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COORDINATION CHEMISTRY REVIEWS

Niobium and Tantalum 1994

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Contents

1. Introduction

This review is intended to cover the literature on the coordination chemistry of niobium and tantalum through the year 1994 as reflected in the Bath Information and Data Services, Science Citation Index database. Searching was performed through keyword analysis using the string [niobium/tantalum + complex*-organo*]. To keep the review to a manageable length we have chosen to limit the study further, in a similar fashion to the 1993 review, to low nuclearity inorganic coordination systems only; consequently several areas have had to be omitted. Organic/organometallic systems have been omitted unless there was good reason for their inclusion on account of the non-carbon based components of the coordination sphere.

The layout of the review focuses on the range of different oxidation states. Many 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

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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 review of niobium and tantalum coordination chemistry for 1993 [2].

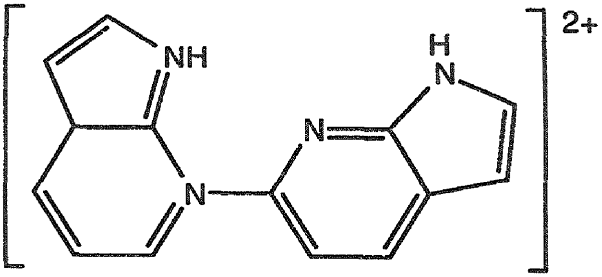
1.1. Niobium(V) and tantalum(V)

1.1.1. Complexes with group 17 donor ligands

Among the most important uses of halide complexes of niobium(V) and tantalum(V) is displacement chemistry in the presence of suitable ligands. Thus it has been shown that sequential removal of chloride ions from $[(\eta^5\text{-}C_5H_5)NbCl_4]$ may be realised using antimony(V) chloride in acetonitrile under controlled stoichiometry. Under these conditions, a variety of cationic species including $[(\eta^5\text{-}C_5H_5)NbCl(MeCN)_4]^{3+}$ and $[(\eta^5\text{-}C_5H_5)Nb(MeCN)_6]^{4+}$ [3] have been synthesised.

In a similar vein, refluxing $[NbCl_5]$ and excess 7-azaindole (Haza) in benzene yields a solid mixture containing $[NbCl_5(Haza)]$, $[NbCl_4(Haza)_2]$, the azaindolium ion $(H_2aza)^+$ and the azaindolylazaindolium ion $(H_2aza\text{-}aza)^+$. The neutral (Haza-aza) molecule was obtained from the hydrolysed mixture and shown by X-ray diffraction (monoclinic, $P2_1/c$, $a=10.025$, $b=13.758$, $c=8.416$ Å; $\beta=102.89°$; $Z=4$, $R=0.035$) to result from the coupling of two azaindole units [4]. This compound was the only oxidation product detected, but concurrent formation of other niobium and/or azaindole-containing products keeps the yield of Haza-aza low. Dark green crystals of $[Cu_4O(aza\text{-}aza)]Cl_2 \cdot 6.5\ H_2O$ were obtained from Haza-aza and $CuCl_2$ in wet methanol, and a single crystal X-ray diffraction study of this material has been reported [4]. A related study by the same group reported that the reaction of $[NbCl_5]$ and $[TaCl_5]$ with 7-azaindole (Haza) at room temperature in benzene or dichloromethane yielded $[MCl_5(Haza)]$ addition compounds [5], the tantalum derivative being formed under more forcing conditions. With $[NbCl_5]$ some reduction to Nb(IV) was observed and $[NbCl_5(Haza)]$, $[NbCl_4(Haza)_2]$ and the $(H_2aza)^+$ ion were identified in the reaction mixture by infrared spectroscopy. Oxidative coupling of two azaindole units also took place during the reaction, since the 7-(azaindol-6-yl)azaindolium cation was found as the counter-ion in the crystal structures of two complex salts [5]. In the crystals of $[(H_2aza\text{-}aza)][Nb(O)Cl_4(Haza)] \cdot 0.5\ CH_2Cl_2$ containing cation (**1**), the anion is composed of the roughly octahedral $[Nb(O)Cl_4(aza)]^-$ species containing a neutral N7-coordinated azaindole *trans* to the Nb=O bond. The $[Nb(O)Cl_5]^{2-}$ salt contains a distorted octahedral anion. Infrared spectroscopy suggests monomeric octahedral structures for the $[MCl_5(Haza)]$ and $[NbCl_4(Haza)_2]$ complexes. A ^{1}H-NMR spectroscopic study reveals that $[NbCl_5(Haza)]$ is not dissociated in CD_2Cl_2 solution [5].

To study complex formation of group 5 elements in aqueous HCl solutions at medium and high concentrations, the electronic structures of anionic complexes of



(1)

these elements $[MCl_6]^-$, $[M(O)Cl_4]^-$, $[M(OH)_2Cl_4]^-$ and $[M(O)Cl_5]^{2-}$ have been calculated using the relativistic Dirac-Slater Discrete-Variational Method [6]. The charge density distributional analysis has shown that tantalum occupies a specific position in the group and has the highest tendency to form the pure halide complex, $[TaCl_6]^-$. This fact, along with the high covalency of this complex, explains its good extractability into aliphatic amines. Niobium has a similar tendency to form pure halide $[NbCl_6]^-$ and oxyhalide species, $[Nb(O)Cl_5]^{2-}$ at medium and high acid concentrations.

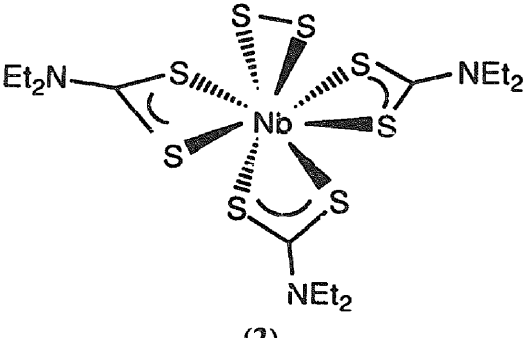
Electrochemical studies continue to be a rich source of study for group 5 elements. The electrochemical behaviour of tantalum in the form of $K_2[TaF_7]$ in an LiF-NaF-KF eutectic melt has been studied by linear voltammetry in the temperature range of 560-815°C with and without the addition of Na_2O [7]. An amperometric titration has been performed by measuring the heights of the cathodic and anodic peaks. It was shown that at a molar ratio of $Na_2O/K_2[TaF_7]=1$, the predominant complex in the melt is $[Ta(O)F_5]^{2-}$, whereas with an Na_2O/K_2TaF_7 molar ratio of 2 it is $[Ta(O)_2F_x]^{(x-1)}$ probably in the form of $[Ta(O)_2F_4]^{3-}$. Increase in the $Na_2O/K_2[TaF_7]$ molar ratio in excess of two, leads to a decrease of tantalum concentration in the melt and precipitation of $K[TaO_3]$ occurs. Both the fluoro complex and the monooxofluoro complex were reduced to metal in a single, five-electron step. The fluoro complexes, in the temperature range 625-815°C with potential scan rates $<0.5\ Vs^{-1}$, discharge quasi-reversibly, but at potential scan rates $>0.5\ Vs^{-1}$ they discharge irreversibly. Monooxofluoro complexes discharge irreversibly at all temperatures and scan rates studied [7]. The diffusion coefficient (D) of the tantalum fluoro complex depends upon the temperature as $\log D=-2.55-(2044/T)$ with an activation energy of 39.1 kJ mol^{-1}. For the monooxofluoro complex the dependence is $\log D=-2.35-(2293/T)$ with an activation energy of 39.1 kJ mol^{-1}.

1.1.2. Complexes with group 16 donor ligands

The interaction of MeI with the complexes, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)XCS_2\text{-}C,S]$ (X = Cl, Br) affords cationic complexes containing a methyldithiocarboxylate group, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)XC(S)SMe\text{-}C,S]$ (X = Cl, Br) as a result of the electrophilic attack of MeI at the *exo* sulfur atom of the coordinated CS_2 molecule [8]. In contrast, the trihydride complex, [Nb(η^5-$C_5H_4SiMe_3$)H_3] interacts under mild conditions in thf solvent with phosphites and other ligands giving rise to new hydridoniobium(III) complexes [Nb(η^5-$C_5H_4SiMe_3$)HL] [L=CO, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$] which undergo subsequent insertion reactions with CS_2 to give products, the nature of which are highly dependent upon L. When L=CO, the product obtained is [Nb(η^5-$C_5H_4SiMe_3$)SCHS(CO)], whereas with L=$P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$, the products are [Nb(η^5-$C_5H_4SiMe_3$)(SCHSSS)]. Using several electrophilic synthons of group 11 metals, two different families of early-late heterodimetallic complexes have been prepared. The compound [Nb(η^5-$C_5H_4SiMe_3$)ClC(S)S-*C,S*] reacts through the *exo*-sulfur atom of CS_2 with [$MPPh_3$]PF_6 to give cationic heterodimetallic complexes [Nb(η^5-$C_5H_4SiMe_3$)Cl(μ-CS_2)(C(S)S-M(PPh_3))][PF_6] (M=Cu, Ag, Au) [8]. In a similar manner, the complexes [Nb(η^5-$C_5H_4SiMe_3$)HL] [L=$P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$] react with [$AuPPh_3$]PF_6 to afford a species containing a hydride bridge, [Nb(η^5-$C_5H_4SiMe_3$)L(μ-H)($AuPPh_3$)][PF_6].

A synthetic and vibrational spectroscopic study on a variety of adducts of [$NbCl_4$], [Nb(O)Cl_3] and [$Nb_2(O)_3Cl_4$] with a range of didentate oxygen and nitrogen donor compounds has been reported [9].

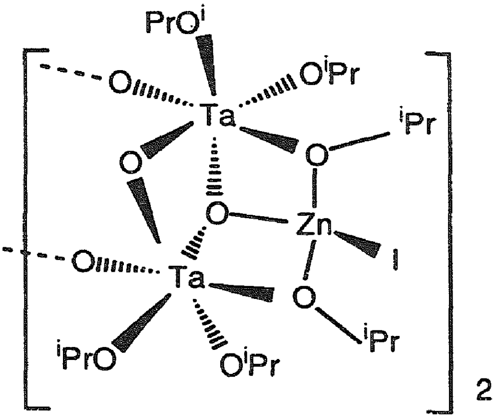
The reaction of [Nb(O)(S_2CNEt_2)$_3$] with boron sulfide has been investigated under a variety of conditions [10]. The major product in all cases was found to be yellow [Nb(S)(S_2CNEt_2)$_3$]. In CH_2Cl_2 solvent at room temperature, orange [Nb(S_2)(S_2CNEt_2)$_3$] and orange-brown [Nb_2(μ-S_2)$_2$(S_2CNEt_2)$_4$] were also formed. At higher temperatures, the same products were formed but a higher proportion of [Nb(S)(S_2CNEt_2)$_3$] was observed. Crystals of [Nb(S_2)(S_2CNEt_2)$_3$]·0.5 CH_2Cl_2, (2)·0.5 CH_2Cl_2, were monoclinic (space group *C*2/*c* with $a=16.360(2)$, $b=10.959(1)$, $c=30.637(3)$ Å; $\beta=92.34(1)°$, $Z=8$). The eight-coordinate complex displays an *mmmm* dodecahedral structure analogous to that of its tantalum counterpart.



(2)

Stereospecific heteroatom and hetero-group transfer from oxiranes, thiiranes and aziridines mediated by a simple alkyl tantalocene have been reported by Bergman's group [11].

A mixed-metal tantalum-zinc oxoisopropoxide complex (3) has been prepared and studied by single-crystal X-ray diffraction [12].



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The reaction of lanthanum isopropoxide with two equivalents of triethanolamine leads to a novel "diatrane" complex $H_3La[(OC_2H_4)_3N]_2$; its reaction with $[Nb(O^iPr)_5]$ provides a soluble and volatile mixed-metal species $[La_2Nb_3]$ whose molecular structure is based on a central diatrane core with eight-coordinate lanthanum whilst all the niobium centres are six-coordinate [13].

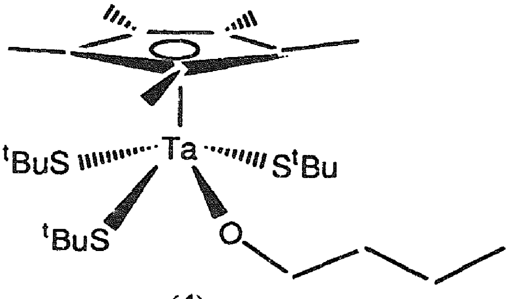
The infrared and ^{13}C-NMR spectra of 1,1-disubstituted chlorodicyclopentadienyloxoniobium complexes have been recorded and their features correlated with structural and substituent effects [14]. Optimized MMX force field and EHT methods have been used to calculate the optimal geometry and charge densities and these have been correlated with corresponding spectral data. In all correlations, a reverse substituent effect was observed, leading to the conclusion that the oxo ligand in chlorodicyclopentadienyloxoniobium complexes exhibits a strong electron-donor effect supported by a through space interaction between the oxygen atom and the two cyclopentadienyl rings.

The complex, $[(\eta^5\text{-}C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-}CHPMe_2)]$ reacts with aryl isocyanates RNCO ($R = C_6H_5$, $4\text{-}MeC_6H_4$) to afford the hydrido-formamido complexes, $[(\eta^5\text{-}C_5Me_5)Ta(PMe_3)(\eta\text{-}OCHNR)(H)(\eta^2\text{-}CHPMe_2)]$ (R as above) which exist in two tautomeric forms in solution [15]. The interconversion of these isomers proceeds via an intramolecular rotation of the (OCHNR) moiety analogous to the equilibration of *syn* and *anti* hydrogens of an η^3-allyl ligand. The complex $[(\eta^5\text{-}C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-}CHPMe_2)]$ inserts two equivalents of CO_2 to afford $[(\eta^5\text{-}C_5Me_5)Ta(PMe_3)(\eta^1\text{-}OCHO)(\eta^2\text{-}OCHO)(\eta^2\text{-}CHPMe_2)]$, a compound containing both η^1 and η^2-formamato ligands.

Dichlorotris(4-*tert*-butylphenoxo)tantalum(V) has been synthesised by reacting tantalum(V) chloride and 4-*tert*-butylphenol in a molar ratio of 1: 3 in dry benzene solvent under reflux and has been characterised subsequently by elemental analysis, conductance, infrared and NMR spectroscopies and mass spectrometric studies [16]. Reaction of dichlorotris(4-*tert*-butylphenoxo)tantalum(V) with equimolar amounts of hydroxyl-containing substrates having labile protons, such as benzoin, 2-hydroxyacetophenone and salicylaldehyde (L) in 1:1 molar ratio, afforded 6-coordinate complexes of composition $[TaCl(OC_5H_4\text{-}Bu^t)_3(L)]$.

The esters $[Ta(O)(OR)_3]$ [(R = ^{t}Bu, $C_6^tBu_3H_2$ (Mes*)], $[Ta(O)(SR)_3]$ (R = ^{t}Bu, 4-MeC_6H_4) have been prepared by the reaction of $[Ta(O)Cl_3]$ and $[Ta(S)Cl_3]$ with the corresponding lithium reagents, LiOR and LiSR. The reaction of $[TaCl_5]$ with an excess of LiOMes* affords the compounds $[TaCl_3(OMes^*)_2]$ and $[TaCl_2(OMes^*)_3]$ [17]. The synthesis of $[TaCl_2(\eta\text{-}C_4H_9)(OMes^*)_2]$, $[Ta(S\text{-}4\text{-}MeC_6H_4)_5]$ and $[TaCl_2(OEt)_3]\cdot NC_5H_5$ are also described. Upon prolonged heating under reduced pressure in benzene solution, $[Ta(O)(OMes^*)_3]$, $[Ta(S)(OMes^*)_3]$, $[TaCl_3(OMes^*)_2]$ and $[TaCl_2(n\text{-}C_4H_9)(OMes^*)_2]$ all decompose to release 2,4,6-tri-t-butylphenol, n-butane and form a cyclometallated product of tantalum(V). A single crystal X-ray diffraction analysis of $[TaCl_2(OEt)_3]$ is also reported, the compound existing in the solid state as an ethoxo-bridged dimer [17].

The tantalum n-butoxide complex of $[(\eta^5\text{-}C_5Me_5)Ta(S^tBu)_3(O^nBu)]$ (4) has been isolated as a minor product from the reaction of $[(\eta^5\text{-}C_5Me_5)TaCl_4]$ with LiS^tBu in thf solvent. The crystal structure of (4) reveals two crystallographically independent molecules with distinctly different Ta-O-C angles, where a larger angle is associated with a longer Ta-O bond and vice versa. Extended Hückel molecular orbital calculations on the model compound $[(\eta^5\text{-}C_5H_5)Ta(SH)_3(OH)]$ showed that the potential energy curve against the Ta-O-H angle is in fact flat while the Ta-O overlap population decreases as the Ta-O-H bond bends [18].



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The 1:1 and 1:2 reactions of $[TiCl_4]$ with $Me_3SiO\text{-}2,6\text{-}(CH_3)_2C_6H_3$ produced $\{TiCl_3[O\text{-}2,6\text{-}(CH_3)_2C_6H_3](thf)_2\}$ and $\{TiCl_2[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2(thf)_2\}$ respectively which both possess 6-coordinate titanium geometries. In the complex, $\{TiCl_2[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2(thf)_2\}$ the two phenoxo ligands are disposed in a *cis*-geometry with thf coordinated *trans* to the phenoxo and chloro ligands [19]. Similarly, the 1:1 and 1:2 reactions of $[NbCl_5]$ with $Me_3SiO\text{-}2,6\text{-}(CH_3)_2C_6H_3$ affords the two complexes $\{NbCl_4[O\text{-}2,6\text{-}(CH_3)_2C_6H_3](thf)\}$ and $\{NbCl_3[O\text{-}2,6\text{-}(CH_3)_2C_6H_3]_2(thf)\}$ respectively, again having octahedral coordination geometries around the metal centre. Again, the phenoxo ligands are orientated mutually *cis* and the thf ligand in $\{NbCl_4[O\text{-}2,6\text{-}(CH_3)_2C_6H_3](thf)\}$ is disposed *trans* to a phenoxo ligand.

1.1.3. Complexes with group 15 donor ligands

Diazoacetates N_2CHCO_2R (R = Et, ${}^tBu$) react readily with $[(\eta^5\text{-}C_5H_5)_2NbH_3]$ to afford $[(\eta^5\text{-}C_5H_5)_2Nb(\eta^1\text{-}N_2CHCO_2R)H]$ as the first identifiable product by ^1H NMR spectroscopy. The complex $[(\eta^5\text{-}C_5H_5)_2Nb(\eta^1\text{-}N_2CHCO_2Et)H]$ converts via a stepwise process into a unique dinuclear niobocene complex, $\{[\eta^5\text{-}C_5H_4CH(CO_2Et)=N\text{-}\mu\text{-}N](C_5H_5)_2Nb\}_2$ which is in fact a product of the Cp-ligand functionalised by the diazoacetate group. Mechanistic features of this transformation are also reported [20].

A derivative spectrophotometric method has been developed for the simultaneous determination of microgram amounts of Nb(V) and Ti(IV). The method is based on fifth order derivative spectra of ternary metal systems with hydrogen peroxide and 2-(5-bromo-2-pyridyazo)-5-diethylaminophenol (5-BrPADAP) [21]. For measurements of the derivative values, the most suitable is the "zero-crossing" technique. The method is selective for Nb(V) and Ti(IV) when they are separated as complexes with *N*-benzoyl-*N*-phenylhydroxylamine (BPHA). The full procedure including such preliminary extraction allows the determination of up to 10 mg of Nb(V) and 15 mg of Ti(IV) in the presence of large amounts of other ions. Niobium and titanium in standard steel and Buffalo River sediment were determined with good precision and accuracy.

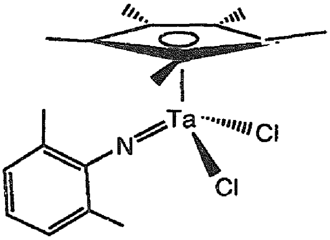
5-Chloro-2,3-pyridinediol (CPD) has been used as a sensitive and selective reagent in some analytical techniques (such as spectrophotometry and potentiometry). A survey of the literature revealed that an omission existed with CPD. This has subsequently been rectified recently by examination of the polarographic behaviour of Nb(V) and Ga(III) with CPD. It is reported also that with this complexing agent it is not necessary to employ a maximum suppressor and the method has found use in the determination of niobium in rock samples [22].

The α-agostic n-ethyl and n-propyl niobium alkyne complexes $[NbL(Cl)(\mu\text{-}H\text{-}CHR)(PhC{=}CR')]$ (L = hydridotris-3,5-dimethylpyrazolylborate; R = Me, Et; R′ = Me, Et, ${}^nPr$) undergo a thermolytic exchange of the niobium and alkyne-bound alkyl groups to afford $NbL(Cl)(R)(PhC{=}CR')]$; first order kinetic parameters have been obtained when R = R′ = Me ($\Delta H = 113$ kJ mol^{-1}; $\Delta S = 4$ J K^{-1} mol^{-1}) [23].

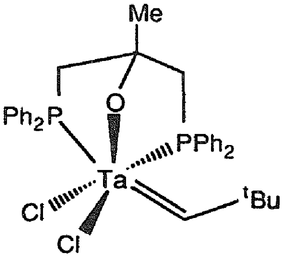
The dimethyl tantalum complex $[Cp^*TaCl_2Me_2]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) reacts readily with isocyanide CNAr ($Ar = 2,6\text{-}Me_2C_6H_3$) to form the azatantalacyclopropane derivative $[Cp^*TaCl_2(\eta^2\text{-}NArCMe_2)_2]$ which may be alkylated subsequently with two equivalents of MeLi to afford the corresponding dimethyl complex of the form $[Cp^*TaMe_2(\eta^2\text{-}NArCMe_2)_2]$ [24]. Reaction of both $[Cp^*TaCl_2(\eta^2\text{-}NArCMe_2)_2]$ and $[Cp^*TaMe_2(\eta^2\text{-}NArCMe_2)_2]$ with an additional equivalent of isocyanide leads to the imido complexes $[Cp^*TaCl_2(NAr)]$ and $[Cp^*TaMe(NArCMe{=}CMe_2)(NAr)]$ respectively. The latter complex is also obtained by reaction of $[Cp^*TaMe_4]$ with two equivalents of isocyanide and the same reaction with $[Cp^*TaClMe_3]$ leads to $[Cp^*TaCl(NArCMe{=}CMe_2)(NAr)]$. The complexes have been characterised by

NMR spectroscopic studies (^{1}H, ^{13}C and ^{13}C-CP MAS) and the crystal structure of [Cp*$TaCl_2(NAr)$] (**5**) has been determined by X-ray diffraction methods. The dynamic behaviour and kinetic parameters were calculated from dynamic ^{1}H-NMR spectroscopic data.

A series of dineopentyl tantalum and titanium complexes which contain phosphinoalkoxide ligands has been prepared. The corresponding alkylidene complexes are formed readily upon expulsion of neopentane [25]. The molecular structure of one of the tantalum complexes (**6**) has been determined by single crystal X-ray diffraction.



(**5**)



(**6**)

Hydrido-trispyrazolylborate complexes of elements from groups 5-7 have been prepared by reaction of d^0-metalloyl chlorides $[M(Y)_nCl_m]_x$ (Y = O, NR) with KTp* [Tp* = $HB(3,5\text{-}Me_2Pz_3)$] [26]. Thus, [$Nb(O)Cl_3$] and [$Ta(O)Cl_3$] are converted into monomeric and well-characterised oxo complexes [Tp*$Nb(O)Cl_2$] and [Tp*$Ta(O)Cl_2$] respectively. Molybdenum and tungsten derivatives are prepared in a similar way. ^{t}Butylamine has been found to react with [$NbCl_5$] and [$TaCl_5$] in the presence of pyridine to afford the imido-pyridine complexes [$Nb(NtBu)Cl_3(Py)_2$] and [$Nb(N^tBu)Cl_3(Py)_2$] in excellent yield. These species react subsequently with KTp* to afford pyrazolyl derivatives, [Tp*$M(N^tBu)Cl_2$] (M = Nb, Ta). Similar derivatives of molybdenum and tungsten are available via similar synthetic routes. From the same laboratory has come a related study in which the half-sandwich complexes [$(\eta^5\text{-}C_5R_5)M(N^tBu)Cl_2$] (R = H, Me; M = Nb, Ta) have been prepared by the reaction of [$(\eta^5\text{-}C_5R_5)MCl_4$] with $^tBuNH_2$ in the presence of bases such as $^tBuNH_2$, $LiNH^tBu$ and $LiN^tBuSiMe_3$ [27]. These complexes are starting materials for the preparation of the corresponding methyl complexes [$(\eta^5\text{-}C_5R_5)M(N^tBu)Me_2$] and of d^0-niobocene and tantalocene complexes [$(\eta^5\text{-}C_5R_5)_2M(N^tBu)Cl$] and [$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)M(N^tBu)Cl$]. The most efficient syntheses of [$(\eta^5\text{-}C_5H_5)_2M(N^tBu)Cl$] make use of the reaction of readily available pyridine imido complexes, [$M(N^tBu)Cl_3(py)_2$] (M = Nb, Ta) with NaC_5H_5. With MeLi, the compounds [$(\eta^5\text{-}C_5H_5)_2M(N^tBu)Cl$] are converted into the methyl derivatives [$(\eta^5\text{-}C_5H_5)_2M(N^tBu)Me$]. One-electron reduction of the compounds [$(\eta^5\text{-}C_5H_5)M(N^tBu)Cl_2$] leads to diamagnetic, dinuclear complexes with bridging imido ligands of the form [$(\eta^5\text{-}C_5H_5)M(\mu\text{-}N^tBu)Cl$]$_2$ (M = Nb, Ta). Similarly, the reduction of the d^0-niobocene imido complex [$(\eta^5\text{-}C_5H_5)_2Nb(N^tBu)Cl$] results in the formation of a dinuclear complex $[(\eta^5\text{-}C_5H_5)_2Nb(N^tBu)]_2$ with spin coupling of both d^1-metal centres [27].

Reaction of $[Cp'_2Nb(\eta^2\text{-}PhRCCNPh\text{-}CN)]$ ($R=Ph$, Me, Et; $Cp'=\eta^5\text{-}C_5H_4SiMe_3$) with one equivalent of $[Cp_2Fe]^+[X]^-$ ($X=PF_6$, BPh_4) in the presence of nitriles (MeCN) or isonitriles (^tBuNC) produces a variety of cationic ketenimine niobocene complexes, $[Cp'_2Nb(\eta^2\text{-}PhRCCNPh\text{-}CN)(L)][X]$ (where L = nitrile or isonitrile ligand) in essentially quantitative yields [28]. Electrochemical oxidation processes were investigated in the same study by cyclic voltammetry. In most cases, the solution state structures have been determined by NMR spectroscopy and in one case, the solid state structure (7) has been examined by single crystal X-ray diffraction (triclinic, $a=9.468(3)$, $b=10.641(2)$ and $c=19.852(2)$ Å; $\alpha=86.30(1)$, $\beta=88.79(1)$, $\gamma=74.64(2)°$, $Z=2$, $R=0.069$).

The molecular structure reveals a typical bent-sandwich geometry around the niobium atom with the ketenimine and MeCN ligands arranged in the plane between the two cyclopentadienyl rings. Those cationic ketenimine complexes isolated as nitrile adducts are readily converted to isonitrile adducts by treatment with an excess of isonitrile. However, the reverse reaction does not occur under the same conditions. Several of the ketenimine complexes react with the water in wet acetone or methanol to produce hydroxo and alkoxo iminoacyl complexes $[Cp'_2Nb(\eta^2\text{-}PhRHCCNPh\text{-}CN)(OR')][BPh_4]$ ($R'=H$, Me).

1.1.4. Complexes with other donor ligands

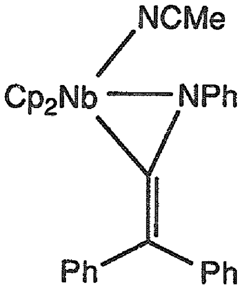
The nucleophilic cyclocarbene 1,3-dimethylimidazolin-2-ylidene (L) (**8**) reveals universal ligand properties in metal coordination chemistry. In addition to the well-known stabilisation of low oxidation state transition metal fragments, this particular class of carbenes also coordinates with metal halides and metal oxides thus resembling the properties of conventional ether (O), amine (N) and phosphine (P) ligands [29]. Complexes of titanium(IV), zirconium(IV), hafnium(IV), vanadium(II), niobium(V) and tantalum(IV) having the general form $[MX_nL_m]$ are reported.

Magic angle spinning ^{31}P NMR spectra of solid niobium half-sandwich compounds are shown to yield values of $^{93}Nb\text{-}^{31}P$ coupling constants which are not accessible from solution state spectra and also provide more accurate values of chemical shifts. Results are reported for eight compounds and the general value of NMR spectra of solids for these and similar cases is emphasised [30].

Although it is well known that cisplatin has been developed into one of the most frequently used and most effective cytostatic drugs for the treatment of solid carcinomas, numerous other metal compounds containing platinum, other platinum group metals and even non-platinum group metals have been shown to be effective against tumours in man and experimental tumours in animals. Among these metals, niobium has featured strongly along with gallium, tin, bismuth, titanium, vanadium, molybdenum, rhenium, ruthenium, rhodium, copper and gold [31].

Regioisomers of the first tantalum boryl complexes, *endo*- and *exo*-$[(\eta^5\text{-}C_5H_5)_2TaH_2(BO_2C_6H_4)]$ **9**, have been reported [32], whilst anionic bis(dicarbollide) complexes of bent-sandwich tantalum(V) such as **10** have also been reported [33].

The telluroformaldehyde complex $[(\eta^5\text{-}C_5Me_5)_2Ta(\eta^2\text{-}TeCH_2)H$ has been prepared



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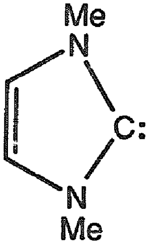
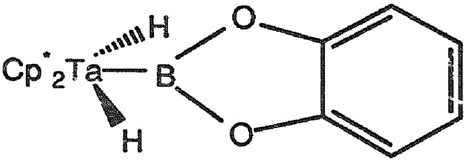


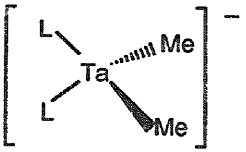
(8)

by the PMe_3-catalysed addition of tellurium to the [Ta=CH_2] double bond of [$(\eta^5\text{-}C_5Me_5)_2Ta(CH_2)H$] [34]. Of the two limiting resonance structures, i.e. metal-telluroformaldehyde versus metallatellurirane, the Te-C bond length of 2.21(2) Å suggests that the latter description might be the more appropriate description for the [$Ta(\eta^2\text{-}TeCH_2)$] interaction. The compound [$(\eta^5\text{-}C_5Me_5)_2Ta(\eta^2\text{-}TeCH_2)H$] is converted to its more stable tellurido-methyl isomer [$(\eta^5\text{-}C_5Me_5)_2Ta(Te)CH_3$] at 130°C. The ditellurido and tellurido-hydrido complexes, [$(\eta^5\text{-}C_5Me_5)_2Ta(\eta^2\text{-}Te_2)CH_3$] and [$(\eta^5\text{-}C_5Me_5)_2Ta(Te)H$] have also been prepared [34].



(9)

The coupled agostic distortion of two methylene groups in the model trigonal bipyramidal complex [$TaH_3(CH_2)_2$] has been studied by means of extended Hückel calculations where it is shown that the conrotatory and outward disrotatory pivoting is unfavourable. These results are discussed using a fragment molecular orbital (FMO) analysis and compared to the experimental structure in which coupled distortion of the two alkylidenes is conrotatory [35].



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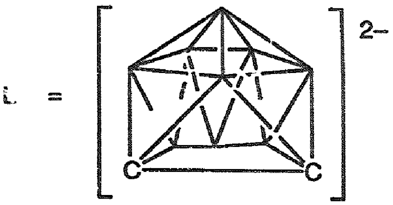


Nine boron vertices
Two carbon vertices

Reaction of $[(\eta^5\text{-}C_5Me_5)Ta(\eta^2\text{-}PhCCPh)Me_2]$ with *tert*-butyl or methyl isocyanides gives high yields of the iminoacyl complexes $[(\eta^5\text{-}C_5Me_5)Ta(\eta^2\text{-}PhCCPh)(\eta^2\text{-}MeCNR)Me]$ ($R={}^tBu$, Me) [36]. When heated in refluxing toluene, $[(\eta^5\text{-}C_5Me_5)Ta(\eta^2\text{-}PhCCPh)(\eta^2\text{-}MeCN^tBu)Me]$ gives the coupled product azatantalacyclopentatriene, $[(\eta^5\text{-}C_5Me_5)Ta(CPhCPhCMeNR)Me]$ in high yield. A similar reaction of CO with $[(\eta^5\text{-}C_5Me_5)Ta(\eta^2\text{-}PhCCPh)Me_2]$ gives the corresponding metallacycle, $[(\eta^5\text{-}C_5Me_5)Ta(CPhCPhCMeO)Me]$, the molecular structure of which reveals a five-membered $[TaC_3O]$-ring folded 124° along the C_a-O axis and containing an alkylidene. Other three-legged piano-stool alkyne complexes of the form $[(\eta^5\text{-}C_5Me_5)Ta(\eta^2\text{-}PhCCPh)XY]$ ($X=Cl$, $Y=Me$; $X=Cl$, $Y=NMe_2$) were prepared and characterised spectroscopically. Reduction of $[(\eta^5\text{-}C_5Me_5)Ta(\eta^2\text{-}PhCCPh)MeCl]$ with Na/Hg gives $[(\eta^5\text{-}C_5Me_5)Ta(\eta^2\text{-}PhCCPh)Cl_2]$ as the only isolable product. The complex $[(\eta^5\text{-}C_5H_5)Nb(\eta^2\text{-}PhCCPh)Me_2]$ reacts with isonitriles, RNC ($R={}^tBu$, CH_2Ph) to produce the corresponding niobium iminoacyl complexes $[(\eta^5\text{-}C_5H_5)Nb(\eta^2\text{-}PhCCPh)(\eta^2\text{-}MeCNR)Me]$.

The new ethyl complexes, [Tp′NbCl(Et)(PhCCR)] Tp′=hydridotris(3,5-pyrazolyl)borate (R=Me, Et) are shown to exhibit an α-hydrogen agostic interaction. The reason why the α-hydrogen agostic interaction is preferred over a more conventional β-agostic interaction is proposed to lie on steric grounds [37]. Accordingly, the bulkier benzyl ligand in $[Tp'NbCl(CH_2Ph)(PhCCMe)]$ coordinates in an η^1-manner whereas the good π-donor methoxy ligand in [Tp′Nb(OMe)(Et)(PhCCMe)] weakens the α-agostic bond.

The early-late heterodimetallic complex, $[Cp_2Ta(\mu^2\text{-}CH_2)_2PdCp]$ has been prepared and aspects of its reactivity investigated [38]. Reactions with phosphines, including the preparation, structural characterisation and reactivity of a [Ta-Pd] cationic complex bearing a naked cyclopentadienyl counter-ion have been detailed. The complex $[Cp_2Ta(\mu^2\text{-}CH_2)_2PdCp]$ was prepared by the reaction of $[Cp_2Ta(CH_2)Me]$ with $[CpPd(C_3H_5)]$. Subsequent treatment of $[Cp_2Ta(\mu^2\text{-}CH_2)_2PdCp]$ with PMe_3 or $P(OMe)_3$ (1 equiv.) in CH_2Cl_2 solvent resulted in the formation of $[Cp_2Ta(\mu^2\text{-}CH_2)_2Pd(L)Cl]$ [$L=PMe_3$, $P(OMe)_3$] and half an equivalent of Cp_2CH_2. Mechanistic studies indicated that the first step in these transformations is the formation of the respective bis-phosphine adducts $[Cp_2Ta(\mu^2\text{-}CH_2)_2Pd(L)_2]Cl$. The reaction of $[Cp_2Ta(\mu^2\text{-}CH_2)_2PdCp]$ with two equivalents of PMe_3 or $P(OMe)_3$ or one equivalent of $Me_2P(CH_2)_2PMe_2$ (dmpe) led to the isolation of $[Cp_2Ta(\mu^2\text{-}CH_2)_2Pd(L)_2]Cl$ [$L=PMe_3$, $P(OMe)_3$, dmpe], the latter dmpe complex being the subject of an X-ray diffraction analysis. Addition of $P(OMe)_3$ to $[Cp_2Ta(\mu^2\text{-}CH_2)_2PdCp]$ in acetonitrile solvent gave the product $[Cp_2Ta(\mu^2\text{-}CH_2)_2Pd\{P(OMe)_3\}_2(CH_3CN)]$ which again proceeded through a bis-phosphite adduct. Indeed, each of the reactions of $[Cp_2Ta(\mu^2\text{-}CH_2)_2PdCp]$ with phosphines suggests the formation of intermediates bearing a free cyclopentadienide ligand. The complex $[Cp_2Ta(\mu^2\text{-}CH_2)_2Pd(dmpe)]Cp$ was isolated from the reaction of $[Cp_2Ta(\mu^2\text{-}CH_2)_2PdCp]$ with dmpe in acetonitrile and was characterised by X-ray diffraction. Reactions of this compound with electrophilic reagents are similar to those observed for sodium cyclopentadienide. Thus, the addition of $FeCl_2$ to the complex $[Cp_2Ta(\mu^2\text{-}CH_2)_2Pd(dmpe)]Cp$ resulted in the formation of half of an equivalent of ferrocene and $[Cp_2Ta(\mu^2\text{-}CH_2)_2Pd(dmpe)]Cl$, whereas treatment of $[Cp_2Ta(\mu^2\text{-}CH_2)_2Pd(dmpe)]Cp$ with 1,2-dibromoethane led to the quantitative formation of half an equivalent of spiro[2.4]hepta-4,6-diene together with the bromide salt $[Cp_2Ta(\mu^2\text{-}CH_2)_2Pd(dmpe)]Br$ [38].

1.2. Lower oxidation states of niobium and tantalum

1.2.1. Complexes with group 17 donor ligands

Electrogenerated bis(trimethylsilyl)cyclopentadienyl niobium(III) complexes $[\eta^5\text{-}C_5H_4SiMe_3)_2NbX_2]$ ($X=Cl$, Br, I) have been shown to be effective catalysts for the reduction of acyl chloride $R^1R^2CHC(O)Cl$ ($R^1=R^2=Ph$; $R^1=Me$, $R^2=Ph$) [39]. Indirect cathodic reduction yields α-diketones $(R^1R^2CHCO)_2$, ketones $R^1R^2CHC(O)CHR^1R^2$ and alkanes $(R^1R^2CH)_2$. The formation of these derivatives involves the homolytic cleavage of the acyl chloride carbon-halogen bond, giving an acyl radical. Several mechanistic aspects are discussed; an oxidative addition of $R^1R^2CHC(O)Cl$ to the niobium(III) complex is followed by a reductive elimination of the acyl radical. On a similar theme, the same group has reported the synthesis of the hydrido-styrene complex of niobium(III) $[(\eta^5\text{-}C_5H_4SiMe_3)_2NbH(\eta^2\text{-}CH_2=CHPh)]$ from the reaction between $[(\eta^5\text{-}C_5H_4SiMe_3)_2NbH_3]$ and styrene or $[(\eta^5\text{-}C_5H_4SiMe_3)_2NbX_2]$ (X as above) with $PhCH_2CH_2MgBr$ [40]. The first method gives rise to two isomeric products (*endo*, where the olefinic substituent is central and *exo*, with the olefinic substituent lateral in the equatorial plane bisecting the two Cp-rings), while the latter leads exclusively to the *endo* isomer. The mechanism of the formation of the styrene complex $[(\eta^5\text{-}C_5H_4SiMe_3)_2NbH(\eta^2\text{-}CH_2=CHPh)]$ is discussed in terms of a model which implies a consecutive reaction with a reversible step and a first order rate dependence with respect to $[(\eta^5\text{-}C_5H_4SiMe_3)_2NbH_3]$. Finally, the kinetics of the olefin-hydride insertion have been studied by ^{1}H-NMR spectroscopy using coalescence techniques.

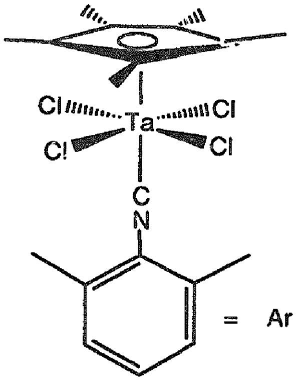
The single crystal X-ray diffraction study on $[(\eta^5\text{-}C_5H_4^tBu)_2NbCl_2]$ has been reported [41], in which it is revealed that the two *tert*-butylcyclopentadienyl ligands are bound in an asymmetric manner to the niobium atom. This asymmetry is accounted for in terms of the steric demand of the *tert*-butyl substituents. The pseudo-tetrahedral geometry is completed by two chloride ligands.

The compound $[Cp^*NbCl_4]$ ($Cp^*=C_5Me_5$) reacts with isocyanides to give the pseudo-octahedral adducts [Cp*NbCl$_4$(CNR)] (R = ^{t}Bu, 2,6-Me$_2$C$_6$H$_3$) [42]. Reduction of these adducts or alternatively [Cp*NbCl$_4$] in the presence of two equivalents of Na/Hg and stoichiometric amounts of isocyanides gives the diamagnetic pseudo-octahedral niobium(III) complexes, [Cp*NbCl$_2$(CNR)$_3$]. A similar reduction of [Cp*NbCl$_4$] in the presence of alkynes and dienes leads to the isolation of new niobium(III) derivatives, [Cp*NbCl$_2$(R'CCR")] (R' = R" = variously Me, Et, Ph and SiMe$_3$) and [Cp*NbCl$_2$(diene)] (diene = isoprene, methyl methacrylate). These complexes can also be prepared by addition of acetylenes to the phosphine complexes of niobium(III) [Cp*NbCl$_2$(L)$_2$] (L = PMe$_3$, PMe$_2$Ph) and by addition of acetylenes to the dichloro niobium(III) dimer, [Cp*NbCl$_2$]$_2$. All complexes have been characterised by mass spectrometry, IR and NMR spectroscopies and the molecular structures of [Cp*NbCl$_4$(CNR)] **11** and [Cp*NbCl$_2$(CNR)$_3$] **12** (R = 2,6-Me$_2$C$_6$H$_3$) determined by single crystal X-ray diffraction; both possess pseudo-octahedral geometries.

The compound [Cp'$_2$NbCl$_2$] (Cp' = η^5-C$_5$Me$_4$Et) has been synthesised from [NbCl$_5$]$_2$ and a slight excess of LiCp' and NaBH$_4$ [43]. Its electrochemical (two-electron, $E_{1/2}$ = -1.6 V) and chemical reductions (2 equiv., Na/Hg) were studied showing that peralkylation of the Cp'-ligand facilitates two-electron reduction compared to the less substituted Cp-derivatives [43]. The reduced solutions of [Cp$^*_2$NbCl$_2$] (Cp* = η^5-C$_5$Me$_5$) and [Cp'$_2$NbCl$_2$] (Cp' = η^5-C$_5$Me$_4$Et) were shown by means of EPR spectroscopy to contain two new paramagnetic species for which bent niobocene and fulvene-like structures are proposed. The high reduction potential of these species led to their reaction with HPF$_6$ and to the first stable difluoroniobocene derivative [Cp'$_2$NbF$_2$][PF$_6$] in good yield. The molecular structures of this compound and a co-crystallate of [Cp'$_2$NbF$_2$][PF$_6$] and [Cp'$_2$NbCl$_2$][PF$_6$], analysing as [Cp'$_2$NbCl(Cl/F)][PF$_6$], were studied by single-crystal X-ray diffraction techniques. Comparison with the structure of [Cp'$_2$NbCl$_2$] (Cp' = η^5-C$_5$Me$_4$Et) reveals a marked decrease in the X-Nb-X angle from 102.3(4)° in the case of X = F to 85.2(1)° for X = Cl. Electrochemical, one-electron reduction of [Cp'$_2$NbF$_2$][PF$_6$] gave rise to the formation of [Cp'$_2$NbF$_2$] which exhibits a much lower potential ($E_{1/2}$ = -2.38V) than other niobocene dihalides. Reaction of [Cp'$_2$NbF$_2$][PF$_6$] with Li$_2$S$_2$ gave [Cp'$_2$Nb(η^2-S$_2$)F], whereas [Cp'$_2$NbCl$_2$][PF$_6$] was reduced by Li$_2$S$_2$ to give [Cp'$_2$NbCl$_2$].

1.2.2. Complexes with group 16 donor ligands

Novel niobium(IV) complexes containing two cyclopentadienyl rings and DMIT, DMIO and DDDT ligands have been synthesised and their voltammetric behaviour investigated in acetonitrile and dichloromethane solvents [44]. These complexes in acetonitrile solution exhibit a reversible one-electron oxidation and a reversible one-electron reduction step, corresponding to niobium(V) and niobium(III) respectively, without any complicating side or subsequent reactions. Among the three niobium(IV) complexes, the reduction potential of the complex with DDDT was notably less negative than those of the complexes with DMIT or DMIO. This fact allows the preparation of the charge-transfer complexes with TCNQ. The niobium(V) DMIT and DMIO complexes with two cyclopentadienyl ligands were also isolated as iodide salts by the oxidation of the corresponding niobium(IV) complex. These niobium(V) complexes gave one-electron reduction steps whose potentials were identical to those of niobium(IV) and niobium(III) DMIT and DMIO complexes [44].



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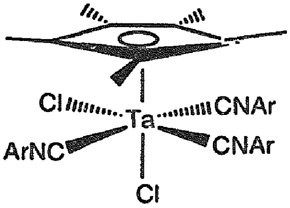

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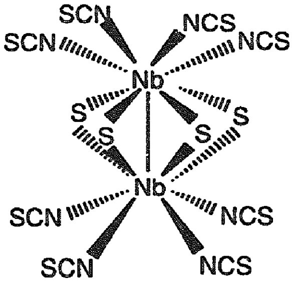
The (arene)tricarbonylchromium (benchrotrenic) oxo compounds BctCOR (Bct = $Cr(CO)_3C_6H_5$; R = H, alkyl, aryl) undergo a reductive coupling reaction with [$NbCl_3$(dme)] leading to the mono- and bis-metallated alkenes, Bct(R)C = C(R)Ar and Bct(R)C = C(R)Bct, respectively. Such a mixture of mono- and bis-metallated products is obtained when the benchrotrenic ketones are used as substrates. Starting from benchrotrenic aldehydes, different products such as mono-tricarbonylchromium *trans*-stilbene are obtained, a process shown to occur in two steps. The niobium(III) induced partial $Cr(CO)_3$ decomplexation of the substrate is followed by the reductive coupling, preferentially between the free aldehyde formed and the benchrotrenic aldehyde. The differences in the reactivity observed are explained in terms of the favoured in-plane s-geometry for the niobium(III)-Lewis acid activation of the carbonyl toward metalloxirane nucleophilic attack [45].

Metal alkoxides are often associated with more accessible precursors such as carboxylates, nitrates, β-diketonates in chemical routes to complex metal oxides. The molecular constitution of such solutions has been examined for systems related to ferroelectrics and based on niobium, titanium or zirconium alkoxides. A variety of oxo and non-oxo mixed metal acetoalkoxides have been characterised in the solid state (X-ray diffraction) as well as solution (FT-IR as well as multinuclear NMR spectroscopy). Conversion from these molecules to the final material through hydrolysis-polycondensation has been estimated [46]. The amorphous and crystalline powders have been characterised by thermogravimetric analysis and X-ray diffraction, respectively. Strategies for a control of the stoichiometry between the metals in the precursors are discussed. Homoleptic alkoxides [$Pb_6Nb_4O_4(OEt)_{24}$] and [$BaTi_4(OEt)_{18}$] were used as models for gaining insight into chemical transformations.

The synthesis, structures and properties of $[(Et_4N)_4Nb_2S_4(NCS)_8]$, $[(EtQuin)_4Nb_2S_4(NCS)_8]$, $[Nb_2S_4(Et_2\text{-}NCS_2)_4]$, $[Nb_2S_4(ROCS_2)_4]$ (R = Et, Cy, ^{i}Pr) and $[Nb_2S_4(^iPrO_2PS_2)_4]$ have been described [47]. The first two of the above compounds have been obtained by fusing together $[NbS_2Cl_2]$ and KNCS, dissolving this melt in water and adding the corresponding organic cations. In this manner, the complex $[(EtQuin)_4Nb_2S_4(NCS)_8]$ **13** has been isolated and characterised by single-crystal X-ray diffraction. The anion contains 8-coordinate niobium atoms ligated by $\eta^2{:}\eta^2{:}\mu^2$ ligands and eight terminal isothiocyanate ligands. The Nb-Nb distance is 2.913(2) Å. The NCS ligands in **13** can be displaced easily to afford the complexes $[Nb_2S_4(Et_2\text{-}NCS_2)_4]$ and $[Nb_2S_4(^iPrO_2PS_2)_4]$ **14**, the latter being examined by X-ray diffraction. Just like **13**, complex **14** possesses a $[Nb_2S_4]$ core with a Nb-Nb distance of 2.898(1) Å. Each niobium atom is, in addition, coordinated by two chelating dithiophosphate ligands. Mass spectrometric data for **13** and **14** have also been collected and studied [47].



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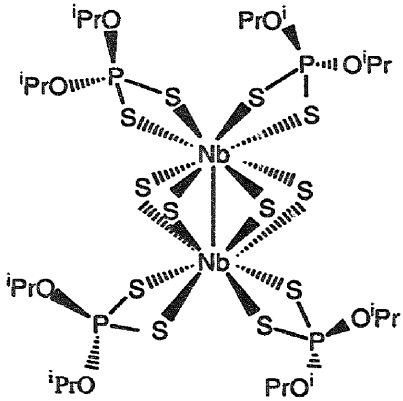

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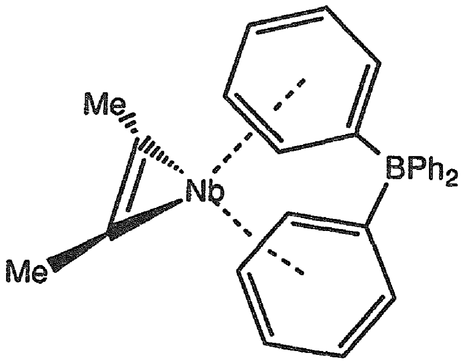
1.2.3. Complexes with group 15 donor ligands

Reaction of the hydride complex, $[TaH(CO)_4(dppe)]$ (dppe = bis-1,2-diphenylphosphinoethane) in benzene with tris(*p*-*tert*-butyphenyl)methyl radical results in the abstraction of the metal-bonded hydrogen atom and formation of tris(p-t-butyphenyl)methane and the 17-electron compound $[Ta(CO)_4(dppe)]$, the latter being the first tantalum(0) carbonyl compound to be synthesised and studied [48].

Previous interpretation of the EPR spectra of the d^1-pseudo-D_{4h} $[NbCl_4(PR_3)_2]$ complexes assumed that the unpaired electron resides in the b_{2g} (d_{xy}) orbital. In contrast, simple molecular orbital considerations suggest that the unpaired electron resides in the Jahn-Teller unstable e_g (d_{xy}, d_{yz}) orbital. *Ab initio* self-consistent field calculations, which should be reasonably accurate for the relative energies of these various d^1-states, predict the ground state to be the Jahn-Teller distorted $2E_g$ [49].



(15)

Although the predicted geometry of this state is in agreement with the X-ray structure, the calculated g-values for this and other possible states are incompatible with the experimental g-values. It is concluded that the observed spectra are due to some other species.

The complexes, $[NbX(CO)_3(PR_3)_3]$ ($PR_3 = PEt_3$, X = I; $PR_3 = PMe_2Ph$, X = Cl, Br, I) and $[NbX(CO)_{4/2}(dppe)_{1/2}]$ (X = Br) have been prepared by oxidative halogenation of carbonyl niobate with pyridinium halides (X = Cl, Br) or iodine (X = I) [50]. In the tricarbonyls, one CO and one PR_3 are labile and can be displaced by a four-electron donating alkyne to give all-trans $[NbX(CO)_2(RCCR')(PR_3)_2]$ ($PR_3 = PMe_2Ph$; X = Cl, Br, I; R,R' = H, Et, Ph; R = H, R' = Ph; $PR_3 = PEt_3$, X = I, R,R' = Pr; R = H, R' = Bu, Ph; R = Me, R' = Et). In the case of acetylene, $[NbI(CO)(HCCH)(PEt_3)_2]$ is also formed. The phosphine ligands can be replaced with phosphites. In the tetracarbonyl, two CO ligands are replaced by two isonitriles to form $[NbI(CO)_2(CNR)_2(dppe)]$ (R = ^{t}Bu, Cy) or by one alkyne to form $[NbX(CO)_2(PhCCPh)(dppe)]$ (X = Br, I). In these complexes, the remaining CO ligands occupy *cis*-positions. The structures of $[NbX(CO)_2(dppe)_2] \cdot L$ (X = Br, L = thf; X = I, L = hexane), $[NbI(CO)_2(PEt_3)_2(MeC{=}CEt)]$ have been determined by X-ray diffraction. The alkyne complexes are best regarded as octahedral with the centre of the alkyne ligand occupying the positions *trans* to the halide and the [C = C] axis aligned with the [OC-Nb-CO] axis. The complexes, $[NbX(CO)(H_2CPhCH_2CH_2PPh_2)_2] \cdot 1/2thf$ has also been determined. The geometry is pentagonal bipyramidal, with one of the bromine atoms and the CO on the axis. Some ^{93}Nb spectroscopic data for the Nb(I) complexes are presented and preliminary observations on the reactions between π-alkyne complexes and H_2 or H-are reported.

Siloxycarbyne complexes of the type $[Ta({\equiv}COSiR_3)(CO)(dmpe)_2]$ ($R_3 = {}^tBuPh_2$, Ph_3) have been prepared by routes analogous to those previously described for $[Ta({\equiv}COSi^iPr_3)(CO)(dmpe)_2]$ [51]. Each of these compounds reacts with R'_3SiCl to afford the acetylene complexes, $[Ta(R_3SiOC{\equiv}COSiR'_3)(dmpe)_2Cl]$ (R, R' = as above). The mechanism of C-C bond formation in these systems has been elucidated by stopped-flow kinetic studies of the reaction of [Ta(=COSi^{i}Pr$_3$)(CO)(dmpe)$_2$] with excess Me$_3$SiCl in thf. Addition of (n-pentyl)$_4$NCl increased the rate of reaction between [Ta(=COSi^{i}Pr$_3$)(CO)(dmpe)$_2$] and excess Me$_3$SiCl, but produced the complex [Ta(Me$_3$SiOC=COSiMe$_3$)(dmpe)$_2$Cl] instead. A pathway for chloride-induced exchange of silyl groups between the starting material and excess Me$_3$SiCl has been elucidated. Addition of [Bu$_4$N]BPh$_4$ also strongly accelerated the observed reaction rates but in this case the product formed was [Ta(R$_3$SiOC=COSiR'$_3$)(dmpe)$_2$Cl] (R=Me, R'=iPr). The observed rate increases were attributed to an increase in the ionic strength of the solution. At a constant salt concentration of 23.9 mM [Bu$_4$N]BPh$_4$, the reaction was first order in both [Ta(=COSi^{i}Pr$_3$)(CO)(dmpe)$_2$] and Me$_3$SiCl, with a second order rate constant of 1.71(4) M^{-1} s^{-1} at 22(1)°. These results are consistent with a mechanism involving electrophilic attack by the silyl reagent on the CO ligand as the rate determining step of reaction [51]. Addition of AlEt$_3$ to [Ta(=COSi^{t}BuPh$_2$)(CO)(dmpe)$_2$] allowed the isolation of the complex [Ta(=COSi^{t}BuPh$_2$)(COAlEt$_3$)(dmpe)$_2$], a model for the initial species formed upon silylation of the CO ligand in the precursor tantalum complex. Comparison of the structural and spectroscopic properties of [Ta(=COSi^{t}BuPh$_2$)(CO)(dmpe)$_2$] and [Ta(=COSi^{t}BuPh$_2$)(COAlEt$_3$)(dmpe)$_2$] revealed that C-C bond formation does not occur upon addition of this particular Lewis acid. The structure of the latter adduct revealed several important features, the most significant of which is a decrease in the C-Ta-C angle to 73.4(4)° from the value of 89.1(3)° in [Ta(=COSi^{t}BuPh$_2$)(CO)(dmpe)$_2$]. The corresponding angle in the reductively coupled product [Ta(R$_3$SiOC=COSiR'$_3$)(dmpe)$_2$Cl], the structure of which is also reported, is 36.5(2)° [51].

Tantalum(III) silyl complexes [Cp$_2$TaL(SiR$_3$)] (Cp=η^5-C$_5$H$_5$, L=PMe$_3$, CO) are reactive towards the C-H bonds of unhindered arenes such as benzene, toluene and *m*-xylene [52]. The sterically hindered silyl complex [Cp$_2$Ta(PMe$_3$)(Si^{t}Bu$_2$H)] reacts in neat arenes to produce the corresponding aryl complexes [Cp$_2$Ta(PMe$_3$)Ar] in high yields. However, complexes with smaller silyl ligands give equilibrium mixtures of silyl and aryl complexes in which the silyl is favoured. Dynamic studies of this system have permitted the first direct comparison of Si-H and C-H bond activation by the same metal centre and allow the estimation of relative Ta-C and Ta-Si bond dissociation enthalpies (BDEs) [52]. It is found that the Ta-Si bonds in [Cp$_2$Ta(PMe$_3$)(Si^{t}Bu$_2$H)] and in [Cp$_2$Ta(PMe$_3$)(SiMe$_3$)] are respectively 5.4 and 7.9 kcal mol^{-1} weaker than the Ta-C phenyl bond in [Cp$_2$Ta(PMe$_3$)Ph]. However, metal-phenyl bonds are generally much stronger than metal-alkyl bonds and the Ta-Si BDEs are probably comparable to or greater than the strength of a tantalum-alkyl bond. As expected, the bulkier silyl group exhibits the weaker BDE, but surprisingly, the lower stability of [Cp$_2$Ta(PMe$_3$)(Si^{t}Bu$_2$H)] with respect to the phenyl complex is primarily due to a large and favourable entropy change (34(3) J K^{-1} mol^{-1}) resulting from the release of steric congestion upon converting the silyl into the phenyl complex. The high reactivity of tantalum silyls towards arene C-H bond activation can also be combined with the facile reaction of tantalum alkyls with silanes to yield the silane-catalysed conversion of [Cp$_2$TaLR]

($R=$alkyl, $L=PMe_3$, $CH_2=CH_2$) complexes into the corresponding aryl complexes. Complexes $[Cp_2Ta(PMe_3)(Si^tBu_2H)]$, $[Cp_2Ta(CO)(Si^tBu_2H)]$ and $[Cp_2Ta(CO)(SiMe_3)]$ have been structurally characterised by single crystal X-ray diffraction analysis.

1.2.4. Other donor sets

The one-electron oxidation of $[Nb(Mes)]_2$ (Mes = 1,3,5-trimethylbenzene) with ferrocenium tetraarylborate produces the 16-electron cation, $[Nb(Mes)_2]^+$ which adds disubstituted symmetrical alkynes to give the ionic compounds $[Nb(Mes)_2(alkyne)]^+[Y]^-$ [alkyne = MeC_2Me, $Y=BPh_4$, $B(p\text{-}FC_6H_4)_4$, $B[3,5\text{-}(CF_3)_2C_6H_3]_4$; alkyne = PhC_2Ph, $Y=BPh_4$, $B(p\text{-}FC_6H_4)_4$] [53]. The latter complex has been examined by single-crystal X-ray diffraction which reveals no startling discoveries. However, thermal treatment in toluene results in mesitylene displacement and formation of a neutral species containing η^6-aryl bonding arrangement of the borate anion such as in complex **15**. This new type of bonding is not restricted to methyl or phenyl-substituted alkyne derivatives, CO is also compatible with the arrangement, such as $[Nb(\eta^6\text{-}C_6H_4X)_2B(C_6H_4X)_2(CO)]$ which has also been the subject of an X-ray diffraction investigation.

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