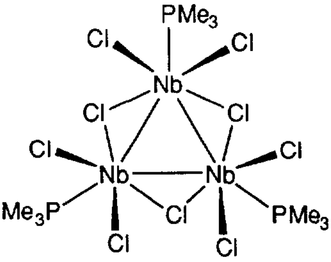
(33)

Along similar lines, deprotonation with ^{n}BuLi in tmen at the propargylic site of the coordinated alkyne in Tp'NbCl(X)(PhCCMe) (R = H, X = Cl, OMe; Tp' = as above) followed by reaction with MeI or $PhCH_2Br$ affords the alkylated alkyne compounds Tp'NbCl(X)($PhCCCH_2R$) (R = Me, X = Cl, OMe; R = CH_2Ph, X = Cl, OMe) in high yield. The addition of $PhCH_2Br$ to deprotonated Tp'NbCl(OMe)($PhCCCH_2Me$) affords a 4:1 diastereoisomeric mixture of Tp'NbCl(OMe)[PhCCCHMe(CH_2Ph)] whereas a 1:6 ratio is obtained under the same conditions starting from Tp'NbCl(OMe)[$PhCCCH_2(CH_2Ph)$] and MeI [47].

Moving on to phosphorus-bound systems, two examples of a new type of face-sharing bioctahedral niobium complex that contain three bridging chloro ligands and two terminal phosphines in a *syn* configuration have been reported by Cotton and co-workers [48]; $(Bu_4N)[Nb_2Cl_7(PEt_3)_2]$ (**34**), the isostructural complex $(Bu_4N)[Nb_2Cl_7(PMe_3)_2]$.thf (**35**) and the related triangular $(Me_3PH)(Bu_4N)[Nb_3Cl_{10}(PMe_3)_3(BF_3)]$.thf (**36**) (the relevant metal containing anions are illustrated below). Compounds (**34**) and (**35**) have effective magnetic moments of 0.84 and 0.99 BM respectively at room temperature. Pathways of interconverting edge-shared bioctahedral $[Nb_2Cl_6(PEt_3)_4]$ to the face-sharing $[Nb_2Cl_7(PEt_3)_2]^-$ and finally to the triangular trinuclear $[Nb_3Cl_{10}(PEt_3)_3]^-$ and even larger clusters is discussed [48].

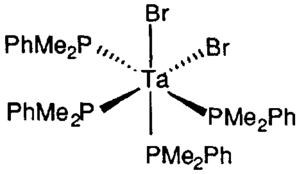


R = Et (34), Me (35)



(36)

The monomeric, paramagnetic tantalum(II) complex, $TaBr_2(PMe_2Ph)_4$ (**37**) has been isolated from the reduction of $TaBr_5$ with $LiBEt_3H$ in toluene solvent in the presence of PMe_2Ph and characterised by single crystal X-ray diffraction techniques [49]. The coordination polyhedron is essentially distorted octahedral with a mutually *cis* arrangement of bromo ligands. However, the structure is severely distorted towards a bicapped tetrahedron with the angle Br-Ta-Br = 84.23(4)°.



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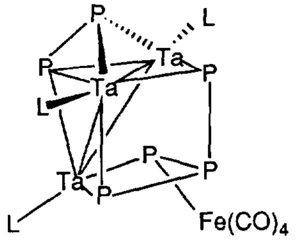

(38)

The phosphido-phosphinidene coordination mode of a P_2 ligand has been realised in the trinuclear complex $[(TaL)_3(P_4)(P_2)]$ (L = 1,3-$^tBu_2C_6H_3$) prepared by reaction of $TaL(CO)_4$ with white phosphorus (P_4) in decalin solvent at 190°C for 4 h. Structural proof was obtained by single-crystal X-ray diffraction of the product of the reaction of $[(TaL)_3(P_4)(P_2)]$ with $Fe_2(CO)_9$, namely $[(TaL)_3[P_4\{Fe(CO)_4\}(P_2)]$ (**38**) [50].

The kinetics of the reaction of $[Ta(COSiPr^i_3)(CO)(dmpe)_2]$, (dmpe = 1,2-dimethylphosphinoethane) with Me_3SiCl in thf to afford $[Ta(Me_3SiOCCOSiPr^i_3)(CO)(dmpe)_2Cl]$ have been studied using stopped flow spectrophotometric techniques [51]. The rate is greatly accelerated by the addition of the salts, $[(n\text{-pentyl})_4N]Cl$ and $[(n\text{-butyl})_4N][BPh_4]$ due to the increased ionic strength of the solution. The reaction is first order in both $[Ta(COSiPr^i_3)(CO)(dmpe)_2]$ and Me_3SiCl in the presence of excess $[(n\text{-butyl})_4N][BPh_4]$. At 22(1)°C, a second order rate constant of 1.71(4) $M^{-1}s^{-1}$ was obtained. These results were interpreted in terms of initial electrophilic attack of the silyl reagent at the oxygen atom of the carbonyl ligand in $[Ta(COSiPr^i_3)(CO)(dmpe)_2]$. In order to model the transition state or intermediate of this rate-determining step in the [C—C] bond-forming reaction, $AlEt_3$ was added to the siloxocarbene complex $[Ta(COSiBu^tPh_2)(CO)(dmpe)_2]$; spectroscopic and structural characterisation of this complex revealed that coupling does not necessarily occur upon addition of a Lewis acid; adduct formation appears to be the initial event resulting in the formation of $[Ta(COSiBu^tPh_2)(COAlEt_3)(dmpe)_2]$. However, further discussion of the organometallic aspects of this work lies outside the scope of this review.

REFERENCES

1. R.W. Berg, *Coord. Chem. Rev.*, 113 (1992) 1.
2. T.P. Kee, *Coord. Chem. Rev.*, 138 (1995) 161; *ibid* 138 (1995) 181.
3. M.E. Ignatov, E.G. Il'in, L.S. Butorina, T.A. Mastryukova and Yu.A. Buslaev, *Zh. Neorg. Khim.*, 38 (1993) 1560; *Chem. Abstr.*, 120 (1993) 152193z.
4. I. Kobayashi, *Nippon Kagaku Kaishi*, (1993) 213; *Chem. Abstr.*, 118 (1993) 204008y.
5. E.G. Il'in, V.V. Kovalev, V.D. Butsky, M.V. Simonov, I.V. Leont'eva, I.M. Aladzheva, G.A. Mastryukova and Yu.A. Buslaev, *Dokl. Akad. Nauk.*, 330 (1993) 60; *Chem. Abstr.*, 119 (1993) 216166g.
6. S. Boghosian and G.A. Voyiatzis, *Polyhedron*, 12 (1993) 2965.

7. A. Khalidi and J. Bouteillon, *J. Appl. Electrochem.*, 23 (1993) 801.
8. B. Therrien and A.L. Beauchamp, *Acta Crystallogr., Sect. C*, 49 (1993) 1303.
9. K.C. Malhotra, B. Bala, N. Sharma and S.C. Chaudhry, *J. Indian Chem. Soc.*, 70 (1993) 187.
10. V.M. Visciglio, P.E. Fanwick and I.P. Rothwell, *Inorg. Chim. Acta*, 211 (1993) 203.
11. Y. Nakayama, K. Mashima and A. Nakamura, *Macromolecules*, 26 (1993) 6267.
12. S. Mathur, A. Singh and R. C. Mehrotra, *Polyhedron*, 12 (1993) 1073.
13. S. Mathur, A. Singh and R. C. Mehrotra, *Indian. J. Chem.*, 32A (1993) 585.
14. R. Gupta, A. Singh and R. C. Mehrotra, *Indian. J. Chem.*, 32A (1993) 310.
15. T. Kauffman, T. Abel and D. Schwarze, *Chem. Ber.*, 126 (1993) 453.
16. V. Sum and T.P. Kee, *J. Chem. Soc., Perkin Trans. 1*, (1993) 2701.
17. D.A. Brown, W. Errington and M.G.H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, (1993) 1163.
18. D.A. Brown, M.G.H. Wallbridge and N.W. Alcock, *J. Chem. Soc., Dalton Trans.*, (1993) 2037.
19. D.F. Evans, A.M.Z. Slawin, D.J. Williams, G.Y. Wong and D.J. Woolins, *Polyhedron*, 12 (1993) 1103.
20. R.L. Miller, R. Toreki, R.E. LaPointe, P. T. Wolczanski, G.D. van Duyne and C.D. Roe, *J. Am. Chem. Soc.*, 115 (1993) 5570.
21. N.G. Chernorukov, N.P. Egorov and E.V. Suleimanov, *Zh. Neorg. Khim.*, 38 91993) 197. *Chem. Abstr.* 119 (1993) 61510p.
22. V.C. Gibson and T.P. Kee, *J. Chem. Soc., Dalton Trans.*, (1993) 1657.
23. S.K. Pandey, G. Srivastava and R.C. Mehrotra, *Transition Metal Chem.*, 18 (1993) 31.
24. R.N. Pandey, L.M. Choudhray, S.P. Roy, A.N. Sahay and R.N. Sharma, *Indian J. Chem.*, 32A (1993) 450.
25. T. Kazuyuki, K. Hiroyuki, I. Matsubara and A. Nakamura, *Inorg. Chem.*, 32 (1993) 2604.
26. H. Braunschweig, P. Paetzold and R. Boese, *Chem. Ber.*, 126 (1993) 1571.
27. T.C. Baldwin, S.R.Huber, M.A. Bruck and D.E. Wigley, *Inorg. Chem.*, 32 (1993) 5682.
28. C.C. Cummins, R.R. Schrock and W.M. Davis, *Angew. Chem. Int. Ed. Engl.*, 105 (1993) 758.
29. V. Christou and J. Arnold, *Angew. Chem. Int. Ed. Engl.*, 105 (1993) 1551.
30. H.C.L. Abbenhuis, N. Feiken, H.F. Haarman, D.M. Grove, E. Horn, A.L. Spek, M. Pfeffier and G. Van Koten, *Organometallics*, 12 (1993) 2227.
31. C.P. Schaller and P.T. Wolczanski, *Inorg. Chem.*, 32 (1993) 131.
32. J.R. Clark, P.E. Fanwick and I.P. Rothwell, *J. Chem. Soc., Chem. Commun.*, (1993) 1233.
33. N. Brnicevic, P. Planinic, J. Basic, R. E. McCarley, V. Rutar and X. Xie, *Inorg. Chem.*, 32 (1993) 3786.
34. S.H. Chan and B.L. Ooi, *Transition Metal Chem. (London)*, 18 (1993) 473.
35. I. Nobuyuki and Y. Iwasawa, *Catal. Today*, 16 (1993) 427.
36. N. Ichikuni and Y. Iwasawa, *Stud. Surf. Sci. Catal.*, 75 (1993) 477; *Chem. Abstr.*, 119 (1993) 270378r.
37. N. Zhang, Z. Yu, X. Wu, Z. Gao, Q. Zhu and F. Kong, *J. Chem. Soc., Faraday Trans.*, 89 (1993) 1779.
38. A.V. Virovets, N.V. Podberezskaya, M.N. Sokolov, I.V. Korobkov, V.P. Fedin and V.E. Fedorov, *Zh. Strukt. Khim.*, 34 (1993) 134; *Chem. Abstr.*, 119 (1993) 253317c.
39. W. Cen, S.C. Lee, J.Li, F.M. MacDonnell and R.H. Holm, *J. Am. Chem. Soc.*, 115 (1993) 9515.
40. S. Deng, H. Zhuang, C. Lu and J. Huang, *Acta Crystallogr., Sect. C*, 49 (1993) 1135.
41. W. Tremel and K.L. Stork, *Z. Naturforsch Teil B*, 48 (1993) 1155.
42. G.J. Miller, J. Lin and V. Young, *Acta Crystallogr., Sect. C*, 49 (1993) 1770.
43. S.D. Gray, P.A. Fox, R.P. Kingsborough, M.A. Bruck and D.E. Wigley, *Prepr. Am. Chem. Soc., Div. Pet. Chem.*, 38 (1993) 707.
44. D.M. Hoffman and S. Suh, *J. Chem. Soc., Chem. Commun.*, 1993, 714.
45. D.M. Hoffman and S.P. Rangarajan, *Polyhedron*, 12 (1993) 2899.
46. M. Etienne, P.S. White and J.L. Templeton, *Organometallics*, 12 (1993) 4010.
47. M. Etienne, P. Zeline, J.L. Templeton and P.S. White, *New. J. Chem.*, 17 (1993) 515.
48. F.A. Cotton and M. Shang, *Inorg. Chem.*, 32 (1993) 969.
49. L.G. Hubert-Pfalzgraf, A. Zaki and L. Toupet, *Polyhedron*, 12 (1993) 1411.
50. O.J. Scherer, R. Winter and G. Wolmershaeuser, *J. Chem. Soc., Chem. Commun.*, (1993) 313.
51. J.D. Protasiewicz, A. Masschelein and S.J. Lippard, *J. Am. Chem. Soc.*, 115 (1993) 808.

3. Scandium 1993

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INTRODUCTION

This review surveys the coordination chemistry of scandium reported during the year 1993 and follows a similar format to the 1992 review [1]. The literature has been searched by using *Current Contents* and the Cambridge Crystallographic Data Base. Structural figures have been redrawn using coordinates taken from the latter, implemented through the ETH, Zürich [2]. Organometallic complexes have, in general, been excluded, although in section 3.2 some fullerene chemistry is described.

A review which includes discussions of zero oxidation state scandium compounds has appeared [3].

3.1 SOLID STATE COMPOUNDS

The reaction of elemental scandium with Sc_2O_3 and iodine in the solid state has been studied by DTA. The product is ScOI, and the structure of this compound has been determined by X-ray crystallography [4]. The crystal structure of $CsScS_3$ has also been elucidated [5].

3.2 FULLERENE DERIVATIVES

Members of a series of endohedral scandafullerenes have been characterised by mass spectrometric and ESR spectral data. In the same study, Shinohara *et al.* have shown that $Sc@C_{82}$ can be separated from $Sc_3@C_{82}$ by using liquid chromatography with an ethanol-deactivated silica-gel column [6]. The same workers have reported that $Sc_2@C_{74}$, $Sc_2@C_{82}$ and $Sc_2@C_{84}$ may be